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CONFIGURATIONS WITH INNER VACANCIES OF FREE ATOMS AND PECULIARITIES OF X-RAY AND AUGER SPECTRA

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CONTENTS

1. INTRODUCTION

Various anomalies, approximate symmetries, strong correlation and dynamical effects as well as other new features of complex atoms with open shells have been revealed due to the recent investigations of free atoms (Mehlhorn 1982, Fano 1983, Connerade 1984, Амусья 1987). The main direction of this progress in the atomic physics as well as in some other fields of physics, is the higher energies. At the strong perturbation of the atom by X-rays or energetic particles the configurations with inner vacancies are arising. Their detailed investigation becomes more accessible with the development of modern experimental tools, such as synchrotron radiation, heavy ion accelerators, electronic spectrometers. A new branch of the atomic physics - atomic inner-shell physics - has formed in the second half of this century (Åberg et al. 1975, Åberg et al. 1985). It was provided by the importance of inner-shell processes in plasma physics, astrophysics, collision physics and by the progress in the area of short wavelength lasers.

After some period, when X-ray and Auger spectroscopy was closely related to the solid state physics, from the 60-ties the high resolution spectra of various free atoms became accessible. They contain the valuable information on the structure of electronic shells and elementary processes within them. It requires the elaboration of the adequate theory of excited many-electron atoms, complex X-ray and electronic spectra.

Such theory has originated from the angular momentum theory of Condon and Shortley (1935), Юцис и др. (1960), and the irreducible tensor operators method, elaborated by Wigner (1955) and Racah (1942, 1943). In the case of atoms with outer closed or half-filled shells perturbation theory has been effectively used (Kelly 1969, Амусья 1987 and others) The second quantization representation, specified for atoms by Judd (1967a) and extended by Рудзикас, Каняускас (1984), and the theory of continuous groups of higher ranks (Judd 1962, Wybourne 1970) are perspective in this field too.

The main aim of the theory of X-ray and electronic spectra is not only to develop effective methods, to calculate and interpret complex spectra, but also to investigate general spectral regularities, to establish the relations between the open shell features and the structure of atomic spectra. Description of complex spectra especially requires the global characteristics, revealing physical phenomena, obscured by their abundant structure (Bauche et al. 1988). Consequently, general summation methods for obtaining explicit expressions for mean characteristics of spectra and groups of lines or levels in them are needed.

The present work was initiated about twenty years ago by Prof. A. Jucys, the head of Vilnius theoretical school, at the request of the experimenters. At that time and later the theoretical work was greatly stimulated by the collaboration with experimenters Profs. L.L.Makarov, T.M.Zimkina, M.A.Elango, Dr. E.T.Verkhovtseva, Doc. A.Širvaitis and others, by the needs and the problems related to the interpretation of particular spectra. The author's aim however was not the extensive calculations of spectra, but the elaboration of theoretical methods, the investigation of spectral regularities and their relations to the structure of open electronic shells.

There have been set the following main problems:

-investigation of the specific features of configurations with vacancies as well as their influence on atomic properties and spectra;

- elaboration of the general summation method over all many electron quantum numbers and its application for obtaining explicit expressions of main global or mean characteristics of energy levels, X-ray and Auger spectra, investigation of their regularities;

- elaboration and application of the methods for obtaining explicit expressions of mean characteristics of the line and level groups;

-investigation of the configuration mixing effects in complex atoms and their influence on X-ray and Auger spectra.

The main results of this work were published in [1-39], presented in the author's review reports at the VI-th All-Union Conference on the Theory of Atoms and Atomic Spectra (Voronezh, 1980), the VII All-Union Conference on the Theory of Atoms and Atomic Spectra (Tbilisi, 1981), the First USSR-Poland Seminar on the Investigation of f Electron Systems (Vilnius, 1988) and reported at various All-Union and international conferences on the theory of atoms and atomic spectra, X-ray and electronic spectra, etc.

2. SPECIFIC FEATURES OF CONFIGURATIONS WITH VACANCIES AND THEIR INFLUENCE ON ATOMIC PROPERTIES AND SPECTRA

Configurations with inner vacancies are considerably less investigated as compared to the configurations with excitations in outer shells. The production of the vacancy essentially changes some characteristics of an atom, increases the configuration mixing effects, leads to the various relaxation and deexcitation processes (Åberg et.al. 1975, 1985). The relativistic effects also become more important in the inner shells. The theoretical investigation of the configurations with vacancies and their influence on corresponding X-ray and electronic spectra are summarized in this Chapter.

2.1. Influence of the vacancy on single-electron characteristics, binding and X-ray energies. The influence of the vacancy $n'l'^{-1}$ on the single-electron quantity χ_{nl} may be characterized by the difference of its values for configurations without and with this vacancy

$$\Delta\chi_{nl}=\chi_{nl}-\chi_{nl}(n'l'^{-1}). \qquad (1)$$

Systematic calculations of the electron screening constants of various electrons in configurations with the inner $1s^{-1}$, $2p^{-1}$ and $3p^{-1}$ vacancies have shown that the influence of the vacancy is the strongest not on the characteristics of neighboring shells, but on the outer weakly binded electrons [10, 11]. The screening constant of the outer electron decreases by 2 and even 3 units at inner vacancy creation (Fig. 1), which is due to the change of the asymptotic behavior of the potential. By the way, it shows, that "Z+1 approximation" for the Auger energies is insufficient in the case of outer electrons.

The application of the Koopmans theorem to the changes of single-electron energies gives the approximate relation [10]

$$\Delta\varepsilon_{nl}(n'l'^{-1}) \approx \Delta\varepsilon_{n'l'}(nl^{-1}), \qquad (2)$$

showing that the influence of vacancy $n'l'^{-1}$ on electron nl is approximately the same as that of the vacancy nl^{-1} on electron $n'l'$.

The generalization of Koopmans theorem for the configurations with vacancies in two (or more) shells $n_1l_1^{-q_1}\, n_2l_2^{-q_2}$ allows one to obtain explicit expressions for the shift of binding energy and X-ray energy in atom with respect to ion, containing these vacancies [7, 12]:

$$\Delta I_{nl}(n_1l_1^{-q_1}\, n_2l_2^{-q_2}) = q_1\, \Delta\varepsilon_{n_1l_1}(nl^{-1}) + q_2\, \Delta\varepsilon_{n_2l_2}(nl^{-1}) +$$
$$+q_1(q_1-1)\, A_{n_1l}(nl^{-1}) + q_2(q_2-1)\, A_{n_2l_2}(nl^{-1}) + q_1q_2\, B_{n_1l_1,n_2l_2}(nl^{-1}), \qquad (3)$$

$$\Delta E_{n_3l_3\rightarrow n_4l_4}(n_1l_1^{-q_1}\, n_2l_2^{-q_2}) = q_1\, C_{n_1l_1} + q_2\, C_{n_2l_2} + q_1(q_1-1)\, A'_{n_1l_1} +$$
$$+q_2(q_2-1)\, A'_{n_2l_2} + q_1q_2\, B'_{n_1l_1,n_2l_2}. \qquad (4)$$

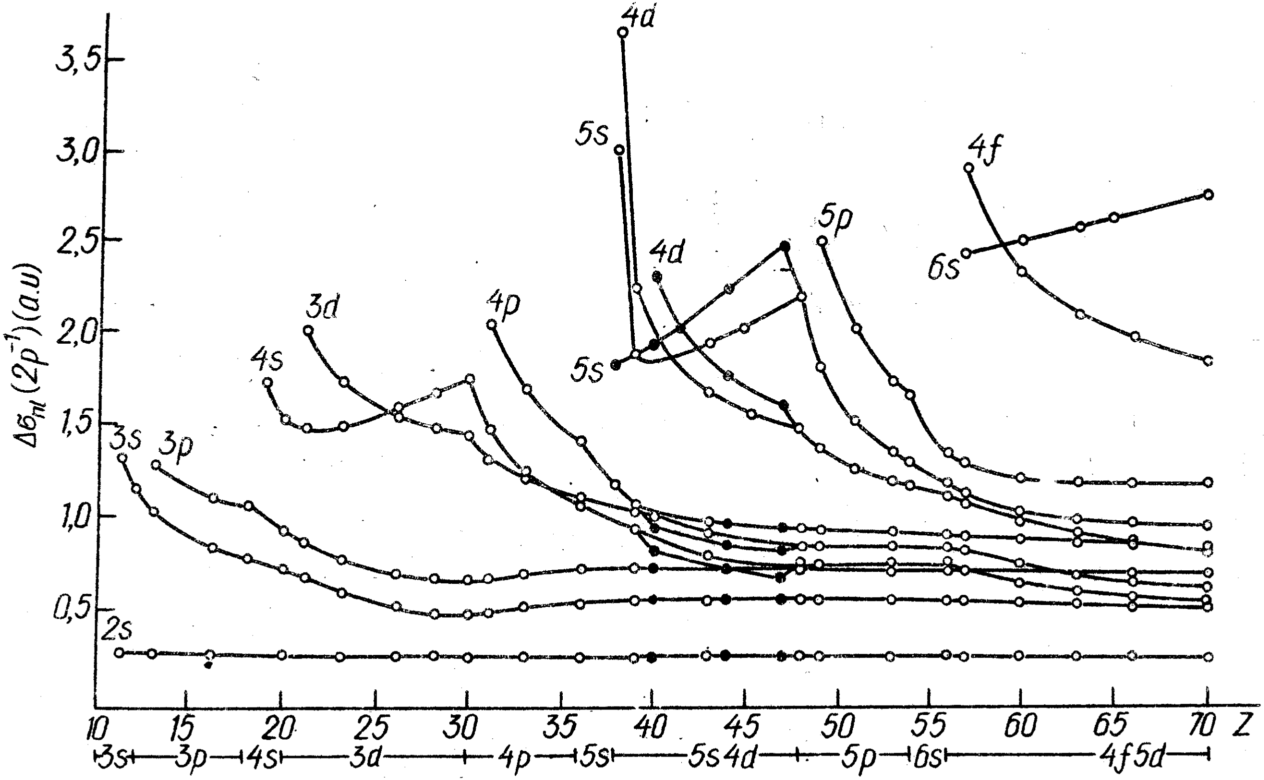

Fig. 1. Shift of the screening constant $\Delta\sigma_{nl}(2p^{-1})$ of electron nl due to $2p^{-1}$ vacancy production as a function of atomic number Z (Hartree-Fock results [10]). In the case of transition elements dark points correspond to the configuration $d^N s$ and light points to configuration $d^{N-1}s^2$.

The simple formulae for the parameters A, A', B, B' and C in nonrelativistic and relativistic approximations have been obtained [7, 12, 1]. For their calculation the wavefunctions of the atom and ion with only one vacancy nl^{-1} and/or $n'l'^{-1}$ are needed, while the accuracy of (3) and especially (4) differs a little from the accuracy of the formula, containing the differences of total energies, as it was shown by Тупицын, Братцев (1979), and exceeds the accuracy of usually employed approximate formula, both requiring calculations of the wavefunctions for all values of q_1 and q_2 (Fig.2). The explicit form and accuracy of (3), (4) as well as a weak dependence of the parameters on the configuration [7, 8, 16] favored their

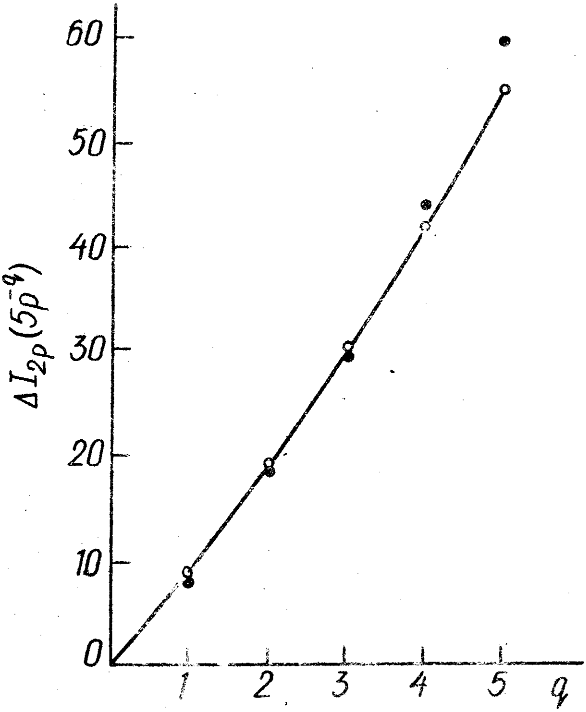

Fig.2. Binding energy shift ΔI_{2p} as a function of the number of $5p^{-1}$ vacancies [12]. Results of calculations using formula (3) (full curve) and by total energy differences (dark points).

use for the investigations of chemical shifts of X-ray and electronic lines (Макаров и др. 1975, Зайцев и др. 1978, Тихонов и др. 1988, [13] и др.).

