Autoionization bands in one- and two-dimensional crystals

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The singularities of the interaction of decay states in the presence of translational symmetry are considered.. It is shown that in the case of low-energy potential resonances observation of weakly decaying autoionization bands, with a nonanalytic dispersion law of the imaginary part of the energy, are possible even within the first Brillouin zone. The dependence of the decay probability $\Gamma(\varkappa)$ on the quasimomentum is investigated within the framework of the exactly solvable model of "muffin-tin" potentials. It is shown that the form of the function $\Gamma(\varkappa)$ reflects the singularities of the angular part of the wave function of an isolated center.

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1. INTRODUCTION

The concepts and conclusions of the band theory are the basis of the present-day premises of solid-state theory, and in particular of the physics of electronic phenomena in crystals. The mechanism of formation of bands of electronic states is well known: exchange interaction[1)] lifts the degeneracy of the discrete levels of the system of identical centers, and collectivized states are formed, which are characterized in the presence of translational symmetry by the quasimomentum vector $\varkappa$. The intraband dispersion law, i.e., the dependence of the energy E on the quasimomentum, determines the basic characteristics of the motion of the electron along the crystal. Calculations of the functions $E(\varkappa)$ at negative energies (the position of the vacuum level is taken to be zero) are among the traditional problems of solid-state physics. The corresponding results are given in numerous reviews and monographs (see, e.g., Refs. 1–3).

At the same it is well known that the spectrum of the discrete states of single-center systems, corresponding to poles of single-center Green's functions, has in many cases a continuation at $E>0$. The complex energy levels E_n with sufficiently small imaginary part (i.e., $\mathrm{Im}E_n \ll |E_n|$) are set in correspondence with quasistationary (autoionization) states whose properties are close in many respects to the properties of the stationary levels.[4] The theory of the interaction of resonant and autoionization states is presently rapidly developed, and its results are extensively used in most diverse branches of physics. This raises the natural question: can energy bands of resonance states be formed, and what are the singularities of the corresponding dispersion laws?[2)] The answer depends on the ratio of the characteristic times, the decay time, of the order of $(\mathrm{Im}\,E_n)^{-1}$, and the exchange time τ_0, which determines the rate of transition between centers. The formation of collectivized states should obviously be expected under the condition

$$\tau_0 \,\mathrm{Im}\, E_n \ll 1, \tag{1}$$

when the electron manages to travel between centers many times by the instant of its detachment.

The behavior of the weakly bound electron in the field of two centers that produce a resonance in the P state was previously investigated in Ref. 5. The intensity of the exchange interaction of two decaying states was investigated in Ref. 6. It was shown that in the case of resonances of Feshbach type[3)] the exchange interaction is proportional to the geometric mean of the autoionization widths of the isolated centers. The act of transition between centers turns out to be strongly suppressed by the required double inelastic transition. In periodic structures, resonances of the Feshbach type (without allowance for the excitonic states that transfer the core excitation from center to center) should yield post-decay rescattering effects, analogous to those considered by Kagan and Afanas'ev[9] with nuclear interactions of the neutron as an example. The situation is entirely different in the case of potential (centrifugal or shape[7,8]) resonances. In fact, at $ka \ll 1$, where k is the electron momentum and a is the distance between centers, the penetrability of the barrier separating two neighboring centers turns out to be large enough,[10] so that the electronic transition is rapid and condition (1) is certainly satisfied.[6] It is shown in the present paper that in periodic structures the potential resonances form rather wide autoionization bands whose dispersion law has qualitatively new singularities.[4)] The possible physical consequences of this deduction are discussed briefly in the Conclusion.

2. DISPERSION LAW OF AUTOIONIZATION BANDS IN ONE-DIMENSIONAL CRYSTALS

We consider the spectrum of the eigenvalues of the Hamiltonian

$$\mathcal{H}(\mathbf{r}) = -\tfrac{1}{2}\Delta + V(\mathbf{r}), \tag{2}$$

which describes the motion of the electron in the combined field of muffin-tin (MT) potentials[1-3] that form a linear chain:

$$V(\mathbf{r}) = \sum_s U_s(\mathbf{r}_s), \quad \mathbf{r}_s = \mathbf{r} - \mathbf{R}_s, \quad \mathbf{R}_s = (0, 0, as), \qquad U_s(\mathbf{r}_s) = \begin{cases} U_s(\mathbf{r}_s), & r_s < r_0 \\ 0, & r_s > r_0,\ 2r_0 < a \end{cases} \tag{3}$$

where $\mathbf{r}$ is the coordinate of the electron, $\mathbf{R}_s$ is the radius vector of the s-th atomic center, a is the constant of the chain, and U_s is the potential of the interaction of the electron with the s-th center. The system of algebraic equations of the theory of multiple scattering for an aggregate of MT potentials was obtained by many workers (see, e.g., Refs. 12 and 13). In our case this system takes the form

$$\tau_{lm}^{(s)} = f_l(E) \sum_{s' \neq s} \sum_{l'm'} F_{mm'}^{ll'}(\mathbf{R}_s, \mathbf{R}_{s'})\, \tau_{l'm'}^{(s')}. \tag{4}$$

