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RELATIVISTIC AND CORRELATION EFFECTS IN AUGER SPECTROSCOPY OF ATOMS AND SOLIDS

It is presented an advanced, consistent theoretical scheme for determination of the energy and spectral characteristics of the Auger process (decay, transition) in atomic systems and solids with correct accounting for the relativistic and nuclear effects. As the basic approach to calculating the Auger spectra of solids there is used a consistent theoretical method, based on the S-matrix formalism by Gell-Mann and Low and relativistic many-body perturbation theory formalism. Universal relativistic Dirac-Hartree-Slater method is taken as a theoretical method for calculating the electronic wave functions and energies of the states and transitions. The advanced data on the Auger electron energy for some solids (Ge,Ag) with accounting for the relativistic and nuclear finite size effects are listed.

1. In the modern atomic, molecular physics, physics of solids and surfaces there are used different methods of spectroscopy of electromagnetic radiation and spectroscopy of charged particles in order to provide an analysis, diagnose and sensing the composition (analysis) of the energy and radiative properties of atomic, molecular systems, surface and near-surface layers of solids. Usually a classification of the main methods of spectroscopy used to analyze the above listed physical systems is based on the type of particles used to excite the spectrum and particles - carriers of information about the composition of the substance.

One of the most effective and spread methods to study the chemical composition of solid surfaces and near-surface layers [1-8] is the Auger electron spectroscopy. Analysis and sensing the Auger spectra in atomic, molecular systems and solids allow to get the important information a for the whole number of scientific and technological physical and chemical applications, including many topics of modern optics and spectroscopy, laser, astrophysics, ultra cold plasma diagnostics, forecasting properties of Rydberg substance, Bose-condensate of Rydberg atoms etc. One should underline the theoretical and practical interest for a such of applications and related physical disciplines, which include atomic, molecular, quantum optics and spectroscopy, quantum electronics, l construction of kinetic models of new short-wave laser circuits, physics of laboratory, astrophysical plasma, quantum , sensor and photoelectronics etc.

Naturally, at the present time there are carried out relatively a great number of different theoretical models and schemes in order to calculate the corresponding energy and s[spectroscopic parameters of the Auger transitions, and, generally speaking, a total set of characteristics of the Auger spectra. Surely there are developed a group of effective experimental methodises in order to measure the Auger transitions characteristics (e.g. [1-12]).

It should be noted that there is a whole group of methods based on the use of data on photoionization cross sections and measurements of the dependence of the intensity of photoelectron lines on the kinetic energy of photoelectrons by varying the energy of the exciting X-ray radiation (for example, using synchrotron radiation) or by choosing an appropriate set of photoelectron lines (see, e.g., [1-5]).

The most popular in the theoretical Auger spectroscopy is so called two-step model, which is used most widely when calculating the Auger spectra (transitions, decay) characteristics [1-16]. The physical aspects of the cited model are quite reasonable. It is known that since the vacancy lifetime in an inner atomic shell is rather long (about 10^{-17} to 10^{-14}s), the

atomic system ionization and the Auger emission processes are considered to be two independent processes. Though the more correct dynamic theory of the Auger effect [3,7-9] is developed and the above mentioned processes are not believed to be independent from one another in this theory. The fact is taken into account that the relaxation processes due to Coulomb interaction between electrons and resulting in the electron distribution in the vacancy field have no time to be over prior to the transition. One should note that the consistent and quantitively correct Auger decay theory should take a definite number of the physically important complicated exchange-correlation effects into consideration. Above them one should separate such effects as exchange-polarization effects, an energy dependence of the vacancy mass operator, a continuum pressure, spreading of the initial state over a set of configurations etc. In a great number of papers it has been shown that in order to ger a current information about energy and spectral characteristics of the Auger process (decay, transition) it is necessary to provide a correct accounting for the relativistic, radiation and nuclear finite size effects contributions especially under consideration of the middle and heavy atomic and molecular systems, solids etc (eg.[10-14]).