2.2. Relativistic corrections to inner electron energies in Hartree-Fock-Pauli approximation. Relativistic effects play an important role in the inner shells of heavy and even intermediate atoms (Grant 1983). Since the complete relativistic calculations were complicated, there was accomplished the investigation accounting for the main relativistic corrections to inner-electron, X-ray and Auger energies in the first order of perturbation theory, i.e. in Hartree-Fock-Pauli approximation (Bethe, Salpether 1957, Богданович и др. 1977). The results for noble gas atoms Ar, Kr and Xe have shown the efficiency of this method for inner and subvalent vacancies, except for the outer ones [14]. There was established the following regularity: the difference between relativistic and experimental values of inner-electron binding energies or correlation correction increases in absolute value at a given principle quantum number with the increas of the orbital quantum number. This regularity has been confirmed by subsequent systematic calculations (McGilp, Weightman 1980, Chen et al. 1985). It is caused by the interaction of the vacancy $n_1l_1^{-1}$ with super-Coster-Kroning and Coster-Kroning continua

$$n_1l_1^{-1} + n_1l_2^{-1}\ n_1l_3^{-1}\begin{pmatrix}\varepsilon\\ n\end{pmatrix}l + n_1l_2^{-1}n_2l_4^{-1}\begin{pmatrix}\varepsilon\\ n\end{pmatrix}l, \qquad l_1<l_2. \tag{5}$$

Their number increases for the shells with the smaller value of l_1 at the given n_1. Such correlation effects, the strongest in the configurations with vacancies, and their influence on X-ray and Auger spectra will be considered in the following chapters. Hartree-Fock-Pauli approximation was used in the majority of calculations, referred to in this thesis.

2.3. Collapse of an excited electron and the peculiarities of atomic spectra. Due to the "centrifugal" repulsion of the electron with the orbital quantum number l>1 from the nucleus and Coulomb exchange interaction, the effective potential can obtain a form of two wells, separated by a barrier. Furthermore, at the change of configuration (Griffin et al. 1969) or even many-electron state of the atom (Кучас и др. 1976), a sudden contraction of the electron orbital may occur. Various manifestations of the collapse and potential barrier effects in atoms were reviewed in [4], where their importance for the configurations with inner vacancy was stressed. In this work the collapse of the slow free electron near the atom was also considered and there were suggested important potential barrier effects for negative ions, the disappearance of some Auger lines at small energies not forbidden energetically and (basing on some anomalies for X-ray line chemical shifts and other characteristics of rare earths) the possibility for the f electrons to take part in the chemical bonding.

The positive barrier disappears for the higher ionization degrees J (Каросене и др. 1973). However it has been shown in [20], that the considerable dependence of the excited electron orbital on many-electron quantum numbers may take place up till J= 8-10.

The existence of the positive barrier can lead to the strong dependence of the Auger transition probability on the free electron energy [22].

2.4. Radiative and Auger widths of levels and their approximate invariance.

In the case of short living states with inner vacancies the width of excited levels mainly consists of their natural width. These states can decay not only by radiative but also by Auger transitions. Supposing radial orbitals are term-independent, the summation in an expression for the partial radiative or Auger width (corresponding to the transitions to all states of the given final configuration) can be accomplished in the second quantization representation and these quantities are expressed in terms of a matrix element of an effective operator. The effective operators for the radiative width were obtained by Богданович и др. (1985, 1988) and in [2]. The effective operators for Auger width follow from the general expressions, referred in Sec. 5.1.

In the case of some configurations only the scalar part of the effective operator gives a contribution to the partial width and then it becomes term-independent. Auger width acquires this property for the following transitions [21, 1]:

$$K_0\, l_1^{N_1}\, l_2^{4l_2+2}\, l_3^{4l_3+2} \rightarrow K_0\, l_1^{N_1+1}\, l_2^{4l_2+1}\, l_3^{4l_3+1}\, \varepsilon l,$$

$$K_0\, l_1^{N_1}\, l_2^{4l_2+2} \rightarrow K_0\, l_1^{N_1+1}\, l_2^{4l_2}\, \varepsilon l \qquad (6)$$

and the radiative width in the cases:

$$K_0\, l_1^{N_1}\, l_2^{4l_2+2} \rightarrow K_0\, l_1^{N_1+1}\, l_2^{4l_2+1},$$

$$K_0\, l_1^{0}\, l_2^{N_2} \rightarrow K_0\, l_1^{1}\, l_2^{N_2-1}\,. \qquad (7)$$

Here any symbol l_i stands for $n_i l_i$. K_0 means "passive" open or closed shells.

When all partial widths of level are term-independent, the total width of level also become invariant (in fact, approximately invariant). This takes place only for configurations with one open shell above closed "passive" shells K'_o. So far as radiative and Auger widths depend on the number of electrons N in this shell through the simple multiplier 4l+2-N, the total radiative or Auger width and the total natural width of levels of such configuration, differing by the number of electrons in an open shell, fulfill relation [21]

$$\frac{\Gamma(K'_0 l^N \gamma J)}{\Gamma(K'_0 l^{N'} \gamma' J')} = \frac{4l+2-N}{4l'+2-N'} . \qquad (8)$$

Then the fluorescence yield also becomes approximately independent on the number of electrons or vacancies in this shell. It corresponds to the experimental data on the approximate equality of fluorescence yield for configurations with one and two vacancies in the same shell (Campbell et al. 1977, Venugopala et al. 1974, Indira et al. 1979). The obtained term-independent formula of the partial and total widths considerably simplifies the calculation of these quantities.

2.5 Sudden perturbation of an atom due to the vacancy production. Many-electron processes, such as simultaneous ionization and excitation or two-electron ionization of the atom play an important role in the inner-shell physics (Åberg et al. 1985), but the accurate probability calculations of such processes for complex atoms are cumbersome. If the initial perturbation of the atom is sudden and electrons are removed from different, weakly correlated shells, the sudden perturbation model can be used (Åberg 1967, Матвеев, Парилис 1982). In this model many-electron process is divided into two steps: production of the initial vacancy in frozen core and subsequent excitation or ionization due to the relaxation of electronic shells. The probabilities of such shake-off and shake-up processes, depending on many-electron quantum numbers, are needed for the calculations of X-ray and Auger spectra, arising at the rearrangement of the electronic shells. Corresponding expressions have been obtained in [15] while integrating the (N-1)-electron density matrices, which describe an electronic system, except the removed electron.

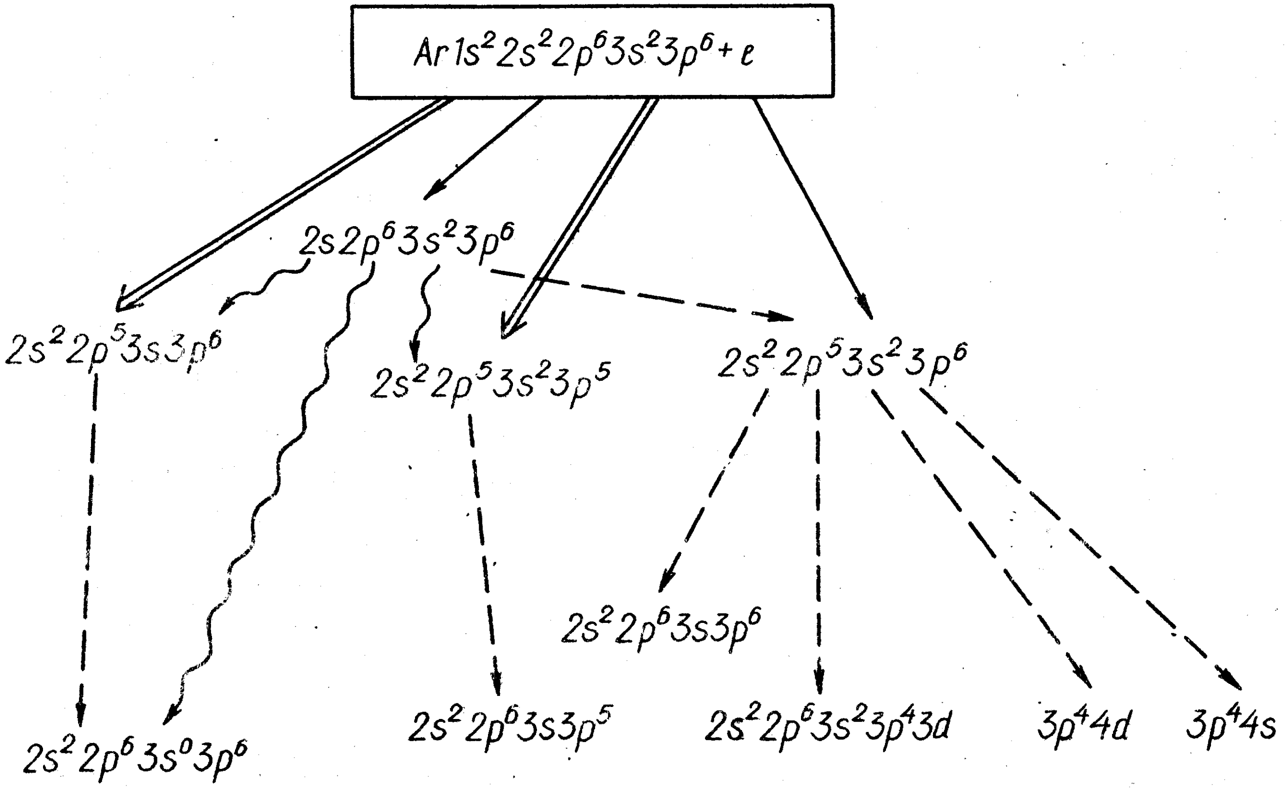

Fig. 3. Cascade of main processes, arising due to the interaction of free Ar atoms with 1 keV electron beam and having influence on the structure of $L_{2,3}$ soft X-ray spectrum: one-electron ionization; ⇒ two-electron ionization; - -→ radiative transition, ↝ Auger transition.

2.6. Cascade of processes, following a vacancy production, and the structure of X-ray spectrum. An inner vacancy production by X-rays, electronic or ionic beams gives rise to the cascade of elementary processes: the excitation and ionization of other shells, radiative and Auger transitions. X-ray or Auger spectra, generated in such a way, depend on the populations of various levels. Therefore the accurate theoretical interpretation of spectra requires to calculate the whole cascade of processes. The first such detailed theoretical investigation was accomplished in [17] for $L_{2,3}$ soft X-ray spectrum of Ar, excited by electronic beam (Верховцева и др. 1976). The main processes of the cascade were defined by the preliminary approximate calculation of the total populations of configurations (Fig.3). Level populations at electron beam energy of 1 keV were calculated by using semiempyrical electron ionization

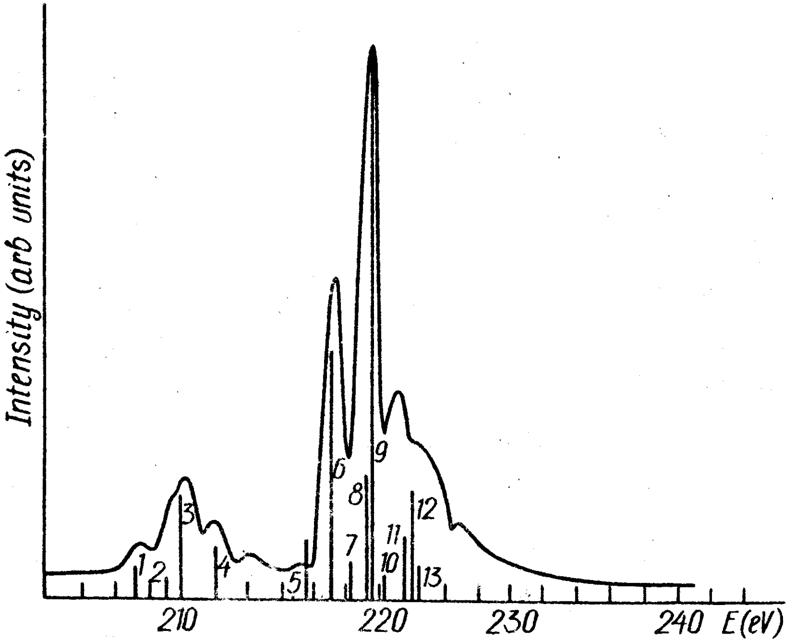

Fig.4. Ar $L_{2,3}$ soft X-ray spectrum. Full curve corresponds to the experiment (Верховцева и др. 1976), separate lines represents the results of calculation taking into account the populations of excited levels.[17].

cross-sections, as well as the expressions for the shake-off probabilities, referred above, and the formulae of Auger transition probabilities, obtained in [9]. The strong mixing of configurations $3s3p^6 + 3s^2 3p^4 3d + 3s^2 3p^4 4s$, corresponding to the specific type of correlations (5), was also taken into account. A reasonable agreement of the theoretical and experimental spectra (Fig.4) has allowed to adjust the interpretation of its structure, proposed by Верховцева и др.(1976). For example, it was shown that the main line at 221 eV corresponds to the satellite, not to a diagram transition and the low energy maximum is caused by two-electron radiative transitions $3p^2 \rightarrow 3s3d$ and $3p^2 \rightarrow 3s4s$. The interpretation of this spectrum was continued by Dyall, Larkins (1982), Сухоруков и др.(1985).

Similar investigation of the ultrasoft X-ray spectrum of Kr was accomplished in [23]. There was analyzed the role of various elementary processes on formation of this spectrum. An estimation of the strong correlation effects in the configuration with $3p^{-1}$ vacancy had shown that they could not explain anomalous high population of $3d^{-2}$ configuration levels.