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The corresponding electron wave functions are

$$\Psi_{\varkappa}(\mathbf{r}) = \text{const} \cdot \sum_{s,lm} Y_{lm}(\mathbf{r}_s) h_l^{(+)}(kr_s) \tau_{lm}^{(s)}. \quad (5)$$

Here $F_{mm'}^{ll'}(\mathbf{R}_s, \mathbf{R}_{s'})$ is the probability amplitude of the transition of the electron from the s-th center with angular momentum l and angular momentum projection m relative to this center to a center s' with respective angular momentum and projection l' and m', i.e.,

$$F_{mm'}^{ll'}(\mathbf{R}_s, \mathbf{R}_{s'}) = \sum_{LM} (-1)^m i^L [4\pi(2L+1)(2l+1)(2l'+1)]^{1/2} \times \begin{pmatrix} l & l' & L \\ -m & m & M \end{pmatrix} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} Y_{LM}(\mathbf{R}_{s'}) h_L^{(+)}(k|\mathbf{R}_s - \mathbf{R}_{s'}|);$$

Y_{LM} is a spherical harmonic, $h_L^{(+)}$ is a spherical Hankel function of the first kind, (:::) is the Wigner $3j$-symbol; $f_l(E)$ is the partial amplitude of the scattering of an electron by an isolated atomic enter; we assume for this amplitude, in accordance with the formulation of the problem, the single-resonance approximation[10]:

$$f_l(E) = -\frac{1}{2k} \frac{\Gamma_0}{E - (E_0 - i\Gamma_0/2)}, \quad (6)$$

where $E_0 - i\Gamma_0/2$ is the complex energy of the single-center resonant level with angular momentum l, whose real and imaginary parts at small kr_0 are connected in known fashion with the parameters of the potentials

$$\Gamma_0 = \alpha_l k^{2l+1}, \quad \alpha_l > 0. \quad (7)$$

Neglecting the contribution of the nonresonant terms[5] and taking into account the translational symmetry of the Hamiltonian (2), we seek a solution of the system (4) in the quasimomentum representation $\varkappa = (0, 0\varkappa)$:

$$\tau_{lm}^{(s)} = \tau_{lm} e^{i\varkappa as}. \quad (8)$$

The dispersion equation, whose roots are the energies of the allowed band resonances, takes in this case the form

$$E_{lm}(\varkappa) = E_0 - \frac{i\Gamma_0}{2} - i\Gamma_0 \sum_{s'}{}' \sum_{\lambda} C_{ll\lambda}^m h_\lambda^{(+)}(kas') \cos \varkappa as'. \quad (9)$$

By virtue of the axial symmetry of the interaction (3), the solution of this equation are classified in accord with the projection of the angular momentum on the axis of the chain and the value of the quasimomentum $\varkappa$. At small ka, the solution of (9) can be sought by iteration over the terms that contain imaginary parts. In the lowest-order approximation we obtain accordingly an equation that determines the dispersion law of the band states without allowance for the autoionization

$$E_{lm}(\varkappa) = E_0 + \Gamma_0 \sum_{s'}{}' \sum_{\lambda} C_{ll\lambda}^m n_\lambda(kas') \cos \varkappa as'. \quad (10)$$

Here

$$C_{ll\lambda}^m = (2\lambda+1)(2l+1) \begin{pmatrix} l & l & \lambda \\ -m & m & 0 \end{pmatrix} \begin{pmatrix} l & l & \lambda \\ 0 & 0 & 0 \end{pmatrix};$$

$n_\lambda(x)$ is a Neumann spherical function. The parameter $\varkappa_a$ takes on a continuous spectrum of values within the interval $[-\pi, \pi]$ (the first Brillouin zone), and the corresponding solutions of (10) determine the resonant-state band whose end points correspond at even values of $(l+m+1)$ to the energies

$$E_{lm}^{\max} = E_{lm}(0) = E_0 + \Gamma_0 D_{lm} \zeta(2l+1)/(ka)^{2l+1},$$
$$E_{lm}^{\min} = E_{lm}(\pm\pi) = E_0 - \Gamma_0 D_{lm}(1 - 2^{-2l}) \zeta(2l+1)/(ka)^{2l+1}, \quad (11)$$

where

$$D_{lm} = (4l-1)!!(2l+1)(4l+1) \begin{pmatrix} l & l & 2l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & 2l \\ -m & m & 0 \end{pmatrix}.$$

$\zeta(x)$ is the Riemann zeta function. At odd $l+m+1$ the connection between the values of the parameter $\varkappa a$ and the end points of the energy band is reversed [i.e., $E_{lm}^{\max} = E_{lm}(\pm\pi)$, $E_{lm}^{\min} = E_{lm}(0)$]. At $E_{lm}^{\min} < 0$ the lower edge of the energy band is under the end point of the continuous spectrum (the vacuum level). Similarly, in the case of strong exchange interaction of the discrete levels, the upper edge of the band can go off into the region $E > 0$. The decay of such states is also of interest.[6]