The aim of the work is to provide a consistent theoretical scheme for determination of the energy and spectral characteristics of the Auger process (decay, transition) in atomic systems and solids with correct accounting for the relativistic, and (relaxation) effects. As the basic approach to calculating the Auger spectra of solids we use an consistent theoretical method, based on the S-matrix formalism by Gell-Mann and Low and relativistic many-body perturbation theory formalism, presented in Refs. [11-14]. However, in contrast to the original version of the theoretical approach used [9-14], a simpler and more universal relativistic Dirac-Hartree-Slater method was taken as a theoretical method for calculating the electronic wave functions and energies of the hundred states. The numerical data on the Auger electron energy for some solids (Ge,Ag) with accounting for the relativistic and nuclear finite size effects are listed. Other details can be found in Refs. [9-16]

2. As the key moments of our method fpor accounting the relativistic and nuclear effects in Auger spectroscopy are shortly have been mentioned in Refs. [9,10], here we are limited only my the principally important model points. It should be recalled that when colliding with an atomic system, the primary electron e, which has energy sufficient to ionize one of the main levels of the atom, knocks out the electron ej from this level, transferring the atom A to an ionized, unstable state A^+ with a hole at the level which in the general case may correspond to some set of final states E_A.

Following to Ref. [9,11], one should determine the uger transition probability and the Auger line intensity through the square of an electron interaction matrix element (the classical golden Fermi rule) having the form [11,13]:

$$V^{\omega}_{1234} = [(j_1)(j_2)(j_3)(j_4)]^{1/2} \sum_{\lambda\mu} (-1)^{\mu} \begin{pmatrix} j_1 j_3 & \lambda \\ m_1 - m_3 & \mu \end{pmatrix} \times \mathrm{Re}\, Q_{\lambda}(1234)$$

$$Q_{\lambda} = Q_{\lambda}^{\mathrm{Qul}} + Q_{\lambda}^{\mathrm{Br}}. \qquad (1)$$

The terms $Q_{\lambda}^{\mathrm{Qul}}$ and $Q_{\lambda}^{\mathrm{Br}}$ correspond to subdivision of the relativistic interelectron potential into Coulomb part $cos|\omega|r_{12}/r_{12}$ and Breit component $cos|\omega|r_{12}\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2/r_{12}$. The real part of the electron interaction matrix element is determined using expansion in terms of the known Bessel functions:

$$\frac{\cos|\omega|\eta_{12}}{\eta_{12}} = \frac{\pi}{2\sqrt{\eta_1 r_2}} \sum_{\lambda=0} (\lambda) J_{\lambda+1/2}(|\omega|r_<) J_{-\lambda-1/2}(|\omega|r_>) P_{\lambda}(\cos \mathbf{r}_1 \mathbf{r}_2) \qquad (2)$$

where J is the 1st order Bessel function, $(\lambda)=2\lambda+1$. The Coulomb part $Q_{\lambda}^{\mathrm{Qul}}$ is expressed in terms of radial integrals R_{λ}, angular coefficients S_{λ} [11-13]:

$$\mathrm{Re}\, Q_{\lambda}^{\mathrm{Qul}} = \frac{1}{Z} \mathrm{Re}\{R_1(1243) S_{\lambda}(1243) + R_{\lambda}(\tilde{1}\,243\tilde{3}) S_{\lambda}(\tilde{1}\,243\tilde{3}) + R_{\lambda}(1\tilde{2}\tilde{4}3) S_{\lambda}(1\tilde{2}\tilde{4}3) + R_{\lambda}(\tilde{1}\,\tilde{2}\tilde{4}\,\tilde{3}) S_{\lambda}(\tilde{1}\,\tilde{2}\tilde{4}\,\tilde{3})\}. \qquad (3)$$

As a result, the Auger decay probability is expressed in terms of $\mathrm{Re}Q_{\lambda}(1243)$ matrix elements:

$$\mathrm{Re}\,R_\lambda(1243)=\iint d\eta r_1^2 r_2^2 f_1(\eta) f_3(\eta) f_2(r_2) f_4(r_2) Z_\lambda^{(1)}(r_<) Z_\lambda^{(1)}(r_>) \quad (4)$$

where f is the large component of radial part of single electron state Dirac function; function Z and angular coefficient are defined in refs. [7,8].

The other items in (3) include small components of the Dirac functions; the sign «~» means that in (3) the large radial component f_i is to be changed by the small g_i one and the moment l_i is to be changed by $\tilde{l}_i = l_i - 1$ for Dirac number æ$_i$> 0 and l_i+1 for æ$_i$<0. The Breit interaction is known to change considerably the Auger decay dynamics in some cases. The Breit part of Q is defined in [7]-9]. The corresponding basis's of the relativistic wave functions are determine within the standard X_a method (e.g. [11,15,16]).