3. MEAN CHARACTERISTICS OF ATOMIC SPECTRA AND THEIR REGULARITIES

The atomic spectra are usually investigated on performing their detailed calculations and considering single electron quantities or radial integrals. A new perspective method in the theory of complex spectra is given by the analysis of their global or mean characteristics, such as average energy ($\bar{E}$), variance (σ^2), scewness (κ_1) and excess (κ_2), which are the central spectral moments

$$\mu_k = \sum_i (E_i - \bar{E})^k \, p_i \tag{9}$$

(E_i is energy of the i-th level or line, and p_i stands for the probability of finding it in the spectrum) or are expressed by them

$$\sigma^2 = \mu_2, \quad \kappa_1 = \mu_3/(\sigma^2)^{3/2}, \quad \kappa_2 = \mu_4/(\sigma^2)^2 - 3. \tag{10}$$

Average energy characterizes the "center" of spectrum, variance represents its width, scewness describes its asymmetry and excess stands for its level or line density. The main problem is to obtain explicit expressions of these characteristics which do not need calculations of spectra. About ten years ago such a general formula was known only for the average energy of energy level spectrum. Bauche-Arnoult et al.(1979, 1982) obtained some new formulae for this and emission spectra and effectively applied them for the approximate description of complex spectra of highly charged ions. Some investigations of spectral regularities were accomplished by using mean characteristics calculated directly from experimental and theoretical spectra (Cowan 1981, Bancewicz, Karwowski 1983 et al.). The authors aim was to elaborate the general summation method for obtaining expressions of spectral moments, to find such formulae for various spectra and to illustrate their usefulness for the investigation of spectral regularities.

3.1. General method of summation over all many-electron quantum numbers. Matrix elements of atomic operators contain fractional parentage coefficients, having a non-standard form, so the direct summation of matrix elements is very cumbersome. (Nomura 1972). Bauche-Arnoult et al. (1979) obtained some explicit formulae combining the second quantization representation with a simple formula for some configurations. However this method becomes insufficient for the third and even for the second moments of some spectra. A general group-theoretical method for deriving the averages of operators, acting in many fermion spaces, was proposed by Ginocchio (1973). To solve this problem the continuous groups of higher ranks were used: the rotation group $R(8l+5)$ and its unitary subgroup $U(4l+2)$. The operator average is expressed by its vacuum expectation value and a unitary scalar coefficient which (due to the fact that every irreducible representation of $U(4l+2)$ appears once and only once in a given irreducible representation of this rotation group) has a simple explicit expression. While evaluating all possible distributions of contractions between operators of creation and annihilation of electrons in the vacuum expectation the special summation diagrams were suggested (Ayik, Ginocchio 1974).

In [30, 32, 2, 5] this method was specified to electronic shells and its diagrammatic form was elaborated. The average of the product of operators is expressed as follows:

$$\langle O_1 O_2 \ldots O_k \rangle^K = \sum_{\mathrm{diag}} N_{\mathrm{diag}} M_{\mathrm{diag}} , \qquad (11)$$

where O_i is the operator of interaction or transition, irreducible with respect to the $R(8l+5)$ and $U(4l+2)$ groups; N_{diag} is the N-multiplier, containing all dependencies on the electron numbers in the shells, and M_{diag} is the minimal sum of one- and two-electron matrix elements. The summation

$$\mathcal{F} = \sum_{\nu\zeta} a^+_\nu a_\zeta \langle\nu|f|\zeta\rangle - \underset{\nu\zeta}{\circ}$$

$$\mathcal{G} = \frac{1}{4}\sum_{\nu\xi\zeta\eta} a^+_\nu a^+_\xi a_\eta a_\zeta \langle\nu\xi|g|\zeta\eta\rangle - \underset{\nu\zeta}{\circ}\quad\underset{\xi\eta}{\circ}$$

$$\langle \mathcal{G}_1\mathcal{F}_1\cdots\mathcal{G}_n\mathcal{F}_k\rangle^K - \begin{array}{lcc} \mathcal{F}_k & \circ & \\ \mathcal{G}_n & \circ & \circ \\ & \cdots & \cdots \\ \mathcal{F}_1 & \circ & \\ \mathcal{G}_1 & \circ & \circ \end{array}$$

Fig. 5. Graphical representation of one electron ($\mathcal{F}$), two electron ($\mathcal{G}$) operators and the average of the product of operators.

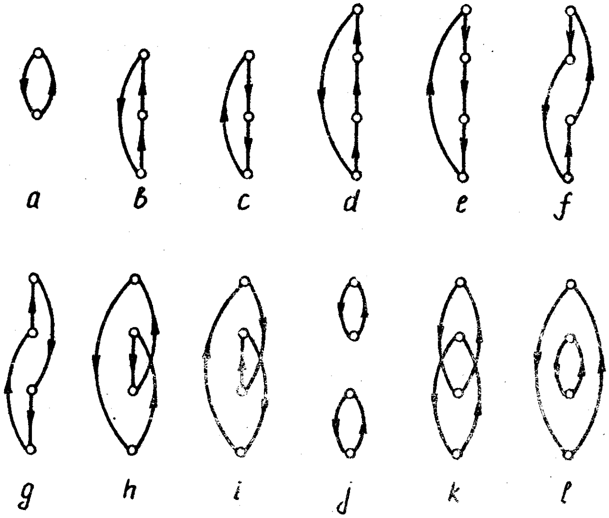

Fig. 6. Nonequivalent diagrams for the averages $\langle\mathcal{F}\rangle^K$ (a), $\langle\mathcal{F}\mathcal{F}\mathcal{F}\rangle^K$ (b.c) and $\langle\mathcal{F}\mathcal{F}\mathcal{F}\mathcal{F}\rangle^K$ (d-l).

in (11) is carried out over all nonequivalent diagrams. The general rules for obtaining all diagrams and excluding topologically equivalent from them as well as the graphical technique for evaluating the expressions of minimal sums were formulated (Fig.5, 6). Also the groups of diagrams, corresponding to the same minimal sum, as well as the permutation operators, acting on the matrix elements, were introduced. It considerably simplifies the evaluation of averages. This diagrammatic method is valid in nonrelativistic and relativistic, single- and many-configuration approximations (the last one will be considered in Chapter 5). It was implemented in a general computer program by S. Kučas.

Various operators can be expressed in terms of the standard unit operators $V^{(kk')}$ [3]. The summation method was applied to obtain the averages of scalar and tensor products of two, three and four such operators [2].

3.2. First four moments of the energy level spectrum and their peculiarities. The k-th central moment of the energy level spectrum of the configuration K is expressed by the average of the product of irreducible traceless Hamiltonians $\mathcal{H}= H-\bar{E}(K)$ in the following way:

$$\mu_k(K)= \frac{1}{g(K)} \sum_{\gamma} [<K |H|K\gamma>-\bar{E}(K)]^k = \frac{1}{g(K)} \sum_{\gamma} <K\gamma|\mathcal{H}|K\gamma>^k = \underbrace{<\mathcal{H}. \dots \mathcal{H}>}_{\text{k operators}}^K, \qquad (12)$$

where $\bar{E}(K)$ is an average energy, and γ is a state of the configuration K.

General formulae for the average energy were obtained by Slater (1960), for the variance by Bauche-Arnoult et al. (1979), for some terms of the third and fourth moments in the jj coupling by Nomura (1972). In [2, 33] there were derived the expressions for any order moment, caused by one-electron spin-orbit interaction, and for the third and the fourth moments of any configuration. They were used to investigate some peculiarities of the spectra for atoms with the open p^N, d^N and f^N shells [33]: the contributions of Coulomb and spin-orbit interactions to variance, scewness and excess as a function of a principal quantum number, the dependence of scewness and excess on a number of electron in a shell (Fig.7) (the symmetry with respect to a half shell is distorted by the contraction of radial wavefunctions and the presence of a noninvariant spin-orbit term). The values of the coefficients κ_1 and κ_2 for atoms with the np^N shell are in a good agreement with experimental data for n=3-5 (Fig.8). Discrepancies for n=2 are caused by the well-

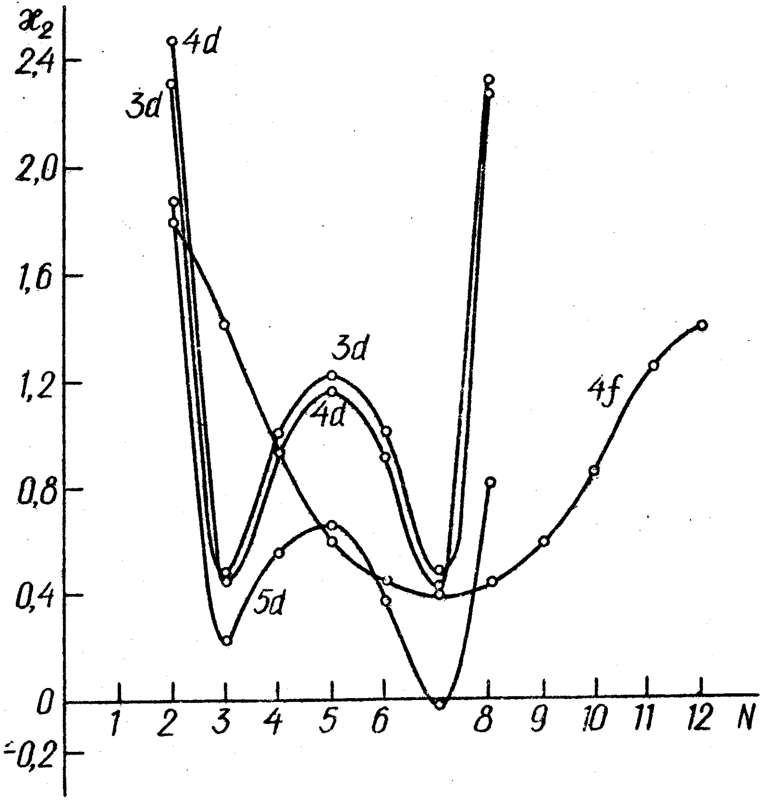

Fig.7. Excess κ_2 for neutral atoms with nd^N and $4f^N$ shells (Hartree-Fock results) [33].

known strong configuration mixing $2s^22p^2 + 2p^4$, changing the energy distances between terms; thus, spectral moments are sensitive to correlation effects.

The ratio $\sqrt{\sigma^2_{so}}/\sqrt{\sigma^2_c}$, where σ^2_{so} and σ^2_c are spin-orbit and Coulomb interaction parts of the variance, may serve as a measure of the coupling in a shell [33]. This is a more accurate measure than the ratio of the main radial integrals as it takes spin-angular parts of the matrix elements into account as well.

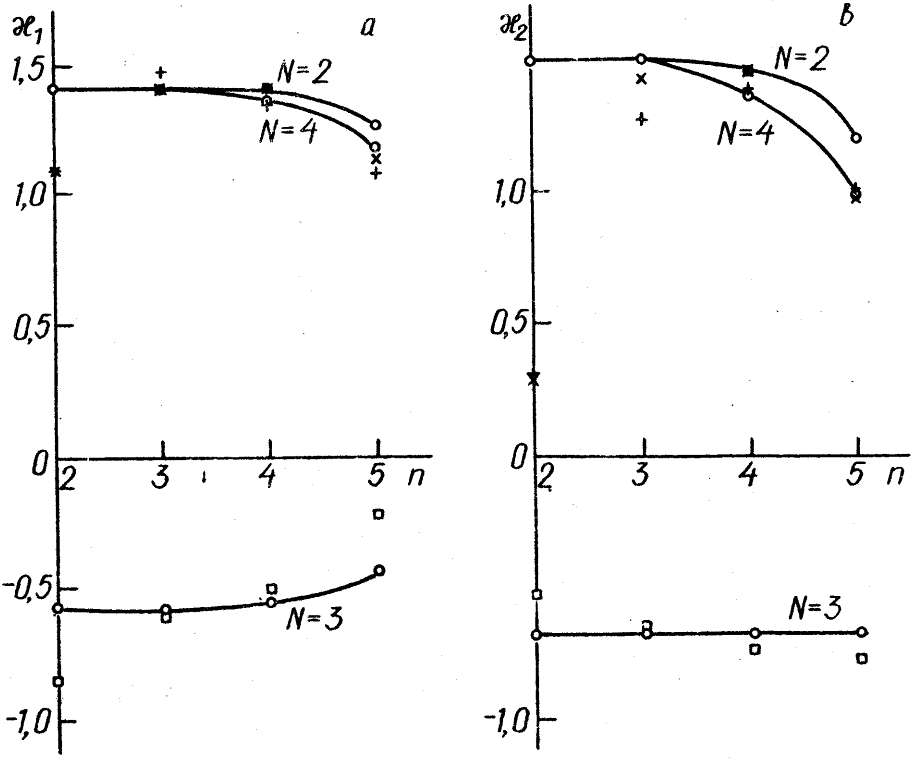

Fig.8. Scewness κ_1(a), and excess κ_2(b) for neutral atoms with np^N shell [33]. ∘ - Hartree-Fock results; x-np^2, -np^3, + - np^4 -experimental results (Moore, 1948, 1952, 1958).

<u>3.3. Moments of the emission spectrum and line strength distribution.</u> Generally the intensity of emission lines and, therefore, the moments of spectrum depend on the excitation conditions, but in some realistic cases the assumption can be made that all states are populated equally (populations of levels are proportional to their statistical weights). This usually corresponds to the physical conditions in high temperature plasma as well as in arcs and sparks. When the energy of a transition between two configurations is much larger as compared to the sum of configuration widths (this condition is as a rule fulfilled for X-ray spectra), the transition

energy in the expression for line probability as an averaging factor may be replaced by the average energy, and the k-th moment is given as follows [5]:

$$\mu_k^{em}(K-K') = \frac{\sum_{\gamma\gamma'} [\langle K\gamma|H|K\gamma\rangle - \langle K'\gamma'|H|K'\gamma'\rangle - \bar{E}(K-K')]^k \, S(K\gamma, K'\gamma')}{\sum_{\gamma\gamma'} S(K\gamma, K'\gamma')} =$$

$$= C_{em}(K,K') \sum_{p=0}^{k} (-1)^p \binom{k}{p} \langle \underbrace{\mathcal{H}_K \dots \mathcal{H}_K}_{k-p \text{ operators}} \mathcal{D}_{KK'} \underbrace{\mathcal{H}_{K'} \dots \mathcal{H}_{K'}}_{p \text{ operators}} \mathcal{D}^{\dagger}_{K'K} \rangle^K =$$

$$= \sum_{p=0}^{k} \sum_{p'=0}^{k-p} (-1)^p \binom{k}{p} \binom{k-p}{p'} \mu_{k-p-p'}(K-K') \, \delta\bar{E}(K-K')^{p+p'}, \qquad (13)$$

where $\mathcal{H}_K$ is the traceless Hamiltonian, $\mathcal{D}_{KK'}$ is a transition operator taken in a dipole form, $\delta\bar{E}$ is the shift of the average transition energy with respect to the difference of average energies of the initial (K) and the final (K') configurations. The factor $C_{em}(K,K')$ has a simple expression, depending on the number of electrons in the shells and single-electron transition line strength.