The dispersion law $E_{lm}(\varkappa)$ has logarithmic singularities at $\varkappa = \pm k$. These singularities, however, appear at $l \geq 2$ in the expansion terms that follow $\varkappa^2$. For resonances with $l = 1$ we have at small ka

$$E(\varkappa) \approx E(0) + \text{const} \cdot \frac{\Gamma_0}{(ka)^3} (\varkappa a)^2 \ln|\varkappa a|. \quad (12)$$

Introduction of the "effective mass" concepts widely used in ordinary band theory[1-3] is impossible in our case. Accordingly, at the boundary of the first Brillouin zone we have

$$E(\varkappa) \approx E(\pm\pi) + \text{const} \cdot \frac{\Gamma_0}{(ka)^3} (\pi - |\varkappa a|)^2. \quad (13)$$

We consider now the rate of autoionization of the states of the resonant bands. According to (9), the imaginary part of the energy, which determines the probability of detachment of an electron per unit time, can be obtained from the formula

$$\Gamma_{lm}(\varkappa) = \Gamma_0 \left\{ \frac{1}{2} + \sum_{s'}{}' \sum_{\lambda} C_{ll\lambda}^m j_\lambda(kas') \cos \varkappa as' \right\}, \quad (14)$$

where $j_\lambda(x)$ is a spherical Bessel function. The Wigner symbols $\begin{pmatrix} l & l & \lambda \\ 0 & 0 & 0 \end{pmatrix}$ differ from zero only at even values of the sum of the indices $2l + \lambda$, therefore the sum over λ in (14) contains only $l+1$ terms corresponding to even values of λ from 0 to $2l$.

The series $\sum j_\lambda(kas') \cos \varkappa as'$ can be summed analytically and expressed in terms of the functions

$$f_\lambda(x) = \sum_s \frac{\sin xs}{s^{\lambda+1}}$$

(see, e.g., Ref. 14). Leaving out the immediate calculations, we obtain ultimately

$$\Gamma_{lm}(\varkappa) = \frac{\pi\Gamma_0}{ka}(2l+1) \frac{(l-|m|)!}{(l+|m|)!} \left(P_l^{|m|}\left(\frac{\varkappa}{k}\right) \right)^2 \eta(k^2 - \varkappa^2). \quad (15)$$

Here $P_l^m(x)$ is an associated Legendre polynomial and $\eta(x)$ is the Heaviside step function. Thus, the autoionization rate turns out to be a nonanalytic function of the quasimomentum even within the first Brillouin zone at the points $\varkappa = \pm \varkappa_0$, which are real roots of the equation

$$\varkappa^2 = 2E_{lm}(\varkappa), \quad (16)$$

where $E_{lm}(\varkappa)$ is determined from (10). At $\varkappa > k$ we

have $\Gamma_{lm} \equiv 0$, i.e., auotionization of states whose quasimomentum exceeds the momentum of the released electrons is impossible. A similar result is known, for example, for molecular excitons,[15] where it applies, however, to all states of one (low-energy) branch of the collective excitations. In our case, however, the transition from nondecaying to decaying states takes place within a single band of allowed states. This conclusion describes a general property of resonant bands and is not connected directly with the considered model of the interactions (3). In fact, autoionization states with $\varkappa > k$ are forbidden by the translational invariance of the Hamiltonian, inasmuch as the decay should take place under the condition $|\mathbf{k}_\parallel| = |\varkappa|$ ($\mathbf{k}_\parallel$ is the projection of the momentum on the axis of the invariant displacements), and the possibility of the decay at large k is obvious.

The dependence of Γ_{lm} on $\varkappa$ in the vicinity of the quasimomentum $\varkappa_0$ is determined by the angular-momentum projection m. For example, for states with $l=1$ and $m=0$ at the point $\varkappa = \varkappa_0$ the autoionization width changes jumpwise from zero to a value $\sim \lambda a^{-1} \Gamma_0$, where λ is the wavelength of the released electron. Actually, at $|\varkappa| < \varkappa_0$, near $\pm\varkappa_0$, the functions $\Gamma(\varkappa)$ increase sharply on a scale

$$\delta\varkappa \sim \frac{d\varkappa}{dE}\Gamma \sim \frac{\Gamma}{\varkappa_0},$$

i.e., a quantity of the order of the quasimomentum uncertainty due to the finite lifetime of the considered states. For states with $m \neq 0$ we have near the autoionization threshold

$$\Gamma_{lm}(\varkappa) \sim (k^2-\varkappa^2)^{|m|}\eta(k^2-\varkappa^2),$$

i.e., the derivative changes jumpwise.