The calculation of radial integrals **Re**R_λ(1243) is reduced to the solution of a system of differential equations [11-13]:

$$y_1' = f_1 f_3 Z_\lambda^{(1)}(\alpha|\omega|r) r^{2+\lambda}$$

$$y_2' = f_2 f_4 Z_\lambda^{(1)}(\alpha|\omega|r) r^{2+\lambda}$$

$$y_3' = [y_1 f_2 f_4 + y_2 f_1 f_3] Z_\lambda^{(2)}(\alpha|\omega|r) r^{1-\lambda} \quad (5)$$

In addition,

$$y_3(\infty) = \mathbf{Re} R_\lambda(1243),$$

$$y_1(\infty) = X_\lambda(13). \quad (6)$$

In order to get the consistent relativistic expressions for the Auger widths and Auger electron transitions energies we use an consistent theoretical method, based on the S-matrix formalism by Gell-Mann and Low and relativistic many-body perturbation theory formalism, presented in Refs. [11-14].

The Auger width is obtained from the adiabatic Gell-Mann and Low formula for the energy shift [7]. In particular, the expression for the key contribution to the Auger level width with a vacancy $n_\alpha l_\alpha j_\alpha m_\alpha$ is given as follows [10-12]:

$$\sum_\lambda \frac{2}{(\lambda)(j_\alpha)} \sum_{\beta\gamma \le f} \sum_{k>f} Q_\lambda(\alpha k\, \gamma\beta) Q_\lambda(\beta\gamma\, k\alpha) \quad (7)$$

And further the corresponding "exchange diagrams" contribution is as:

$$\frac{2}{(j_\alpha)} \sum_{\lambda_1\lambda_2} \sum_{\beta\gamma \le f} \sum_{k>f} Q_{\lambda_1}(\alpha k\gamma\beta) Q_{\lambda_2}(\beta\gamma k\alpha) \begin{Bmatrix} j_\alpha & j_\gamma & \lambda_2 \\ j_k & j_\beta & \lambda_1 \end{Bmatrix} \quad (8)$$

The partial items of the $\sum_{\beta\gamma} \sum_k$ ❑ sum answer to contributions of $\alpha^{-1} \to (\beta\gamma)^{-1} K$ channels resulting in formation of two new vacancies $\beta\gamma$ and one free electron k: $\omega_k = \omega_\alpha + \omega_\beta - \omega_\alpha$. The final expressions for the width in the representation are listed in Refs. [9-13].

Regarding the accounting for the exchange-correlation corrections. The standard Slater potential and the modified correlation potential of the Gunnarson-Lundqvist type has been added into the Dirac-Hratree-Slater equations (see details, e.g., [10-15]).

The key element of novelty is the generation of optimized bases of relativistic Dirac-Hartree-Slater orbitals. To achieve this goal, one should use the formally accurate iterative approach, which is based on the procedure of minimizing the contribution to the imaginary part of the electronic energy shift due to the relativistic perturbation theory second order polarization diagrams associated with the exchange of longitudinal photons. The contribution of these diagrams depends on the calibration of the photon propagator. It is also important to correctly take into account exchange-correlation effects of "2" and higher PT orders, in particular, corrections for the polarization. The standard many-body polarization functional is usually used and added to the inter-electron interaction operator (see the details, for example, in refs. [10-16]). Very important point of the whole scheme is application of correct procedure for taking into account the states of the continuum within the Dirac-Slater-Sturm method (see details in Refs. [10,12]). The contribution of the lower order radiative corrections to the energy and spectral characteristics can be also taken into account with using the methodology [9-15], however,

one should wait for a quite little contribution into studied characteristics.

The formulas for the Auger decay probability include the radial integrals $R_\alpha(\alpha k\gamma\beta)$, where one of the functions describes electron in the continuum state. Following to Ref. [10], the energy of an electron formed due to a transition *jkl* is defined by the difference between energies of atom with a hole at *j* level and double-ionized atom at *kl* levels in final state:

$$E_A\left(\mathrm{jkl}, L_J\right) = E_A^{+(j)} - E_A^{2+(\mathrm{kl}, L_J)} \qquad (10)$$

To single out the above-mentioned correlation effects, the equation (12) can be presented as:

$$E_A(jkl, {}^{2S+1}L_J) = E(j) - E(k) - E(l) - \Delta(k,l; {}^{2S+1}L_J) \qquad (11)$$

where the item Δ takes into account the dynamic correlation effects (relaxation due to hole screening with electrons etc.)

Further, in order to take these effects into consideration, one should use the standard procedure, which is elaborated in an atomic spectroscopy (e.g.[2,3,11,15]).