The general expression of the average energy was obtained by Bauche-Arnoult et al. (1982). In the case of frozen wavefunctions the formula of variance was presented by Bauche-Arnoult et al. (1982) and the general formula for this quantity was obtained in [30]. Some terms of the third moment were given by Bauche-Arnoult et al. (1984) and the expression of this moment in terms of the minimal sums in [2].

An "electron-vacancy" symmetry of the average, containing an even number of spin-orbit interaction operators [32, 2], leads to the symmetry of the first and the second moments of emission spectrum with respect to the substitutions

$$N_1 \to \Omega_1 - N_1 - 1 , \qquad N_2 \to \Omega_2 - N_2 + 1, \qquad (14)$$

where Ω_i is the number of states in a shell, and N_i is the number of electrons in the initial configuration.

Some terms of the emission spectrum moments can be expressed by the corresponding terms of the energy level spectra moments. As it was shown in [32, 2], the relation

$$\frac{\sum_{\gamma\gamma'} \langle K\gamma|H|K\gamma\rangle^k \, S(K\gamma, K'\gamma')}{S(K, K')} = \frac{\sum_{\gamma} \langle K\gamma|H|K\gamma\rangle^k}{g(K)} \qquad (15)$$

($S(K\gamma, K'\gamma')$ is a line strength and, $S(K, K')$ is a total line strength) holds for transitions (7). The similar relation

$$\frac{\sum\limits_{\gamma\gamma'} \langle K'\gamma'|H|K'\gamma'\rangle^k \, S(K\gamma, K'\gamma')}{S(K, K')} = \frac{\sum\limits_{\gamma} \langle K'\gamma'|H|K'\gamma'\rangle^k}{g(K')} \qquad (16)$$

takes place for the transitions

$$K_0 \, l_1^{4l_1+1} \, l_2^{N_2} \to K_0 \, l_1^{4l_1+2} \, l_2^{N_2-1}, \qquad K_0 \, l_1^{N_1} \, l_2 \to K_0 \, l_1^{N_1+1}. \qquad (17)$$

Bauche et al. (1983) introduced the concepts of the "emissive zone" and "receptive zone", defined by its initial moments

$$\alpha_k^{em}(K) = \frac{\sum\limits_{\gamma\gamma'} \langle K\gamma|H|K\gamma\rangle^k \, S(K\gamma, K'\gamma')}{S(K, K')}, \qquad (18)$$

$$\alpha_k^{rec}(K') = \frac{\sum\limits_{\gamma\gamma'} \langle K'\gamma'|H|K'\gamma'\rangle^k \, S(K\gamma, K'\gamma')}{S(K, K')}. \qquad (19)$$

They are useful for the estimation of the spectrum array, taking part in given transitions, and reveal deep relations between the properties of energy levels and structure of the emission spectrum. As it follows from (15), (16), the "emissive zone" is identical to the array of initial levels in the case of transitions (7) and the "receptive zone" coincides with the array of final levels for transitions (17). When the moments of zone and configuration differ, the first one is shifted up by Coulomb exchange interaction - it follows from the formula for $\delta\bar{E}(K-K')$ [2].

As far as the distribution of emission lines is close to the Gaussian, usually the knowledge of only three or even two moments enables one to describe approximately the envelope of the complex spectrum (Fig.9).

The analysis of the moments and their parts reveals the role of various interactions on main features of spectrum and their variation along the sequences of atoms or ions. An example is given in Fig.10.

The above considered mean characteristics correspond to the array of lines, the width of which is not taken into account. Usually the X-ray or Auger line width is not small in comparison with the spacings of lines, but the line profiles depend weakly on the many-electron quantum numbers. Let us suppose that all lines are described by the same profile, and its moments μ_k^o

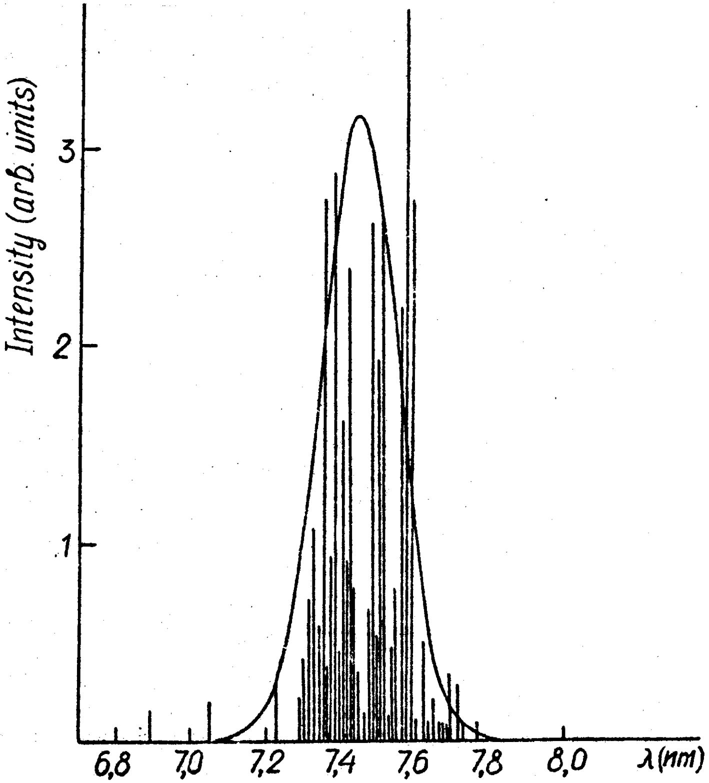

Fig. 9. SrXII $3d^84p-3d^9$ experimental emission spectrum excited by the vacuum spark of small inductivity (Заикин и др. 1983) and its envelope, calculated using first two moments [2].

exist. Then the moments μ'_k of the array of broadened lines are expressed [2, 5]

$$\mu'_k = \sum_{p=0}^{k} \left[\begin{matrix} k \\ p \end{matrix} \right] \mu_p \, \mu^0_{k-p} \, , \tag{20}$$

where μ_p is the moment (13).

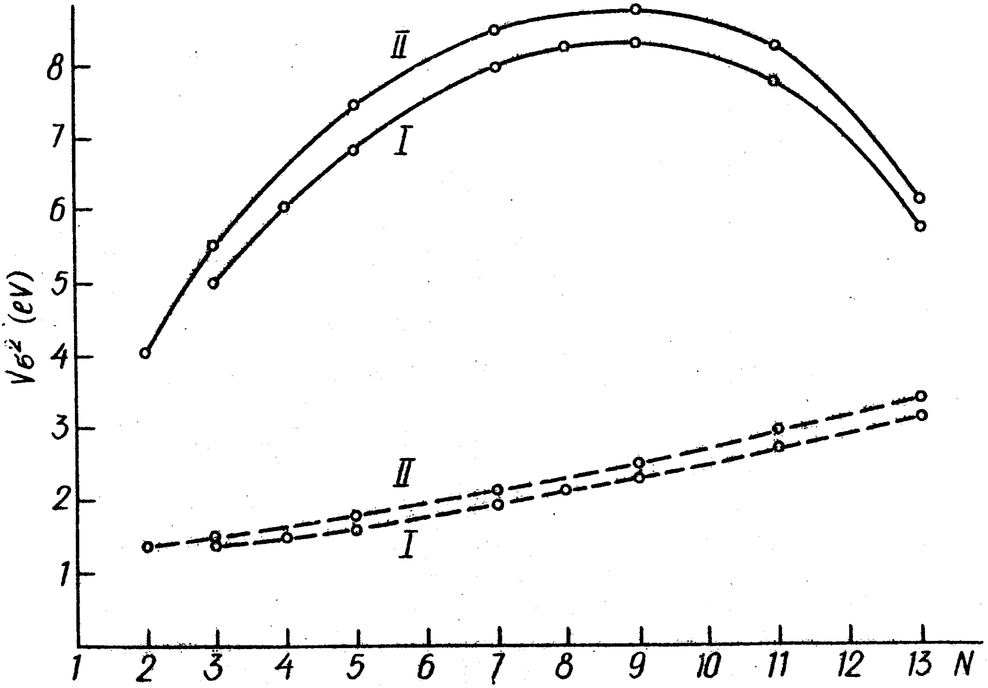

Fig. 10. Square root of the variance of emission spectrum, corresponding to the transitions $4d^9 4f^N - 4d^{10} 4f^{N-1}$ for neutral atoms(I) and first ions(II) of rare earths. Dashed line represents the spin-orbit part of this quantity [2].

3.4. Mean characteristics of the Auger spectrum. Mean characteristics of the Auger spectrum were practically uninvestigated. The expression for the average energy of Auger transitions array, corresponding to the transitions

$$K_0 \lambda_1^{N_1} \lambda_2^{N_2} \to K_0 \lambda_1^{N_1+1} \lambda_2^{N_2-2} \varepsilon\lambda , \qquad (21)$$

$$K_0 \lambda_1^{N_1} \lambda_2^{N_2} \lambda_3^{N_3} \to K_0 \lambda_1^{N_1+1} \lambda_2^{N_2-1} \lambda_3^{N_3-1} \varepsilon\lambda \qquad (22)$$

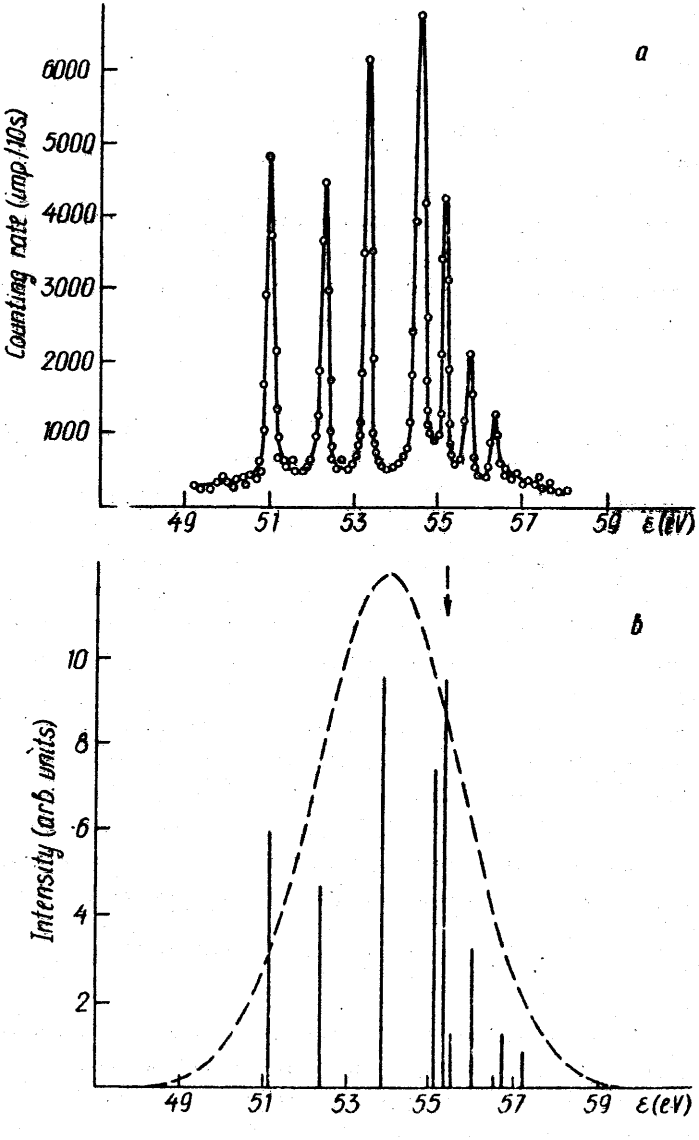

Fig. 11. Kr $M_{4,5}N_{2,3}N_{2,3}$ Auger spectrum: a - experiment (Werme et al. 1972); b - calculation in Hartree-Fock-Pauli approximation [22]. The envelope of the spectrum is obtained using two first moments [2]. The arrow marks position of the average energy without taking into account its shift.

(K_o means the "passive" shells, λ denotes l in the LS or lj in the jj coupling within a shell) were obtained in [29, 2]. The formula of the variance was derived by the computer program [39]. As in the case of the emission spectrum the intensities of Auger lines are supposed to be proportional to their probabilities as well as the radial integrals being term-independent. All or only some shells can be treated in the jj coupling.

The first two moments of the Auger spectrum can be used to calculate approximately its envelope (Fig.11). The shift of the average energy of Auger spectrum, describing its change due to the distribution of transition probabilities, can reach several eV and its account essentially improves the position of the intensity center.

