

## QUANTUM CALCULATION OF AUGER SPECTRA FOR Na, Si ATOMS AND SOLIDS

On the basis of calculation in characteristics of Auger decay in the atomic systems and solids within S-matrix Gell-Mann and Low formalism there are presented data on the cross-sections of ionization of internal shells for a number of atoms (Na, Si) and energies of Auger electron transitions in solids (Na, Si).

### INTRODUCTION

Auger electron spectroscopy is the effective method to study the chemical composition of solid surfaces and near-surface layers [1-8]. When considering the method principles, the main attention is given as a rule to the models to draw chemical information from Auger spectra and to the surface composition determination methods by Auger spectrum decoding. It is just the two-step model that is used most widely when calculating Auger decay characteristics. Since the vacancy lifetime in an inner atomic shell is rather long (about  $10^{-17}$  to  $10^{-14}$ s), the atom ionization and Auger emission are considered to be two independent processes. In the more correct dynamic theory of Auger effect [1-3] the processes are not believed to be independent from one another. 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. In fact, the consistent Auger decay theory has to take into account correctly the number of correlation effects, including energy dependence of vacancy mass operator, continuum pressure, spreading of the initial state over a set of configurations etc. [1-6]. Note that the effects are not described adequately to date, in particular within Auger decay theory [2]. In this paper a novel calculation method of Auger decay characteristics for complex atomic systems basing on S-matrix formalism by Gell-Mann and Low [8-12] is applied to calculation of those characteristics for atoms, quasi-molecules and solids. The novel element consists in using of the optimal basis for electron state functions derived from the condition that calibration-non-invariant contribution of the second order polarization diagrams to the imaginary part of multi-electron system energy is minimized already at the first non-disappearing approximation of the perturbation theory (PT) [9-11]. The method has been applied to calculate the ionization cross-sections of inner shells in various atoms and Auger electron energy in solids (Na, Si).

### METHOD FOR CALCULATING THE LINE INTENSITIES AND WIDTHS IN THE AUGER SPECTRA

Within the frame of QED PT approach [8-11] to Auger effect description, Auger transition probability and, accordingly, Auger line intensity are defined by the square of an electron interaction matrix element having the form:

$$V_{1234}^{\omega} = [(j_1)(j_2)(j_3)(j_4)]^{\frac{1}{2}} \times \sum_{\lambda\mu} (-1)^{\mu} \begin{pmatrix} j_1 j_3 & \lambda \\ m_1 - m_3 & \mu \end{pmatrix} \times \text{Re } Q_{\lambda}(1234);$$

$$Q_{\lambda} = Q_{\lambda}^{\text{oul}} + Q_{\lambda}^{\text{Br}}. \quad (1)$$

The terms  $Q_{\lambda}^{\text{oul}}$  and  $Q_{\lambda}^{\text{Br}}$  correspond to subdivision of potential into Coulomb part  $\cos|\omega|r_{12}/r_{12}$  and Breat one,  $\cos|\omega|r_{12}\alpha_1\alpha_2/r_{12}$ . The real part of electron interaction matrix element is determined using expansion in terms of Bessel functions:

$$\frac{\cos|\omega|r_{12}}{r_{12}} = \frac{\pi}{2\sqrt{r_1 r_2}} \times \sum_{\lambda=0} (\lambda) J_{\lambda+\frac{1}{2}}(|\omega|r_{<}) J_{-\lambda-\frac{1}{2}}(|\omega|r_{>}) P_{\lambda}(\cos r_1 r_2). \quad (2)$$

where  $J$  is the 1<sup>st</sup> order Bessel function,  $(\lambda) = 2\lambda + 1$ . Coulomb part  $Q_{\lambda}^{\text{oul}}$  is expressed in terms of radial integrals  $R_{\lambda}$ , angular coefficients  $S_{\lambda}$  [9]:

$$\text{Re } Q_{\lambda}^{\text{oul}} = \frac{1}{Z} \text{Re} \{ R_{\lambda}(1243) S_{\lambda}(1243) + R_{\lambda}(\tilde{1}24\tilde{3}) S_{\lambda}(\tilde{1}24\tilde{3}) + R_{\lambda}(1\tilde{2}\tilde{4}3) S_{\lambda}(1\tilde{2}\tilde{4}3) + R_{\lambda}(\tilde{1}\tilde{2}\tilde{4}\tilde{3}) S_{\lambda}(\tilde{1}\tilde{2}\tilde{4}\tilde{3}) \}. \quad (3)$$

As a result, Auger decay probability is expressed in terms of  $\text{Re} Q_{\lambda}(1243)$  matrix elements [9]:

$$\begin{aligned} \text{Re}R_\lambda(1243) = & \iint dr_1 r_1^2 r_2^2 f(r_1) f_3(r_1) f_2(r_2) f_4(r_2) \times \\ & \times Z_\lambda^{(1)}(r_1) Z_\lambda^{(1)}(r_2), \end{aligned} \quad (4)$$

where  $f$  is the large component of radial part of single electron state Dirac function and function  $Z$  is [8]:

$$Z_\lambda^{(1)} = \left[ \frac{2}{|\omega_{13}| \alpha Z} \right]^{\lambda+1/2} \frac{J_{\lambda+1/2}(\alpha |\omega_{13}| r)}{r^\lambda \Gamma(\lambda + 3/2)}.$$