It is important also to note that in states with $l \geq 2$ the function $\Gamma_{lm}(\varkappa)$ can have zeros also at $k > \varkappa$. The condition $\Gamma_{lm}=0$ reflects in this case the position of the zeros of the associated Legendre polynomial $P^{|l|m|}(\varkappa/k)=0$. At this ratio of k and $\varkappa$, the directions along which the electron might leave the system correspond to the nodes of the wave function of the isolated center. In this case, naturally, no decay is possible.

3. DISPERSION LAW OF RESONANT STATES IN TWO-DIMENSIONAL CRYSTALS

We consider now the case when the centers of the resonant scattering are located at the points of a regular two-dimensional lattice

$$V(\mathbf{r}) = \sum_s U_s(\mathbf{r}-\mathbf{R}_s), \quad \mathbf{R}_s = (a_x n, a_y m, 0). \tag{17}$$

We introduce first some transformations in Eqs. (14) to reduce them to a form more convenient for the investigation of the decay characteristics of the system. To this end, we introduce the operator

$$Y_{l\pm|m|}(\nabla) = \left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2}\left(\frac{\partial}{\partial ikx} \pm \frac{\partial}{\partial iky}\right)^{|m|} P_l^m\left(\frac{\partial}{\partial ikz}\right)$$

and, using the relation[12]

$$Y_{lm}(\mathbf{R}_s) h_l^{(+)}(kR_s) \equiv (-1)^l Y_{lm}(\nabla_s) h_0^{(+)}(kR_s),$$

and taking into account the theorems for the addition of spherical functions, we write[7)]

$$\tau_{lm}^{(s)} = 8\pi^2 f_l(E) \sum_{s'\neq s}\sum_{l'm'} Y_{lm}(\nabla_s) Y_{l'm'}^*(\nabla_{s'}) G_0^{(+)}(\mathbf{R}_s, \mathbf{R}_{s'}, E)\tau_{l'm'}^{(s')}.$$

We next rearrange the system (18) in such a way that the operators $Y_{ln}(\nabla)$ are replaced by their linear combinations

$$g_{lm}(\nabla) = \frac{1}{\sqrt{2}}\begin{cases} Y_{lm}(\nabla) + Y_{lm}^*(\nabla), & m>0 \\ -i(Y_{lm}(\nabla) - Y_{lm}^*(\nabla)), & m\leqslant 0 \end{cases} \tag{19}$$

(the normalization of the spherical functions corresponds to the normalization assumed in Ref. 10). This rearrangement makes it easy to separate the real and imaginary parts in (18). The system of algebraic equations takes the final form

$$A_{lm}^{(s)} = 8\pi^2 f_l(E) \sum_{s'\neq s}\sum_{m'} g_{lm}(\nabla_s) g_{lm'}(\nabla_{s'}) G_0^{(+)}(\mathbf{R}_s, \mathbf{R}_{s'}, E) A_{lm'}^{(s')}. \tag{20}$$

The differentiation operators ∇_s and $\nabla_{s'}$ act here on the variables $\mathbf{R}_s$ and $\mathbf{R}_{s'}$ in the Green's function $G_0^{(+)}(\mathbf{R}_s, \mathbf{R}_{s'}, E)$ at the locations of the two-dimensional lattice points, and $A_{lm} = (\tau_{lm} \pm \tau_{lm}^*)$. We seek the solution of the system (20) in the form

$$A_{lm}^{(s)} = A_{lm}\exp(i\varkappa\mathbf{R}_s), \quad \varkappa = (\varkappa_x, \varkappa_y, 0),$$

is a two-dimensional quasimomentum in the plane of the lattice. Using the spectral representation for the Green's function

$$G_0^{(+)}(\mathbf{R}_s, \mathbf{R}_{s'}, E) = \frac{1}{2\pi}\frac{\exp(ik|\mathbf{R}_s - \mathbf{R}_{s'}|)}{|\mathbf{R}_s - \mathbf{R}_{s'}|} = \frac{1}{(2\pi)^2}\int d\mathbf{q}\frac{\exp[i\mathbf{q}(\mathbf{R}_s - \mathbf{R}_{s'})]}{\varepsilon - (E+i\gamma)}$$

and changing to summation over the reciprocal-lattice vectors $\mathbf{b}$:

$$\sum_{s'\neq 0}\exp[-i(\mathbf{q}-\varkappa)\mathbf{R}_{s'}] = \frac{(2\pi)^2}{S_0}\sum_{\mathbf{K}}\delta(\mathbf{q}_\parallel - \mathbf{K}) - 1 \tag{21}$$

(S_0 is the area of the unit cell and $\mathbf{K} = \varkappa + 2\pi\mathbf{b}$) we have

$$A_{lm} = \frac{1}{\pi} f_l(E)\sum_{m'} A_{lm'}\int d\mathbf{q}\frac{g_{lm}(\mathbf{q}) g_{lm'}(\mathbf{q})}{\varepsilon - (E+i\gamma)}\left\{\frac{(2\pi)^2}{S_0}\sum_{\mathbf{K}}\delta(\mathbf{q}_\parallel - \mathbf{K}) - 1\right\}. \tag{22}$$