3.5. Mean characteristics of the photoelectron and photoexcitation spectra. The photoelectron and photoexcitation spectra of free atoms belong to the other type of atomic spectra, corresponding to the transitions from some levels, usually from one ground level of the initial configuration, to all levels of the final configuration. The formulae of their moments can be obtained by accomplishing the summation over all states of the final configuration in the second quantization representation and are expressed by the matrix element of a certain effective operator with respect to the ground state wavefunctions [2].

The evaluation of the mean characteristics of photoelectron spectrum is considerably simplified by the fact that the operators of creation and annihilation of the photoelectron appear only in transition operators and are absent in the Hamiltonian. As a result the transition operators do not enter into the effective operator and the shift of the average energy is expressed by the matrix element of the traceless Hamiltonian [2, 37]

$$\delta\bar{E}_{el}(K_0\ l_1^{N_1}\ \gamma \rightarrow K_0\ l_1^{N_1-1}) = -\sum_p \frac{N_1-p}{N_1} \langle K_0\ l_1^{N_1}\ \gamma | \mathcal{H}^p | K_0\ l_1^{N_1}\ \gamma \rangle_{K'}, \quad (23)$$

where $\mathcal{H}^p$ is a p-electron part of the effective operator, the subscript at the matrix element indicates the configuration, radial orbitals of which are used in this matrix element. Similarly the effective operator

$$\mathcal{H}^{ef} = \mathcal{H}_{K'}, \qquad \mathcal{H}_{K'} = \sum_p H_{ef}^p \qquad (24)$$

is used in the expression of the variance

$$\sigma^2_{el}(K_o l^{N_1}\gamma \rightarrow K_o l^{N_1-1}) =$$

$$= \sum_p \frac{N_1-p}{N_1} \langle K_0\, l_1^{N_1}\,\gamma|\mathcal{H}^p|K_0\, l_1^{N_1}\,\gamma\rangle_{K'} - \delta\bar{E}_{el}(K_0\, l_1^{N_1}\,\gamma \rightarrow K_0\, l_1^{N_1-1}). \qquad (25)$$

The "excitation zone" can be introduced for the photoelectron spectrum too. As it was shown in [37], it is much narrower than the energy level array of the upper configuration.

During soft X-ray absorption the ionisation process is competing with the excitation process, especially when an electron from the subvalent shell is excited into an open shell with the same principal quantum number. If its radial orbital in the final state is collapsed, the intense photoexcitation

$$nl_1^{4l_1+2}\, nl_2^{N_2} \rightarrow nl_1^{4l_1+1}\, nl_2^{N_2+1}, \qquad l_2=l_1+1 \quad , \qquad (26)$$

leads to the rising of giant photoabsorption resonances (Connerade 1984, [4]). In the case of such transitions the expression of the average energy was obtained in [26] and that of the variance by Грудзинскас (1986). These formulae are also valid for the complementary transitions

$$nl_1^{N_1} \rightarrow nl_1^{N_1-1}\, nl_2 \;, \qquad (27)$$

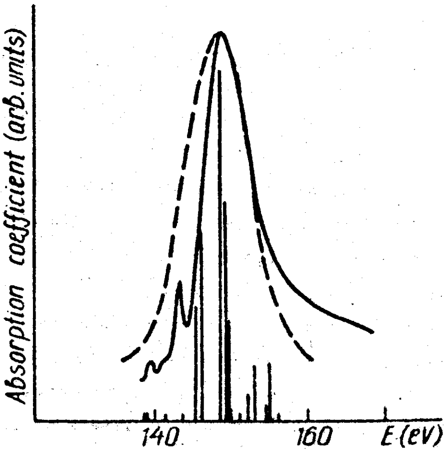

Fig. 12. Gd photoabsorbtion spectrum corresponding to the transitions $4d^{10}4f^7$-$4d^9 4f^8$ (Демехин, Шелкович 1974) (solid line), and its envelope, calculated using two first moments (broken line) [2].

considered by Bauche et al. (1988).

An example of the photoexcitation spectrum envelope, computed with the aid of two first moments, is shown in Fig. 12

4. LEVEL AND LINE GROUPS IN THE SPECTRA

When one interaction in a configuration mostly predominates over the others, the atomic spectra are separated into level or line groups. These groups often maintain their characteristic features in various atoms and are monotonously depending on the number of electrons in the open shell or ionization degree. In such cases it is useful to introduce the mean quantities, characterizing not the whole spectrum, but the separate group of levels or lines. A work in this direction only begins. The average energy and variance of levels with given spin for the configuration l^N was obtained by Slater (1968). Some formulae for the first two moments of spin-orbit split arrays were presented by Bauche-Arnoult et al. (1985). The author's aim was to develop the methods of summation over some quantum numbers, to obtain new formulae of lower moments and ,in certain cases, to perform the analysis of the existence and regularities of such groups as well as to reveal the dependence of energy on the more important quantum numbers.

4.1. Mean characteristics of level or line groups, formed by the spin-orbit interaction. For the atom with the inner vacancy nlj^{-1} $(l\ 0)$ the spin-orbit interaction within this shell predominates over other interactions. Thus energy levels of such configuration are separated into two spin-doublet groups and the emission or Auger spectrum, corresponding to the transitions to this configuration, in spin-doublet groups of lines (Fig. 13). In heavy atoms or high ions the splitting of other shells becomes important as well. When all the shells split into subshells, the mean characteristics of the subarray, corresponding to the transitions between two subconfigurations, can be obtained by the general summation method, referred in Sec. 3.1. This method is also useful for finding the mean characteristics of spin-doublet groups of levels or lines in the case of the LS coupling within shells. A shell containing a single vacancy with the given total momentum quantum number j can be separated definitely into two subshells

$$l^{4l+1}j \to j^{2j}\, j'^{2j'+1}, \quad \text{where } j' = l \pm 1/2 \text{ at } j = l \mp 1/2. \tag{28}$$

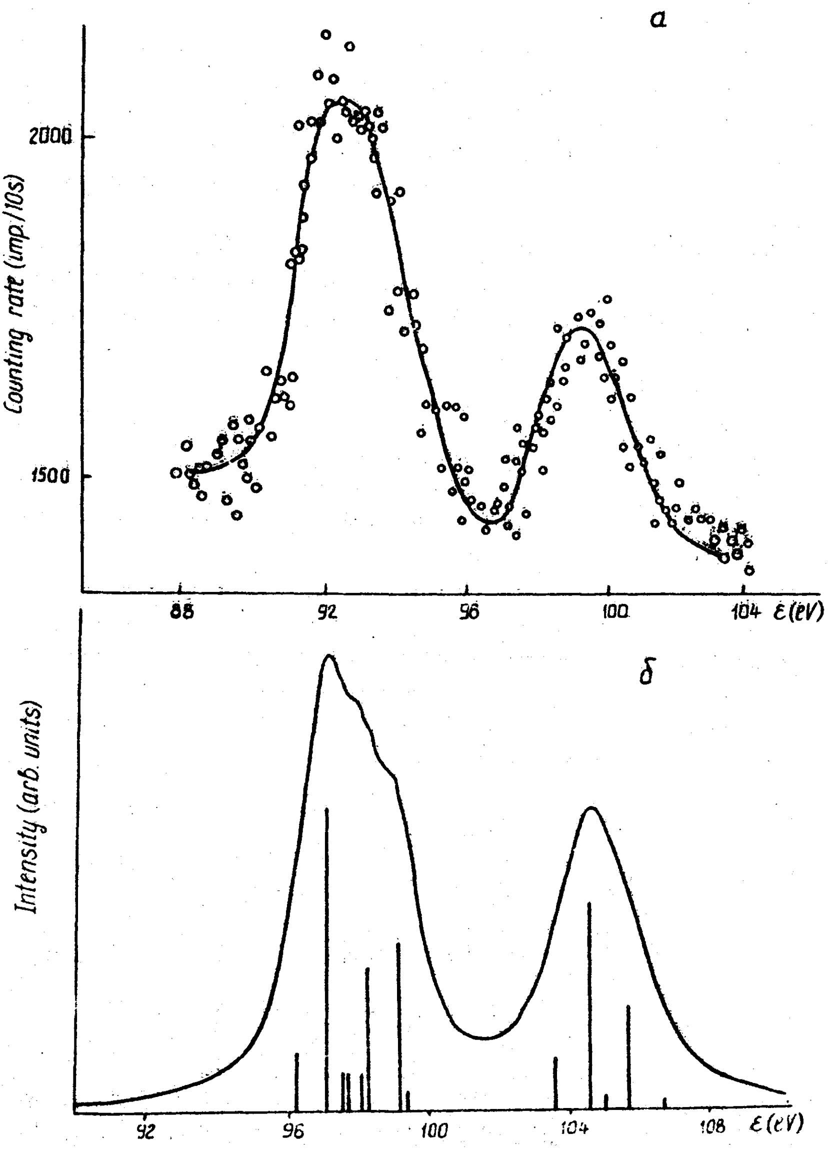

Fig. 13. Kr $M_{2,3}M_{4,5}N_{2,3}$ Auger spectrum: a - experiment (Siegbahn K. et al. 1967); b - calculation in Hartree-Fock-Pauli approximation on taking into account natural width of lines [22]. Arrows mark the average energies of spin-doublet groups of lines.

A closed subshell does not give a contribution to the mean characteristics of spectrum. Thus accomplishing the summation in spaces of inner subshell and outer shells independently, we obtain the mean characteristics, depending only on the total quantum number of the inner vacancy [2].

As in the case of Auger spectrum (Sec.3.4) the general expressions of moments can be presented in such form, that they would remain in force for both coupling schemes in any shell.

The independence of summation in the spaces of separate shells or subshells can also be used for obtaining the mean characteristics of spin-doublet groups of lines in photoexcitation or photoelectron spectra [2] (some of the operators are acting on the single electron states nljm and the others on states $nlm\mu$).

The mean characteristic method is useful for the calculation of spin-doublet lines, which are broadened by the multiplet splitting due to the interaction between a vacancy and an outer open shell. Some preliminary results on the $K_{\beta 1,2}$ lines multiplet broadening in transition elements were presented in [36].

4.2. Coulomb exchange interaction in the complex configurations and peculiarities of spectra.

Decomposition of Coulomb exchange interaction operator into scalar product of two one-electron operators and the electron number operator reveals the structure of exchange matrix elements, coefficients of which can be presented in the form [2, 38]

$$g_k(K_0\, l_1^{N_1}\, l_2^{N_2}\, \gamma\gamma' J) = \Big\{(2J+1)^{-1} \sum_{\gamma'' J''} \langle K_0\, l_1^{N_1}\, l_2^{N_2}\, \gamma J \| W^{(k)} \| K_0\, l_1^{N_1+1}\, l_2^{N_2-1}\, \gamma'' J'' \rangle \times$$

$$\times \langle K_0\, l_1^{N_1}\, l_2^{N_2}\, \gamma' J \| W^{(k)} \| K_0\, l_1^{N_1+1}\, l_2^{N_2-1}\, \gamma'' J'' \rangle - \delta(\gamma,\gamma')\, \frac{N_2}{2l_2+1} \Big\} \langle l_1 \| C^{(k)} \| l_2 \rangle^2 =$$

$$= \Big\{(2J+1)^{-1} \sum_{\gamma'' J''} \langle K_0\, l_1^{N_1}\, l_2^{N_2}\, \gamma J \| W^{(k)} \| K_0\, l_1^{N_1-1}\, l_2^{N_2+1}\, \gamma'' J'' \rangle \times \qquad (29)$$

$$\times \langle K_0\, l_1^{N_1}\, l_2^{N_2}\, \gamma' J \| W^{(k)} \| K_0\, l_1^{N_1-1}\, l_2^{N_2+1}\, \gamma'' J'' \rangle - \delta(\gamma,\gamma')\, \frac{N_1}{2l_1+1} \Big\} \langle l_1 \| C^{(k)} \| l_2 \rangle^2,$$

where $W^{(k)}$ is the general unit operator. If the term structure of configuration $nl_1^{N_1}\, nl_2^{N_2}$ is mainly determined by the largest member of a matrix element with g_{mink}, then its terms have a tendency to separate into two groups: the lower group with the negative term-independent Coulomb exchange energy and the upper group of terms, which are linked by the matrix elements of $W^{(k)}$ with the terms of configurations $l_1^{N_1 \pm 1}\, l_2^{N_2 \mp 1}$.

The simplest such configurations are $n(l-1)^{-1}nl$ (Hansen 1972, Кучас и др. 1976), which have one high-lying level ^1P and a lower group of remaining levels. The upper group in configurations $n(l-1)^{-1}nl^N$ and $nl^{4l+2-N}n(l+1)$ at N=2 consists of three terms, which at l=3 are usually lying quite distant from the lower group (Fig. 14). At a larger number of electrons or vacancies N the levels of both groups tend to overlap. It is expedient to describe the

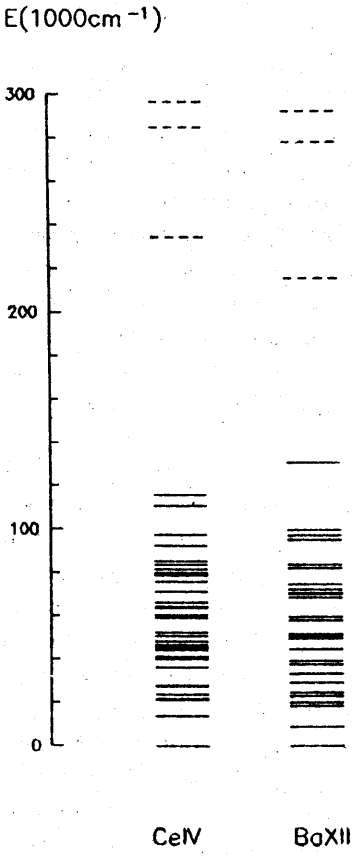

Fig. 14. Energy term spectra of CeIV $4d^9 4f^2$, and Ba XII $4d^8 4f$ (with respect to the lowest term of configuration) calculated in Hartree-Fock-Pauli approximation [38].

distant groups by different radial orbitals. For these purposes the expressions of the average exchange coefficient for the upper group were obtained [27, 2].