The angular coefficient is defined by standard way [7]. The other items in (3) include small components of 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  $\alpha_i > 0$  and  $l_i + 1$  for  $\alpha_i < 0$ . Breat interaction is known to change considerably Auger decay dynamics in some cases (c. f. [6]). Breat part of  $Q$  is defined as the sum:

$$Q_\lambda^{\text{Br}} = Q_{\lambda, \lambda-1}^{\text{Br}} + Q_{\lambda, \lambda}^{\text{Br}} + Q_{\lambda, \lambda+1}^{\text{Br}}, \quad (5)$$

where the contribution of our interest is determined as:

$$\begin{aligned} Q_\lambda^{\text{Br}} = & \frac{1}{Z} \text{Re} \{ R_\lambda(12\tilde{4}3) S_\lambda'(12\tilde{4}3) + \\ & + R_\lambda(\tilde{1}243) S_\lambda'(1243) + R_\lambda(\tilde{1}2\tilde{4}3) S_\lambda'(\tilde{1}2\tilde{4}3) + \\ & + R_\lambda(1\tilde{2}4\tilde{3}) S_\lambda'(1\tilde{2}4\tilde{3}) \}. \end{aligned} \quad (6)$$

The Auger width is obtained from the adiabatic Gell-Mann and Low formula for the energy shift [9]. The contribution of  $A_d = \text{---}$  diagram to Auger level width with vacancy  $n_\alpha l_\alpha j_\alpha m_\alpha$  is:

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

while contribution of  $A_{\text{ex}} = \text{---}$  one is:

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

The formulas (7), (8) define the full Auger level width. The partial items of the  $\sum_{\beta\gamma} \sum_k$  sum answer to contributions of  $\alpha^{-1} \rightarrow (\beta\gamma)^{-1} K$  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 expression for width in the representation of jj-coupling scheme of single-electron moments has the form:

$$\Gamma(2j_1^o l_1^o, 2j_2^o l_2^o; J) = 2 \sum_{l_k l_\alpha} \Gamma(2j_1^o l_1^o, 2j_2^o l_2^o; l_\alpha, k j l)^2. \quad (9)$$

Here the summation is made over all possible decay channels. The basis of electron state functions was defined by the solution of Dirac equation (integrated numerically using Runge-Cutt method). The calculation of radial integrals  $\text{Re}R_\lambda(1243)$  is reduced to the solution of a system of differential equations [8]:

$$\left. \begin{aligned} y_1' &= f_1 f_3 Z_\lambda^{(1)}(\alpha |\omega| r) r^{2+\lambda}, \\ y_2' &= f_2 f_4 Z_\lambda^{(1)}(\alpha |\omega| r) r^{2+\lambda}, \\ y_3' &= [y_1 f_2 f_4 + y_2 f_1 f_3] Z_\lambda^{(2)}(\alpha |\omega| r) r^{1-\lambda}. \end{aligned} \right\} \quad (10)$$

In addition,  $y_3(\infty) = \text{Re}R_\lambda(1243)$ ,  $y_1(\infty) = X_\lambda(13)$ . The system of differential equations includes also equations for functions  $f/r^{|\alpha|-1}$ ,  $g/r^{|\alpha|-1}$ ,  $Z_\lambda^{(1)}$ ,  $Z_\lambda^{(2)}$ . The formulas for Auger decay probability include the radial integrals  $R_\alpha(\alpha k \gamma \beta)$ , where one of the functions describes electron in continuum state. When calculating this integral, the correct normalization of function  $\Psi_k$  is a problem. The correctly normalized function should have the following asymptotic at  $r \rightarrow 0$

$$\left. \begin{aligned} f \\ g \end{aligned} \right\} \rightarrow (\lambda \omega)^{-1/2} \begin{cases} [\omega + (\alpha Z)^{-2}]^{-1/2} \sin(kr + \delta), \\ [\omega - (\alpha Z)^{-2}]^{-1/2} \cos(kr + \delta). \end{cases} \quad (11)$$

When integrating the master system, the function is calculated simultaneously:

$$N(r) = \left\{ \pi \omega_k \left[ f_k^2 [\omega_k + (\alpha Z)^{-2}] + g_k^2 [\omega_k + (\alpha Z)^{-2}] \right] \right\}^{-1/2}.$$