Calculating the imaginary part of the second term in the curly brackets of (22) and using the explicit form of the amplitude of the resonance scattering of the electron (6), we write

$$(E-E_0)A_{lm} = -\frac{\Gamma_0}{2\pi k}\sum_{m'} A_{lm'}\left\{\int d\mathbf{q}\frac{g_{lm}g_{lm'}}{\varepsilon - (E+i\gamma)}\left[\frac{(2\pi)^2}{S_0}\sum_{\mathbf{K}}\delta(\mathbf{q}_\parallel - \mathbf{K}) - \right.\right. \\ \left.\left. - \int d\mathbf{q}\frac{g_{lm}g_{lm'}}{\varepsilon - E}\right]\right\}. \tag{23}$$

The integration in the second term in the curly brackets of (23) is performed in the sense of the principal value. Recognizing further that $d\mathbf{q} = d\mathbf{q}_\parallel dq_z$, where z is perpendicular to the lattice plane, we obtain ultimately after integrating with respect to $\mathbf{q}_\parallel$

$$(E-E_0)A_{lm} = \sum_{m'} A_{lm'}\left(\Delta_{(m,m')}^{(l)} - \frac{i}{2}\Gamma_{(m,m')}^{(l)}\right), \tag{24}$$

where

$$\Delta_{(m,m')}^{(l)} = -\frac{\Gamma_0}{k}\left\{\frac{4\pi}{S_0}\sum_{\mathbf{K}}\int_{-\infty}^{+\infty}\frac{dq_z g_{lm}g_{lm'}}{q_z^2/2 + K^2/2 - E} - \frac{1}{\pi}\int\frac{d\mathbf{q} g_{lm}g_{lm'}}{\varepsilon - E}\right\}, \tag{25}$$

$$\Gamma^{(l)}_{(m,m')}=\frac{4\pi^2\Gamma_0}{S_0 k k_z}[g_{lm}(\mathbf{k})g_{lm'}(\mathbf{k})+g_{lm}(\mathbf{k}_r)g_{lm'}(\mathbf{k}_r)]\eta(k^2-\varkappa^2). \quad (26)$$

Here $k_z=(2E-\varkappa^2)^{1/2}$ and $\mathbf{k}_r$ is a vector with components $(\varkappa_x, \varkappa_y, -k_z)$ and coincides with the vector $\mathbf{k}$ mirror-reflected in the lattice plane. It is seen from (25) and (26) that only states of like parity relative to reflection in the lattice plane interact with one another (the parity of these states coincides with the parity of $l+|m|$). For example, for $l=1$ the system (24) breaks up into two subsystems, one of which corresponds to $m=0$ (odd state) and the other to $m=\pm 1$ (even states). For the odd state we have the dispersion equation

$$E^{(-)}(\varkappa)=E_0+\Delta^{(-)}(\varkappa, k)-{}^1/_2 i\Gamma^{(-)}(\varkappa, k). \quad (27)$$

where

$$\Delta^{(-)}(\varkappa,k)=-\frac{3\alpha}{2\pi}\left[\frac{4\pi}{S_0}\sum_{\mathbf{K}}\int_{-\infty}^{+\infty}\frac{q_z^2dq_z}{q_z^2/2+K^2/2-E}-\frac{1}{\pi}\int\frac{q_z^2d\mathbf{q}}{\varepsilon-E}\right]$$

$$=-3\alpha\sum_{s'}{}'\frac{\cos\varkappa\mathbf{R}_{s'}}{R_{s'}}\left[\left(k^2-\frac{2}{R_{s'}^2}\right)\cos kR_{s'}-\frac{2k}{R_{s'}}\sin kR_{s'}\right], \quad (28)$$

$$\Gamma^{(-)}(\varkappa,k)=\frac{12\pi\Gamma_0 k_z}{S_0 k^3}\eta(k^2-\varkappa^2). \quad (29)$$

The dispersion law for the even states is given by

$$E^{(+)}_{1,2}(\varkappa)=E_0+\frac{\Delta_{11}+\Delta_{22}-{}^1/_2 i(\Gamma_{11}+\Gamma_{22})}{2}\pm\left[\left(\frac{\Delta_{11}-\Delta_{22}-{}^1/_2 i(\Gamma_{11}-\Gamma_{22})}{2}\right)^2+\left(\Delta_{12}-\frac{i}{2}\Gamma_{12}\right)^2\right]^{1/2}. \quad (30)$$

We have introduced here the notation

$$\Gamma_{11}=\frac{6\pi\Gamma_0}{S_0 k^3}\frac{\varkappa^2}{k_z}\eta(k^2-\varkappa^2)\sin^2\varphi,$$

$$\Gamma_{22}=\frac{6\pi\Gamma_0}{S_0 k^3}\frac{\varkappa^2}{k_z}\eta(k^2-\varkappa^2)\cos^2\varphi,$$

$$\Gamma_{12}=\frac{6\pi\Gamma_0}{S_0 k^3}\frac{\varkappa^2}{k_z}\eta(k^2-\varkappa^2)\sin\varphi\cos\varphi;$$

the angle φ is defined by

$$\varphi=\arccos\left(\frac{\varkappa\mathbf{a}}{|\varkappa||\mathbf{a}|}\right), \quad \mathbf{a}=(a_x, a_y, 0).$$