By diagonalising the matrix of main coefficients $g_{|l_1-l_2|}$ it is possible to obtain the wavefunction basis, which is more exact than the usual coupled momenta basis [27,38] (Due to the cancellation effect, the mixing of terms, belonging to both groups, remains small on taking into account all Coulomb interaction). This basis can be constructed explicitly by using the operator $W^{(k)}$, in particular, on obtaining the wavefunctions of this operator. At $l_1=l_2$ and min $k=0$ this operator is proportional to the isospin operator (Рудзикас, Канялускас 1984), while at $l_1 \neq l_2$ to the electric multipole transition operator; the last basis, elaborated mathematically by Bernotas et al. (1990), was named particle-hole basis.

Relationship (29) between the exchange coefficient g_1 and electric dipole transition amplitudes explains the known pattern of photoexcitation spectra, corresponding to transitions (28). In the dipole approximation the photoexcitation is possible only to those terms of a final configuration, which belong to the upper group of terms, and the main maximum of spectra is shifted to the higher energies (Sugar 1972).

4.3. Dependence of atomic quantities on spin, isospin and quasispin quantum numbers. Levels with given spin quantum numbers are rarely resolved into separate groups, but the tendency to arrange levels with the higher multiplicity lower in the spectrum is peculiar to the electronic configurations, especially with one open shell. Even if such groups do not arise, sometimes it is important to determine the dependence of the energy and other atomic quantities on the approximately good spin quantum numbers.

In the case of the LS coupling within shells, the summation in orbital and spin spaces can be accomplished independently. Since only the scalar part of the operator gives a contribution to its average, we can put all the resulting orbital ranks of the operator in the subspaces of all shells equal to 0 [2]. When the operator is one-electron operator in all subspaces, the averaged spin operator is obtained immediately, its matrix element has the explicit expression. (In this way the dependence of the Coulomb exchange interaction energy between shells on the spins is easily determined.) If the operator is of two-electron type in certain subspace, it can be transformed into a spin operator in the following way [2]. The pairing operator (its eigenvalue gives the number of electron pairs in a shell) is transformed into a coupled form

$$\mathcal{P} = -\frac{1}{2} \sum_{L_1 S_1} \left[[a^{\dagger} \times a^{\dagger}]^{(L_1 S_1)} \cdot [\tilde{a} \times \tilde{a}]^{(L_1 S_1)} \right], \qquad (30)$$

where $\tilde{a}_{nlm\mu} = (-1)^{l+s-m-\mu} a_{nl-m-\mu}$. Each term of sum (30) over S_1 represents the operator of pairing with the given moment S_1. Multiplying its eigenvalue

$$\langle l^N \gamma LS | \mathcal{P}(S_1) | l^N \gamma LS \rangle = N(S,\ S_1) \qquad (31)$$

by the average energy of the electron pair with the spin S_1 and summing over all possible values of S_1 we obtain the average energy of the terms with the spin S

$$\bar{E}(l^N\ S) = \sum_{S_1} N(S,\ S_1)\ \bar{E}(l^2\ S_1). \qquad (32)$$

The corresponding operator (obtained replacing in the right hand of (32) the eigenvalue $N(S,\ S_1)$ by the paring operator $\mathcal{P}(S_1)$) represents an average spin operator, introduced by Рудзикас, Канялускас (1984). It can be used for evaluating other moments of the term group with given multiplicity.

The averaging of the transition probabilities can be accomplished by using the relation for the fractional parentage coefficients

$$\sum_{\bar{\gamma}\,\bar{L}} (l^N \gamma LS \| l^{N-1}\ \bar{\gamma}\ \bar{L}\ \bar{S})^2 = \frac{2\bar{S}+1}{N(2S+1)} \left[\frac{2N+3}{4} + S(S+1) - \bar{S}(\bar{S}+1) \right] \qquad (33)$$

and the corresponding relation for the two electron coefficients ([31], Шимонис, Бернотас 1983).

A similar method can be applied for obtaining the energy dependence on the isospin quantum number T. By treating the creation and annihilation operators as triple tensors in orbital, spin and isospin spaces and introducing the operators of pairing with a given isospin number, it is possible to evaluate the coefficients for Coulomb interaction matrix elements averaged over all many-electron quantum numbers except T [31]:

$$\bar{f}_k(l^{N_1}\ l^{N_2}\ T) = -\frac{2\langle l \| C^{(k)} \| l \rangle^2}{(2l+1)(4l+1)(4l+3)}\ [l(l+1)N_1N_2 + (2l+1)X\ ],\quad k=0, \qquad (34)$$

$$\bar{g}_k(l^{N_1}\ l^{N_2}\ T) = -\frac{2\langle l \| C^{(k)} \| l \rangle^2}{(2l+1)(4l+1)(4l+3)} \left[\frac{8l+5}{2}\ N_1N_2 + X \right],\quad k=0, \qquad (35)$$

$$\bar{g}_0(l^{N_1}\, l^{N_2}) = \frac{1}{2} N_1 N_2 + X , \tag{36}$$

where

$$X = T(T+1) - \frac{N_1(N_1+1)}{2} - \frac{N_2(N_2+1)}{2} . \tag{37}$$

At $T=(N_1-N_2)/2$ $(N_1 \geq N_2)$ these formulae describe the Coulomb interaction energy, averaged over all terms, absent in the lower configurations l^{N_1} l^{N_2-p} $(p>0)$ [18]. Their use in Hartree-Fock equations gives the wavefunctions, which are automatically orthogonal to the functions of lower states with the same symmetry.

The quasispin Q, the second analog of the spin, is related to the seniority quantum number v. Using the pairing operator $\mathcal{P}(Q)$ it is possible to obtain the interaction energy, averaged over all quantum numbers, except v [31], De Shalit, Talmi (1963). The coefficient at the integral $F^k(nl,nl)$ reads:

$$\bar{f}_k(l^N v) = \left\{ \frac{N(4l+2-N)}{4l(2l+1)} - \frac{(4l+4-v)v}{4l(4l+3)} \right\} \langle l \| C^{(k)} \| l \rangle^2 . \tag{38}$$

The shell l^N has only one term with $v=0$ or $v=1$, which is usually the highest term of this configuration [25], so (38) gives the formula for such term and, together with the expression for the ground level (see Sec.4.4), enables to find the width of the energy spectrum.

4.4. Peculiarities of the ground state and regularities of the binding energies. Levels of the ground term often form a separate group of levels. Thus, at normal temperatures ($T \leq 500$K) only this group of levels or usually only the ground level are populated, so they are playing an important role in the formation of spectra. In the LS coupling the ground term often is of the highest multiplicity. The other quantum numbers of this term and its lowest level also have simple expressions in the case of one open shell

$$S = \mathcal{N}/2, \quad v = \mathcal{N}, \quad L = \mathcal{N}(2l+1-\mathcal{N})/2, \quad J = \mathcal{N}(2l-N)/2, \tag{39}$$

where N is the number of electrons at $N<2l+1$ and the number of vacancies at $N \geq 2l+1$. The formulae for W and U quantum numbers of the ground term of the f^N shell were obtained in [25].

A shell in its highest multiplicity state can be separated into two

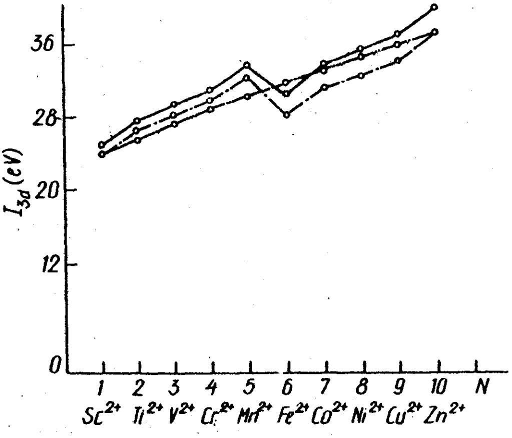

Fig. 15. Binding energy of 3d electron in third ions of transition elements as a function of the number of electrons in $3d^N$ shell. - experiment (data, taken from Cowan (1981)); -·- calculation in Hartree-Fock-Pauli approximation; -·· calculation taking into account only average energies [35].

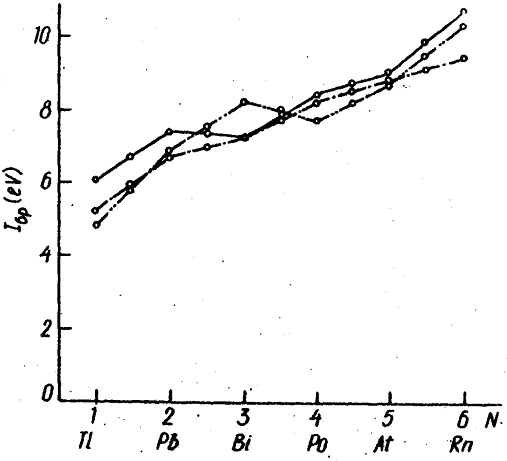

Fig. 16. Binding energy of 6p electron in neutral atoms as a function of the number of electrons in $6p^N$ shell. - experiment (data, taken from Cowan (1981)), -·- calculation in Hartree-Fock-Pauli approximation; -··- the same, but missing spin-orbit interaction contribution [35].

subshells with electron spins directed up and down (Judd 1967b), one of which is empty or closed. The additional relations for scalar products of standard unit operators can be found in the spin-directed space. It leads to the explicit expressions for the energies of the highest multiplicity terms [25]. The substitution of the ground term quantum numbers (39) gives the formulae of the ground term energy as the polynomial of the electron number in a shell [25].

A subshell remains invariant on replacing electrons by vacancies (at frozen radial wave functions). Thus a shell in its highest multiplicity state obtains an additional symmetry with respect to a half of shell $l^N \to l^{2l+1-N}$

The electron binding energy in an atom is expressed by the difference of ion and atom ground state energies. So while using the obtained formulae for them, it was possible to evaluate explicit expressions of the term-dependent part of the binding energy and to show their approximate symmetry with respect to the numbers of electrons $N=l+1$ and $3l+2-N$. This dependence has a different pattern in the cases, when Coulomb or spin-orbit interactions are dominating in a shell. The experimental results usually correspond to the Coulomb pattern, imposed on the linearly increasing difference of average energies (Fig. 15), but in a row of atoms with the $6p^N$ open shell a spin-orbit pattern gives an evidence (Fig. 16). Taking into account all parts of the binding energy the "interval rules" for this quantity were derived [35]

$$\left[I_{nl}(l^{l+1-N}) + I_{nl}(l^{l+1+N}) \right] / I_{nl}(l^{l+1}) = 2\,, \tag{40}$$

$$\frac{I_{nl}(l^{l+1-N}) + I_{nl}(l^{l+1+N})}{I_{nl}(l^{l+1-N'}) + I_{nl}(l^{l+1+N'})} = 1, \qquad l>1, \tag{41}$$

where $N=0,1,\ldots,l$. Corresponding rules for the almost filled shell follow from (40), (41) on replacing in them $l+1$ by $3l+2$. These rules were established empirically for f electrons by Спицын и др. (1987). Their applications to p, d and f electrons of various atoms and ions have shown a high accuracy even at high degree of ionization.

5. CONFIGURATION MIXING AND ITS INFLUENCE ON X-RAY AND AUGER SPECTRA.

The investigation of correlation or many-body effects is one of the main problems in atomic theory and in particular in inner-shell physics. Configuration mixing (CM) or configuration interaction method is the mostly used correlation method. Besides the numerous calculations, performed by this method, some attempts to investigate the regularities of configuration mixing effects (Layser 1959, Froese-Fisher 1977, Cowan 1981, Beck, Nicolaides 1982, and others) and to introduce their mean characteristics (Rajnak, Wybourne 1963, Bauche et al. 1988) were made. Such a theoretical approach was developed in this work by introducing the new mean characteristics, evaluating their expressions and applying them, sometimes together with detailed calculations, for the investigation of strong mixing effects in X-ray and Auger spectra.

5.1. Mean characteristics of the configuration mixing. The complex of two or more mixing configurations and the transitions between such two complexes can be described by their moments. It is very important that these moments can be expressed in terms of the averages of the operators in a single-configuration approximation [2]. Instead of the central (μ_k) and the initial (α_k) moments it is useful to introduce their changes due to the configuration mixing

$$\Delta\mu_k = \mu_k^{CM} - \mu_k^{sum}, \qquad \Delta\alpha_k = \alpha_k^{CM} - \alpha_k^{sum}, \tag{42}$$

where the subscripts "CM" and "sum" indicate moments of complex in CM and single-configuration approximations. For example, the changes of the second and the third initial moments of energy level spectrum are expressed by the averages as follows [2]:

$$\Delta\alpha_2^{CM}(\mathcal{K}) = \frac{2}{g(\mathcal{K})} \sum_{i<j} g(K_i) \langle H_{K_iK_j} H_{K_jK_i} \rangle^{K_i}, \tag{43}$$

$$\Delta\alpha_3^{CM}(\mathcal{K}) = \frac{3}{g(\mathcal{K})} \left\{ \sum_{i\neq j} g(K_i) \langle H_{K_i} H_{K_iK_j} H_{K_jK_i} \rangle^{K_i} + \right.$$

$$\left. +2 \sum_{i<j<k} g(K_i) \langle H_{K_iK_j} H_{K_jK_k} H_{K_kK_i} \rangle^{K_i} \right\}. \tag{44}$$

where H_K and $H_{K_iK_j}$ are the Hamiltonians, acting in the configuration K_i or between the configurations K_i and K_j. The summation in (43), (44) is carried out over all configurations of the complex $\mathcal{K}$.