For solid phase, the more precise form of equation (11) is given by the following equation [9]:

$$E^s{}_A(jkl, {}^{2S+1}L_J) = E_A(jkl, {}^{2S+1}L_J) + \Delta E^s + R_{rel} + e\Phi \qquad (12)$$

where ΔE^s is a correction for the binding energy change in the solid; R_{rel}, the same for out-of-atom relaxation; $e\Phi$ takes into account the standard work of output. The other topics can be, for example, found in refs. [9-16].

3. In table 1 we present our theoretical data (column "This") the data on the Auger electron energy for some solids (Ge, Ag) as well as the experimental data (column E), theoretical semi-empirical method data within the Larkins' equivalent core approximation [2,3] (column A), non-gauge-invariant relativistic Dirac-Fock method (colimn B), the gauge-invariant relativistic Dirac-Fock method (column C) [1,3,10].

Table 1. Experimental and theoretical data for Auger electron energy: E- experiment; A, semi-empirical method - [2]; B- [8]; C – [15]; D – [3], E- this work;

Solid	Auger line	E	Th: A	Th: B
Ge	$L_3M_{4,5}M_{4,5}\,{}^1G_4$	1146.2	1147.2	1146.6
Ag	$M_5N_{4,5}N_{4,5}\,{}^1G_4$	353.4	358.8	354.1
Solid	Auger line	E	Th: C	This
Ge	$L_3M_{4,5}M_{4,5}\,{}^1G_4$	1146.2	1146.2	1146.3
Ag	$M_5N_{4,5}N_{4,5}\,{}^1G_4$	353.4	353.4	353.6

The analysis of the presented data shows that, firstly, the computational accuracy of the classical Larkins' method is about a few eV as an average. The data, obtained within the relativistic perturbator theory methods ([10] and ours) are more correct. The corresponding improvement of the calculational accuracy is reached due to a considerable extent to more correct and consistent accounting for complex interelectron (vacancy) exchange-correlation effects as well as the relativistic and other solid state corrections. The data in the columns "C" and "This work" are more correct in comparison with data in the column B because of the more correct gauge-invariant procedure of generating the relativistic wave functions basis's. Besides, application of correct procedure for taking into account the states of the continuum within the Dirac-Slater-Sturm method (see details in Refs. [10,12] is also very important for adequate model. Naturally, accounting for the effects of the polarization interaction of quasiparticles (electrons and vacancies) and the screening on the basis of the using effective relativistic exchange-correlation functionals is important too. There is of a great interest an application of the method to studying the Auger processes in more heavy systems.

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Summary. It is presented an advanced, consistent theoretical scheme for determination of the energy and spectral characteristics of the Auger process (decay, transition) in atomic systems and solids with correct accounting for the relativistic and exchange-correlation (relaxation) nuclear effects. As the basic approach to calculating the Auger spectra of solids there is used a consistent theoretical method, based on the S-matrix formalism by Gell-Mann and Low and relativistic many-body perturbation theory formalism. Universal relativistic Dirac-Hartree-Slater method is taken as a theoretical method for calculating the electronic wave functions and energies of the states and transitions. The advanced data on the Auger electron energy for some solids (Ge,Ag) with accounting for the relativistic and nuclear finite size effects are listed.

Key words: atomic spectroscopy; Auger spectroscopy; relativistic theory; energy approach; atomic, plasmas, solids systems.

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Софронков О.Н., Тюрін О.В.

РЕЛЯТИВІСТСЬКІ ТА КОРЕЛЯЦІЙНІ ЕФЕКТИ В ОЖЕ-СПЕКТРОСКОПІЇ АТОМІВ ТА ТВЕРДОГО ТІЛА

Резюме. Представлено вдосконалену послідовну теоретичну схему для визначення енергетичних і спектральних характеристик процесу Оже (розпаду, переходу) в атомних системах і твердих тілах з коректним врахуванням релятивістських і кореляційних (релаксаційних) ефектів. В якості основного підходу до розрахунку Оже-спектрів атомних систем, і далі твердих тіл використовується послідовний теоретичний метод, заснований на формалізмі S-матриці Гелл-Манна і Лоу та формалізмі релятивістської теорії збурень багатьох тіл. Універсальний релятивістський метод Дірака-Хартрі-Слетера береться як теоретичний метод розрахунку електронних хвильових функцій і енергій станів та переходів. Наведено передові дані про енергію оже-електронів для деяких твердих тіл (Ge,Ag) з урахуванням релятивістського та ядерного ефектів кінцевого розміру.

Ключові слова: атомна спектроскопія; Оже-спектроскопія; релятивістська теорія; енергетичний підхід; атомні системи, плазмове середовище, тверде тіло.

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