We note the difference between the near-threshold values of the function $\mathrm{Im}E^{(\pm)}(\varkappa)$ with changing k_z at $k^2-\varkappa^2\ll\varkappa^2$. Whereas for the odd states with $l=1$ and $m=0$ the rate of autoionization is $\Gamma^{(-)}\sim k_z$, for the even states at $m=\pm 1$ we have $\Gamma^{(+)}\sim 1/k_z$, just as in the decay of the Feshbach autoionization S state.[9] This result is due to the form of the distribution of the electron density relative to the plane of the lattice for different projections of m. A specific property of the lattice of centers having an autoionization state with $l\neq 0$ is the dependence of the decay probability on the direction of the quasimomentum $\varkappa$. We illustrate this using as an example $l=1$ for the autoionization band of the even states in the case of a quadratic lattice $(a_x=a_y=a)$. The point group of this lattice contains a fourfold symmetry axis, through which pass two pairs of mirror-symmetry planes: one is made up of the symmetry planes σ_x and σ_y, and the other of two diagonal planes passing through the origin. Accordingly the angle φ, reckoned from the vector a directed along the diagonal of the unit cell, takes on values 0, $\pm\pi/4$, and $\pi/2$. For these values of φ it follows from (25) and (30) that

$\Delta_{12}=0$, $\Delta_{11}=\Delta_{22}$.

Thus, even states on the symmetry axis of the crystal decay into symmetrical (g) and antisymmetrical (u) states, with

$$E_g^{(+)}(\varkappa)=E_0+\Delta^{(+)}(\varkappa,k)-{}^1/_2 i\Gamma_g^{(+)}(\varkappa,k), \quad (31)$$

$$E_u^{(+)}(\varkappa)=E_0+\Delta^{(+)}(\varkappa,k) \quad (\Gamma_u^{(+)}\equiv 0), \quad (32)$$

where

$$\Delta^{(+)}(\varkappa,k)=\frac{3\alpha}{4\pi}\left[\frac{4\pi}{S_0}\sum_{\mathbf{K}}\int_{-\infty}^{+\infty}\frac{K^2dq_z}{q_z^2/2+K^2/2-E}-\frac{1}{\pi}\int\frac{(q^2-q_z^2)d\mathbf{q}}{\varepsilon-E}\right]$$

$$=-3\alpha\sum_{s'}{}'\frac{\cos\varkappa\mathbf{R}_{s'}}{R_{s'}}[\cos kR_{s'}+kR_{s'}\sin kR_{s'}], \quad (33)$$

$$\Gamma_g^{(+)}(\varkappa,k)=\frac{6\pi\Gamma_0}{S_0 k^3}\frac{\varkappa^2}{k_z}\eta(k^2-\varkappa^2).$$

The stabilization of the autoionization states for a two-dimensional lattice, at quasimomenta directed along the symmetry axes of the crystal, has a simple physical explanation. In fact, since decay is possible only in planes passing through the vector $\varkappa$ and the z axis, the antisymmetrical (u) state, which has a wave-function node in these planes, has zero width. It is easy to show that for a rhombic lattice this takes place at $\varphi=(0,\pi/2)$.

We examine now the question of the width, position, and singularities of the autoionization bands for even and odd states in the case $l=1$. It follows from (28) and (33) that for the even states ($m=0$) and for the odd states the point $\varkappa=0$ corresponds respectively to the upper and lower edges of the energy band, with the width of the band of the even states double the width of that of the odd states, with a value of the order of $\sim\alpha/a^3$. In the case of a quadratic lattice it is also easy to establish that the lower edge of the band of odd states (and accordingly the upper edge for the even states) corresponds to the value $\varkappa a=\pm\pi$ and to the point X in the Brillouin zone. The singularities of the behavior of $E(\varkappa)$ near $\varkappa=0$ and on the boundary of the first Brillouin zone are also analogous to the singularities of the one-dimensional crystal (see the Appendix).

4. CONCLUSION

In conclusion, we discuss the question of the possibility of observing effects connected with the population and autoionization of the considered state in one-dimensional and two-dimensional systems (these systems include polymer molecules, monolayers produced on the surface of a solid by adsorption of atomic particles, quasi-one-dimensional crystals, etc.). We can point out two processes in which the band structure of the autoionization states manifests itself quite distinctly. These are photoionization from the inner electron shells under the influence of monochromatic x radiation and scattering of a monoenergetic electron beam. The energy and direction of the produced (or scattered) electrons therefore fix in this case the quasimomentum $\varkappa$ of the electron in the intermediate autoionization state. The function $E(\ )$ is therefore obtained directly from the threshold, given by Eq. (16), of the appearance of photoelectrons (or of resonantly scattered electrons). For photoionization, for example, the frequency threshold is $\mathscr{E}=I+E(\varkappa)$, where I is the

ionization potential. On the other hand, information on the decay characteristics of the band states is carried by the intensity of the corresponding process $J \sim \Gamma(\varkappa)$. The most interesting effects should then be expected near the threshold $\varkappa = \pm k$.