The main problem of the CM method is a choice of the configuration basis. So far as the CM is stronger at the larger absolute value of interconfiguration matrix elements and at the smaller distances between interacting levels, the following measure of the configurations K and K' mixing, the configuration mixing strength, can be introduced [24, 1]

$$T(K,K')= \frac{\sum\limits_{\gamma\gamma'} \langle K\gamma|H|K'\gamma'\rangle}{\sigma^2(K,K')} = \frac{M(K,K')}{\sigma^2(K,K')}, \tag{45}$$

where $\sigma^2(K,K')$ is the variance of spacings between interacting levels

$$\sigma^2(K,K')= \frac{\sum\limits_{\gamma\gamma'} [\langle K\gamma|H|K\gamma\rangle - \langle K'\gamma'|H|K'\gamma'\rangle]^2 \langle K\gamma|H|K'\gamma'\rangle^2}{\sum\limits_{\gamma\gamma'} \langle K\gamma|H|K'\gamma'\rangle^2}. \tag{46}$$

Approximately $T(K,K')$ has a meaning of a square of an average coefficient in a wavefunction expansion. This quantity was used to investigate the mixing of $(s+d)^{N+1}$ configurations in the iron group ($\sigma^2(K,K')$ in (45) was approximately replaced by the squared difference of the average energies $(\bar{E}(K)-\bar{E}(K'))^2$). As Fig. 17 shows, the CM between d^Ns and $d^{N-1}s^2$ configurations is prevailing in the second half of the period, mainly due to the strong overlap of these configurations.

The shift of the level $K\gamma$ energy due to its CM with all levels of the distant configuration K' can be calculated approximately in the second order of perturbation theory by replacing the energy difference in the denominator by the average difference

$$\bar{E}(K\gamma,K')= \frac{\sum\limits_{\gamma\gamma'} [\langle K\gamma|H|K\gamma\rangle - \langle K'\gamma'|H|K'\gamma'\rangle] \langle K\gamma|H|K'\gamma'\rangle^2}{\sum\limits_{\gamma\gamma'} \langle K\gamma|H|K'\gamma'\rangle^2}. \tag{47}$$

Thus the average energy shift may be expressed in the form

$$\Delta\bar{E}(K\gamma,K')= \frac{\sum\limits_{\gamma} \langle K\gamma|H|K'\gamma'\rangle^2}{\bar{E}(K\gamma,K')} = \frac{\langle K\gamma|H^{eff}|K\gamma\rangle}{\bar{E}(K\gamma,K')}. \tag{48}$$

The formulae of the effective operator H^{eff} for different configurations with one or more open shells were given by Rajnak, Wybourne (1963), Богданович, Жукаускас (1983), Uylings (1985), the general formulae were presented in [2].

The average shift of the level energy of configuration K is given by

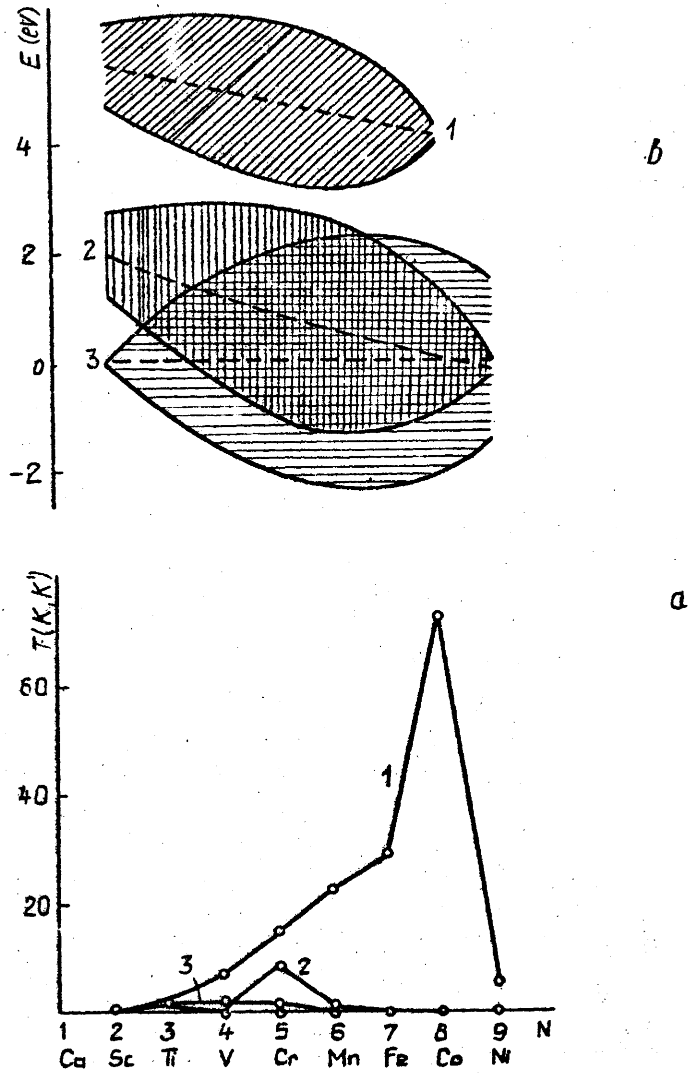

Fig. 17. $(s+d)^{N+1}$ mixing in iron series [24]. Dashed line corresponds to the average energies of configurations d^{N+1}(1), $d^{N}s$ (2) and $d^{N-1}s^{2}$ (3) with respect to the energy of configuration $d^{N-1}s^{2}$; shaded areas show the bands E± 1,178 $\sqrt{\sigma^2}$ for configurations $d^{N}s$ (vertical shading), $d^{N-1}s^{2}$ (horizontal shading) and d^{N+1} (oblique shading). Solid lines in the bottom represents the mixing strength T(K,K') (45): 1- $d^{N}s$- $d^{N-1}s^{2}$; 2-d^{N+1}-$d^{N+1}s^{2}$; 3-d^{N+1}-$d^{N}s$.

$$\Delta\bar{E}(K,K') = \frac{1}{g(K)} \sum_{\gamma} \Delta\bar{E}(K\gamma,K') = \frac{M(K,K')}{g(K)\ \bar{E}(K,K')}. \tag{49}$$

The expression of the sum M(K,K') was obtained in [28, 2].

5.2. Narrowing of the emission spectrum due to configuration mixing. The general summation method, referred in Sec.3.1, is also useful for evaluating the mean characteristics of the emission spectrum, corresponding to the transitions between two complexes of mixing configurations. The changes of the spectral moments due to CM are defined similarly to (42). For example, taking into account correlations among three shells in the initial state, the change of the average energy may be written [34]:

$$\Delta\bar{E}_{CM}(l_1^{N_1-1}\ l_2^{N_2+1}\ l_3^{N_3} + l_1^{N_1}\ l_2^{N_2-1}\ l_3^{N_3+1} \rightarrow l_1^{N_1}\ l_2^{N_2}\ l_3^{N_3}) =$$

$$= \frac{2}{4l_2+1} \left[\frac{(4l_1+2)\ d^2_{l_2,l_3}}{N_1(4l_2+2-N_2)} + \frac{(4l_3+2)\ d^2_{l_1,l_2}}{N_2(4l_3+2-N_3)} \right]^{-1} d_{l_1,l_3}\ d_{l_3,l_2} \times \tag{50}$$

$$\times \sum_k \left[\frac{2\ \delta(k,1)}{3} - \begin{Bmatrix} l_1 & l_2 & k \\ l_3 & l_2 & l_1 \end{Bmatrix} \right] \langle l_1 \| C^{(k)} \| l_2 \rangle\ \langle l_3 \| C^{(k)} \| l_2 \rangle\ R^k(l_1 l_3, l_2 l_2),$$

where d_{l_1,l_2} is a single electron submatrix element of the transition operator, R^k is a Coulomb radial integral. In the case $N_1=4l_1+2$, $N_3=0$ shift (50) was obtained by Bauche et al.(1987). The formula of the variance for these transitions was given in [2]. Using the symmetry between N-particle and N-vacancy averages it is possible to transform these expressions for the transitions from one upper configuration to two-configuration complex [2].

The obtained explicit formulae of the mean characteristics $\Delta\bar{E}_{CM}$ and σ^2_{CM} were used to investigate the narrowing of the emission spectrum through configuration mixing. This effect called an attention, when it allowed to explain the intense quasicontinuum bands in soft X-ray spectra of highly ionized rare-earth elements (Mandelbaum et al. 1988).

The most important special case of transitions (50) corresponds to the decay of a vacancy at the presence of outer open shell

$$sp^N + s^2p^{N-2}d \rightarrow s^2p^{N-1}, \quad p^5d^N + p^6d^{N-2}f \rightarrow p^6d^{N-1},$$
$$d^9f^N + d^{10}f^{N-2}g \rightarrow d^{10}f^{N-1}. \tag{51}$$

In atoms and first ions the configuration with inner vacancy strongly mixes with many configurations of the second type (5) (outer electron is excited into a Rydberg series or even corresponding continuum), but in highly ionized atoms it mixes efficiently with only one nearest configuration. The largest shift $\Delta\bar{E}_{CM}$ takes place at equal principal quantum numbers of all electrons. The analysis of (50) shows, that shift of the average energy for such transitions is always positive, i.e., the intensity of transitions from a higher configuration decreases and from a lower configuration increases. The results of calculation at various numbers of electrons in outer shell, ionization degrees and principal quantum numbers of ns^{-1} and np^{-1} vacancies [34] show a linear dependence between $\Delta\bar{E}_{CM}$ and $\Delta\sigma^2_{CM}$. The narrowing of the spectrum and its shift to the higher energies due to CM increase with increasing the degree of ionization, decreasing the principal quantum number and increasing the orbital quantum number.

Initial and final configurations of considered transitions (51) are the same as the related ones in the expression of the coefficient g_1 (29). Once more, the main coefficient χ_1 of the interconfiguration matrix element is expressed by the same matrix elements of operator $W^{(1)}$ [38]. It reveals a deep relation between the structure of energy levels and emission spectra. The diagonalization of the matrix $\|g_1+\chi_1\|$ gives a new two-configuration basis, which takes into account a considerable part of mixing effects.

5.3. Mixing of the Brillouin's configurations. In the case of some configurations, differing by the principal quantum number of one electron the interconfiguration matrix elements with frozen orbitals are vanishing. This result is known as the Brillouin's theorem. The knowledge of such configurations in various approximations allows one to exclude them from the basic sets. Some Brillouin's configurations were determined by Bauche, Klapisch (1972), Labarthe (1972), Froese-Fisher (1973), Cowan (1981).

The variation of a Hartree-Fock radial orbital

$$P_{nl}(r) = P^{HF}_{nl}(r) + \varepsilon P_{n'l}(r) \tag{52}$$

and its substitution into the energy functional on requiring its stationarity, leads to a general relation for matrix elements (Froese-Fisher 1973). It was used in [28] to establish all the configurations, for which the Brillouin's theorem is holding in Hartree-Fock (for the average energy and LS-term) and isospin bases. In HF-av basis such configurations are:

$$K_0\, nl - K_0\, n'l, \quad K_0\, nl^{4l+2} - K_0\, nl^{4l+1}\, n'l,$$
$$K_0\, nl^{4l+2}\, n'l^{4l+1} - K_0\, nl^{4l+1}\, n'l^{4l+2}, \tag{53}$$

where K_o means closed shells.

In HF-LS basis the list of Brillouin's configurations becomes more extended

$$K'_0\,nl - K'_0\,n'l,\quad K_0\,nl^2 - K_0 nl\,n'l,\quad K_0\,nl^{4l+2} - K_0\,nl^{4l+1}\,n'l,$$
$$K'_0\,nl^{4l+2}\,n'l^{4l+1} - K'_0\,nl^{4l+1}\,n'l^{4l+2},$$
$$K_0\,nl^{4l+2}\,n'l^{4l} - K_0\,nl^{4l+1}\,n'l^{4l+1}, \qquad (54)$$

where the core K'_o may contain one electron or one vacancy above closed shells. In isospin basis some more interconfiguration matrix elements disappear [18], but the list of Brillouin's configurations remains the same as in HF-LS basis [28].

When the Brillouin's theorem does not hold, some compensation of the interconfiguration matrix elements of Coulomb interaction operator with the ones of kinetic energy and Coulomb interaction with the nucleus operator takes place. All such terms were determined in [28]. An explicit expression of the total sum M(K,K') for configurations K,K' differing by quantum numbers of one electron, was also obtained.

5.4. Satellite lines in Auger and photoelectron spectra due to configuration mixing. Strong correlation effects for configurations with inner vacancy, mainly of type (5), lead to the rising of a pronounced satellite structure in various X-ray and electronic spectra, especially of noble gases and neighboring elements (Mehlhorn 1982). The efficiency of CM method, taking into account only few strongly mixing configurations, was demonstrated by Mehlhorn (1982), Демехин и др. (1976) and others as well as in [17, 19, 22]. An interpretation of satellite lines of X-ray spectrum was demonstrated in Sec.2.6., here such interpretation is given for some Auger and photoelectron spectra.