It can be shown that at  $r \rightarrow \infty$ ,  $N(r) \rightarrow N_k$ , where  $N_k$  — normalization of functions  $f_k, g_k$  of continuous spectrum satisfying the condition (11). The energy of electron formed due to transition  $jkl$  is defined by the difference between energies of an atom with a hole at  $j$  level and double-ionized atom at  $kl$  levels in the final state:

$$E_A(jkl, {}^{2S+1}L_J) = E_A^+(j) - E_A^{2+}(kl, {}^{2S+1}L_J). \quad (12)$$

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

$$E_A(jkl, {}^{2S+1}L_J) = E(j) - E(k) - E(l) - \Delta(k, l; {}^{2S+1}L_J), \quad (13)$$

where the item  $\Delta$  takes into account the dynamic correlation effects (relaxation due to hole screening with electrons etc.) To take these effects into account, the set of procedures elaborated in the atomic theory [2, 3] is used. For solid phase, the more precise form of equation (13) is [1]:

$$E_A^s(jkl, {}^{2S+1}L_J) = E_A(jkl, {}^{2S+1}L_J) + \Delta E^s + R_{rel} + e\Phi, \quad (14)$$

where  $\Delta E^s$  — correction for the binding energy change in the solid;  $R_{rel}$  — the same for out-of-atom relaxation;  $e\Phi$  takes into account the work of exit. In real Auger spectra, a specific line shape characteristic for the given transition and for each element arises due to the line blurring caused by Auger electron interaction with electrons of inner shells, outer bands, overlapping individual multiplet lines, multi-particle effects etc. In solids, Auger spectra are broadened in the low-energy region due to non-elastic scattering of Auger electrons emitted by an atom when those move within the crystal [1].

## CALCULATION RESULTS AND CONCLUSIONS

Now let us describe some calculated data for Auger transitions, ionization cross-sections of inner atomic shells and Auger electron energy in solids. As mentioned above, the exit probability of Auger electrons from an atom via different channels associated with ionization from core level is defined by the matrix element (1). In addition, the proportionality coefficient in the equation coincides with electron impact ioniza-

tion cross-section  $\sigma_j$  of level  $j$ . Of course, two aspects are to be considered when determining the exit probability of Auger electrons from an atom, namely, the radiative transition under neutralization of a hole at level  $j$  and the possibility of the considerable change in the initial hole distribution at the core levels at Auger decay via the radiative channel  $ijkl$  associated as a rule with the considerable distinctions in non-radiative transition probabilities. For definiteness sake, let the ionization of L levels in multi-electron atom be considered. The probability of Auger electron emission from the atom via channel  $L_3Kl$  (taken as an example) is defined by ionization cross-section of the level  $L_3$  as well as by a certain effective cross-section depending on ionization cross-sections of the levels  $L_1, L_2$ . Auger line intensity is defined by three atomic constants:  $A_{ijkl} = \sigma_j f_i a_{ijkl}$ , where  $a_{ijkl}$  — non-radiative transition probability;  $f_i$  — Korster-Kronig coefficient;  $\sigma_j$  — ionization cross-section defined by matrix element (1) calculated for wave functions of bound state and continuum one. The ionization cross-sections ( $\text{cm}^2$ ) calculated for inner shells of some atoms basing on the method proposed in this paper as well as the experiment data available [1] are presented in Table 1.

Inner shell ionization cross-sections for some atoms

Table 1

Element	Level	Ionization Energy, $E_i, \text{eV}$	Incident electrons energy, eV ( $U=E/E_i$ )	Ionization cross-section: Experiment	Ionization cross-section: Theory
Na	K	1075	4	$0,7 \cdot 10^{-20}$	$0,8 \cdot 10^{-20}$
Si	$L_3$	103	4	$6,15 \cdot 10^{-19}$	$6,33 \cdot 10^{-19}$

Note that, unlike the widely used calculation method of cross-sections within the frame of Born approximation (c. f. [2, 3]) our approach is more correct theoretically, thus resulting in rather good agreement between theory and ex-

periment. Table 2 presents data on Auger electron energy for some solids calculated using the method of this work (formulas 7–13) and the semi-empirical method under Larkins' equivalent core approximation [2] as well as experimental data.

Experimental data for Auger electron energy for solids and calculated values (A, semi-empirical method [2]; B, this work)

Table 2

Element	Auger line	Experiment	Theory: A	Theory: B
Na	$KL_{2,3}L_{2,3}^1D_2$	994,2	993,3	994,1
Si	$KL_{2,3}L_{2,3}^1D_2$	1616,4	1614,0	1615,9

The calculation accuracy of the using method [2] is within about 2 eV on average. Our approach provides more accurate results that is due to a considerable extent to more correct accounting for complex electron interaction.

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#### КВАНТОВЫЙ РАСЧЕТ ОЖЕ СПЕКТРОВ АТОМОВ И ТВЕРДЫХ ТЕЛ: Na, Si

На основе расчета характеристик Оже распада в твердых телах в рамках S-матричного формализма Гелл-Мана и Лоу получены данные по сечениям ионизации внутренних оболочек атомов (Na, Si) из энергий Оже переходов в твердых телах (Na, Si).

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#### КВАНТОВИЙ РОЗРАХУНОК ОЖЕ СПЕКТРІВ АТОМІВ ТА ТВЕРДИХ ТІЛ: Na, Si

На підставі розрахунку характеристик Оже розпаду в твердих тілах в межах S-матричного формалізму Гелл-Мана та Лоу отримані данні по перерізам іонізації внут-рішніх оболонок ряду атомів (Na, Si) та енергій Оже переходів у твердих тілах (Na, Si).