States with zero width $\Gamma = 0$ are not excited in resonant scattering of the electrons, but can become populated by photoabsorption (a curious fact in this case is the ve very possibility of electron motion in states that are located against a continuum background and are stable with respect to autoionization). We note that the use of a directional beam of light quanta makes it possible to vary the conditions of population of different decay states. For example, in the process of photoionization from the K shell, when the chains are irradiated parallel to their direction, the states predominantly populated should be those with angular momentum projection $|m| = 1$. Similar conditions for preferred population can be produced also for a two-dimensional crystal.

The search for autoionization bands is of interest in itself because of the present intensive research on the interaction of electrons with polymer molecules and monatomic films on solid surfaces.[16] The predicted states might be expected, for example, for a monolayer of molecular nitrogen, which has a low-energy resonance ($E_0 = 2.3$ eV),[9] of for a monolayer of alkali-metal atoms (having a p-resonance at energies $E_0 \sim 0.2$–0.3 eV) on the surface of crystalline nickel.

APPENDIX

We investigate the singularities of $\mathrm{Re}E^{(\pm)}(\varkappa)$ near the point $\varkappa = 0$ and on the boundary of the first Brillouin zone. To this end we use an expression for $\Delta^{(-)}$ in terms of a sum over the vectors of the reciprocal lattice [see (28)]. Closing from above the integration contour and recognizing that at infinity the integrals cancel each other, we obtain

$$\Delta^{(-)}(\varkappa) = 3\alpha \left\{ \frac{2\pi}{S_0} \sum_{\mathbf{K}} [(|\varkappa+\mathbf{K}|)^2 - 2E]^{1/2} - \int_{\sqrt{2E}}^{\infty} K dK (K^2-2E)^{1/2} \right\}. \quad (A.1)$$

In the case of a square lattice

$$|\varkappa+\mathbf{K}| = [(\varkappa_x + 2\pi n/a)^2 + (\varkappa_y + 2\pi m/a)^2]^{1/2}, \quad (A.2)$$

Therefore in the lowest-order approximation in the parameter $ka \ll 1$ the expression (A.1) can be written in the form

$$\Delta^{(-)}(\varkappa) = \frac{12\pi^2\alpha}{a^3} \left\{ \sum_{n,m} [(\xi_x+n)^2 + (\xi_y+m)^2]^{1/2} - \int_0^{\infty} \xi^2 d\xi \right\}, \quad (A.3)$$

where $\xi_x = \varkappa_x a/2\pi$, $\xi_y = \varkappa_y a/2\pi$. Representing

$$\frac{1}{[(\xi_x+n)^2+(\xi_y+m)^2]^{1/2}} = \frac{\partial^2}{\partial\lambda^2} \frac{\exp\{-\lambda[(\xi_x+n)^2+(\xi_y+m)^2]^{1/2}\}}{[(\xi_x+n)^2+(\xi_y+m)^2]^{1/2}} \Big|_{\lambda=0},$$

and also using the formula[14]

$$\frac{\exp\{-\lambda[(\xi_x+n)^2+(\xi_y+m)^2]^{1/2}\}}{[(\xi_x+n)^2+(\xi_y+m)^2]^{1/2}} = \frac{2}{\pi} \int_0^{\infty} K_0[(\xi_x+n)(\lambda^2+z^2)^{1/2}] \cos(\xi_y+m) z dz,$$

we ultimately obtain for the expression (A.3), by the procedure described in Ref. 17,

$$\Delta^{(-)} = S_1 + S_2, \quad (A.4)$$

where

$$S_1 = \frac{6\alpha}{a^3} \sum_{n=1}^{\infty} \frac{1}{n^3} [\cos \varkappa_x a n + \cos \varkappa_y a n]$$

is the sum along the chain of centers passing through the origin,

$$S_2 = \frac{24\pi^2\alpha}{a^3} \frac{\partial^2}{\partial\lambda^2} \int_0^{\infty}\int_0^{\infty} dz dt \Big\{ (T_x(y) + T_y(x)) \times \frac{\exp[-(\lambda^2+z^2)^{1/2} \mathrm{ch}\, t]}{1-\exp[-(\lambda^2+z^2)^{1/2} \mathrm{ch}\, t]} \sum_{p=-\infty}^{+\infty} \delta(z-2\pi p) - \frac{2\delta(z)}{(\lambda^2+z^2)^{1/2} \mathrm{ch}\, t} \Big\}_{\lambda=0},$$

$$T_x(y) = \cos\frac{\varkappa_x a z}{2\pi} \mathrm{ch}\left(\frac{\varkappa_y a z}{2\pi} (\lambda^2+z^2)^{1/2} \mathrm{ch}\, t\right).$$

It is easily seen that S_2 has no singularities near $\varkappa = 0$ (the corresponding expansion in powers of $\varkappa$ begins with $k = 2$), nor near the Brillouin-zone boundary. Thus, the singularities of the behavior of $\Delta^{(-)}$ are determined by the singularities of the sum S_1, which can be investigated in analytic form [see (12) and (13)]. This result should be expected, since the divergence of the series (28) at large R_s, when expanded in powers of $\varkappa$, corresponds exactly to the divergence near the origin for the reciprocal lattice, i.e., near the point taken into account in the analysis of the one-dimensional sums. It follows also from the obtained expressions that on the boundary of the Brillouin zone, for one-dimensional and quadratic lattices, the condition $\mathrm{grad}_{\varkappa} \mathrm{Re}E(\varkappa) = 0$ is satisfied, in agreement with the properties of ordinary bands located below the vacuum level ($E < 0$).

[1)] The interaction responsible for electron transition from one atomic center to another.

[2)] This question is meaningful only for structures having a channel for free departure of the electron to infinity, i.e., linear, two-dimensional, and semi-bounded crystals.

[3)] A classification of the autoionization states of atomic (molecular) particles is given in the reviews[7,8].

[4)] The effects investigated by us, which are connected with the interaction of resonances of the Breit-Wigner type, differ substantially from those that take place in exchange interaction of one-center states of the Bethe-Peierls type. A brief investigation of the latter is reported in the monograph of Demkov and Ostrovskiĭ[11] for a chain of zero-radius potentials that describe S-scattering of an electron by each of the centers. Owing to the lack of a centrifugal barrier (or of some other stabilization mechanism) on the isolated centers, the problem of bands of quasistationary states obviously does not arise within the framework of this model.

[5)] Their contribution has a relative smallness $\sim kf_0$, where f_0 is the amplitude of S scattering of an electron by an isolated center.

[6)] This question is considered within the framework of the model of zero-radius potentials ($l = 0$) in the monograph of Demkov and Ostrovskiĭ.[11]

[7)] Another method of deriving Eqs. (18) is given in Ref. 5.

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Self-consistent description of metal-insulator phase transition in the two-band model

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A two-band model is proposed for a metal-insulator transition with lattice distortion, with account taken of the intraband and interband Coulomb interaction, as well as of the anisotropy of the Fermi surface. The phase diagram of the system as a function of the degree of band occupation is constructed by solving the system of self-consistency equations for the chemical potential and for the gap. It is shown that two dielectric phases exist, and one or the other is stable, depending on the band occupation. The results are compared with experiments on oxides and sulfides of transition metals.

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1. INTRODUCTION

It is known[1,2] that a narrow-band metal whose electron spectrum satisfies the condition

$$\varepsilon_1(\mathbf{k})-\mu=-\varepsilon_1(\mathbf{k}+\mathbf{Q})+\mu \tag{1}$$

where the wave vector $2\mathbf{Q}$ coincides with the reciprocal-lattice vector, is unstable to doubling of the period of the cell and goes over into the insulator state. At the same time, the band structure of narrow-band transition-metal compounds is characterized by the presence of several bands that intersect in the vicinity of the Fermi level. Therefore more general is a two-band model, in which band 1 satisfies condition (1) while band 2 does not satisfy it. Such a model was proposed in Ref. 3, and it was shown that allowance for the second band greatly broadens the class of possible solutions of the self-consistency equation for the order parameter $\Delta=g(\mathbf{Q})\langle b_Q+b_{-Q}^+\rangle/\sqrt{N}$, where b_q is the annihilation operator of a phonon with wave vector $\mathbf{q}$, and $g(\mathbf{q})$ is the electron-phonon interaction constant. In particular, several nontrivial solutions appear, thus indicating the presence of metastable states.

In Ref. 3, however, no account was taken of the Coulomb interaction. More accurately, account was taken of only that part of this interaction which leads to a renormalization of the interaction constants. In the two-band case there appears also a coupling between the bands on account of the self-consistent occupation numbers, and this changes the self-consistency equation. In addition, it was assumed in Ref. 3, in the course of the solution of the system of self-consistency equations for the chemical potential μ and for the gap Δ, that μ depends little on the temperature T, and $\mu(T=0)$ was substituted in the equation for Δ.

The aim of the present paper is a fully self-consistent description of the metal–insulator transition (MIT) in the two-band model, with account taken of the Coulomb interaction. In addition, we consider the influence of the anisotropy of the Fermi surface, of the pressure, of doping, and of the magnetic field on the MIT.

2. HAMILTONIAN AND GREEN'S FUNCTIONS

We consider a system of electrons and phonons described by a Hamiltonian

$$\mathcal{H}=\mathcal{H}_{el}+\mathcal{H}_{ph}+\mathcal{H}_{el-ph}, \tag{2}$$

where

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