Very intense satellite lines were observed in $M_{4,5}NN$ Auger spectrum of Kr and $N_{4,5}OO$ spectrum of Xe by Werme et al. (1972). These satellites were discussed and interpreted in many papers but mainly using the results for line energies only. The full calculation of intensities and energies of satellite lines was accomplished in [19]. The superposition of the following configurations was taken into account:

$$4s4p^5 + 4s^24p^34d + 4s^24p^35d + 4s^24p^35s,$$
$$4s^24p^4 + 4s^04p^6 + 4s4p^44d + 4s4p^45d + 4s^24p^35p. \qquad (55)$$

The interpretation of this Auger spectrum was accomplished together with the reexamination of the energy level spectrum, the level positions of which in the lower part of the spectrum correspond very well to the experimental results (Fig. 18). The main satellite lines are produced by the double Auger transitions, taking place due to the mixing $4s4p^6 + 4s^24p^34d$ (Fig. 19). Some reassignments of the Auger lines and Kr III energy levels were proposed.

The results of calculation by CM method of Xe $N_{4,5}OO$ Auger spectrum allowed an interpretation of its satellite lines by $5p^35d$ and $5p^36s$ mixing with $5s5p^5$. In the case of transitions $N_{4,5}OO$ and $N_{4,5}O_{2,3}O_{2,3}$ the

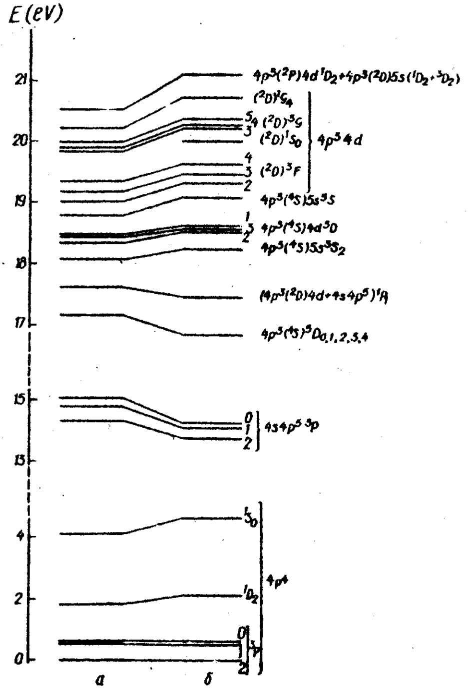

Fig. 18. Energy levels of KrIII (lower part of the spectrum): a- experiment (Moore 1952), b - calculation in configuration mixing approximation (55) [19].

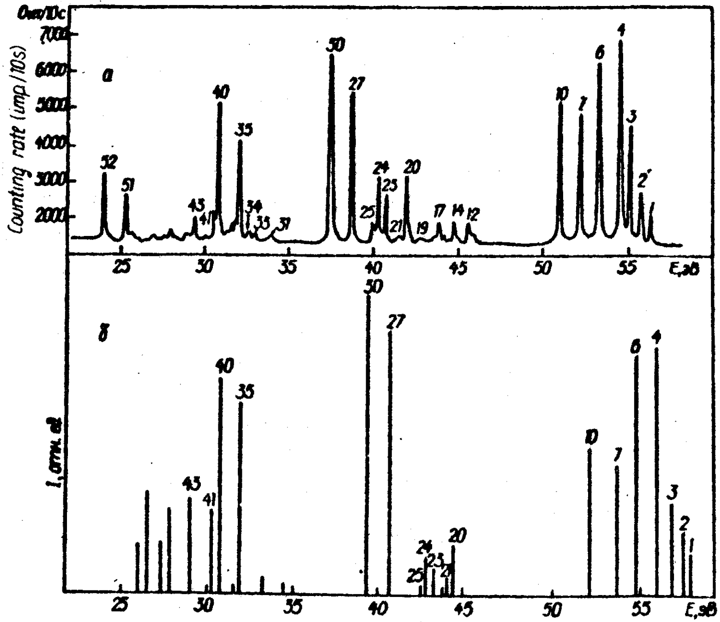

Fig. 19. $M_{4,5}$NN Auger spectrum of Kr: a- experiment (Werme et al. 1972); b- calculation, taking into account configuration mixing (55). The theoretical spectrum is normalized with experiment for $M_4N_{2,3}N_{2,3}$ line [19].

correlation effects in the final configuration of the ion are also important [19, 22].

At the presence of an inner vacancy in the atoms of alkali earth elements the $(s+d)^2$ mixing increases due to the collapse of d orbital (Connerade 1978, [24]). It manifests in Ba 4d electron spectrum (Fig. 20), which was obtained by Wuilleumier et al. 1982 and calculated in [24] using the following approximation:

$$4d^9(6s^2+5d^2+6s5d+6p^2+6d^2+4f^2). \qquad (56)$$

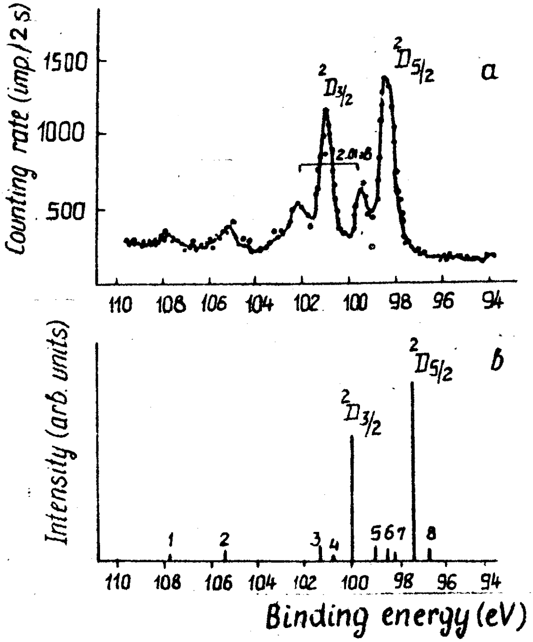

Fig. 20. 4d photoelectron spectrum of Ba: a - experiment (Wuilleumier et al. 1982), hν= 130,2 eV; b - calculation by configuration mixing method [24]. Individual satellite lines correspond to the transitions into following final states 1- $4d^9_{3/2}6p^2(^1S)$; 2- $4d^9_{5/2}6p^2(^1S)$; 3 - $4d^9_{3/2}5d^2(^1S)$; 4- $4d^95d^2(^1D)^2D_{3/2}$; 5 -$4d^9_{5/2}5d^2(^1S)$; 6-$4d^96s(^1D)5d\ ^2D_{3/2}$; 7-$4d^96s(^3D)5d\ ^2D_{5/2}$; 8- $4d^95d^2(^1D)5d\ ^2D_{5/2}$.

The main satellite lines correspond to the final states of configuration $4d^95d^2$, two $5d^2$ electrons having the same term ^1S as $6s^2$ electrons.

6. MAIN RESULTS AND CONCLUSIONS.

1. Expressions for binding energy and X-ray energy shifts due to vacancy production explicit (quadratic) with respect to the number of vacancies have been derived. They exceed in accuracy the formula, widely used for the interpretation of energy shifts, and differ only a little in accuracy from the general formula, expressed in terms of total energies, which is not explicit and requires considerably more calculations. The parameters of obtained expressions were calculated for various atoms and two principal X-ray lines, their weak dependence on the configuration and other regularities were established. This method was systematically used to interpret experimental chemical shifts of X-ray lines.

2. The efficiency of Hartree-Fock-Pauli method (taking into account relativistic corrections in the first order of perturbation theory) for inner and subvalent vacancies, except the deeper and the outer ones, was shown. The regularity was established: the difference between relativistic and experimental values of inner electron binding energy or the correlation correction increases in absolute value for the given quantum number with an increasing orbital quantum number, what is caused by the interaction of the vacancy with super-Coster-Kronig and Coster-Kroning continua.

3. The general expression for the Auger width of the level and some approximate expressions for the radiative width were obtained. Independence of the partial widths for configurations with one open "active" shell on many-electron quantum numbers was proved. The same peculiarity of the total natural width and fluorescence yield is taking place for a narrower class of configurations with one open shell above closed shells. This considerably simplifies the calculation of these quantities for such configurations.

4. At the nonstatistical population of levels the reliable theoretical interpretation of X-ray and Auger spectra requires the investigation of all the cascade of processes, following a vacancy production and its decay. The method of such calculations was elaborated (the determination of main processes by a preliminary calculation of total populations of configurations, approximate estimation of correlation effects, evaluation of the expressions for some elementary processes (many-electron transitions in sudden perturbation approximation, Auger transitions). The first such calculation for some transitions was accomplished, taking into account CM

effects.

5. The general diagrammatic summation method has been elaborated, useful for obtaining explicit expressions for mean characteristics of various atomic spectra in nonrelativistic and relativistic, single-configuration and configuration mixing approximations. It can be realized in a universal heuristic program. This diagrammatic method is applicable also in nuclear physics.

6. Expressions for the third and the fourth moments of energy level spectrum were obtained, which allow one to investigate its asymmetry and levels density difference from the normal density. Some regularities of the scewness and excess were determined for p^N, d^N and f^N shells and it was shown, that these coefficients are very sensitive to the correlation effects. It was suggested, that the ratio of the square roots of Coulomb and spin-orbital parts of the variance may serve as a measure of a coupling type in a shell.

7. General formula of the main mean characteristics - variance and excess - of the emission spectrum were obtained. It was shown that some terms of the emission spectrum moments can be expressed by the corresponding terms of the energy level moments. All the configurations, for which "emissive zone" and "receptive zone" coincide with the configuration array, were established. In the case of unifomly broadened lines the formula for the emission spectrum moments, expressed by the moments of widthless lines and a single line, was derived.

8. Mean characteristics of the Auger, photoelectron and photoexcitation spectra were introduced and examined for the first time, the expressions of the average energy and variance were derived and their usefulness for the approximate description of the spectra was illustrated.

9. It was shown, that general summation methods over all or only final configuration many-electron quantum numbers can be modified to obtain mean characteristics of spin-doublet groups of lines. In such a way some principal formulae for the energy levels, emission and other spectra were obtained.

10. New expression for the coefficient of Coulomb exchange interaction between two open shells $l_1^{N_1} l_2^{N_2}$ was derived, revealing the existence of two groups of terms, caused by this interaction. Such groups are separated energetically in the configurations $n(l-1)^{-1}nl^N$ and nl^{4l+2-N} $n(l+1)$ at $N=1,2$. This expression explains the known pattern of some photoexitation spectra, i.e., the shift of their main maximum to the higher energies.

By diagonalizing the matrix of main coefficients $g_{|l_1-l_2|}$ it is possible to obtain new wavefunction basis, more exact than the usual coupled momenta basis. This result led to the construction of the particle-hole basis for many-electron atoms.

11. The method for determining the dependence of atomic quantities on spin quantum numbers was developed, useful for the evaluation of the mean characteristics of spin groups. Its extension to the spin analog isospin leaded to an expression for Coulomb interaction energy, averaged over all quantum numbers, except isospin. In a separate case it presents the energy, averaged over terms, absent in the lower configurations of the same symmetry, which is useful for obtaining wavefunctions orthogonal to the functions of lower states.

12. Considering the electronic shell in a state of its highest multiplicity as consisting of two subshells with electron spins directed up and down, the formulae for the energy and quantum numbers of the ground level were derived. They were used to explain the regularities in the electron binding energy as a function of a number of electrons in a shell. The interval rules for the binding energies were derived and their high accuracy for various ions, even at a high degree of ionization, was shown.

13. Mean characteristics of the configuration mixing in atoms: the configuration mixing strength, variance of spacings between interacting levels, shift of (statistical) moments due to CM were introduced and expressed by the averages of the products of operators. The usefulness of the configuration mixing strength for the investigation of CM in $(s+d)^{N+1}$ complex of iron group elements was demonstrated.

14. The formulae or the shift of the average energy and variance due to CM were derived in the case of transitions from two mixing configurations or into two mixing configurations. It was shown, that mixing of the configurations $n(l-1)^{-1}nl^{N}$ and $nl^{N-2}n(l+1)$ always leads to the shift to higher energies and narrowing of the emission spectrum, corresponding to the electric dipole transitions into the configuration nl^{N-1}. This effect increases while increasing the degree of ionization, decreasing the principal quantum number and increasing the orbital quantum number.

15. All the configurations, for which the Brillouin's theorem is fulfilled in Hartree-Fock approximation for the average energy and LS-term or in isospin basis, were determined. When this theorem does not hold, the quenching terms were established for single-electron excitations.

16. The efficiency of the CM method, taking into account few strongly mixing configurations $n(l-1)^{-1}nl^{N}+ nl^{N-2}n(l+1)$ or $(s+d)^{N}$, for the interpretation of satellite structure of Auger, X-ray and photoelectron spectra was demonstrated. The calculations of the energies and intensities of the satellite lines in Kr $M_{4,5}NN$, Xe $N_{4,5}OO$ Auger spectra, Ar $L_{2,3}$ X-ray spectrum and Ba 4d electron spectrum were accomplished and the interpretation or reassignment of some lines was proposed.

Consequently as the result of this work the theory of atoms with vacancies, X-ray and Auger spectra was essentially extended: new features of the configurations with vacancies (approximate invariance of the Auger and radiative widths and fluorescence yields, appearance of the level groups, caused by Coulomb exchange interaction) and the relations between such configurations structure and X-ray or Auger spectra peculiarities (shift of the photoexcitation spectrum, narrowing of the emission spectrum, regularities of the binding energies) were revealed, general methods for obtaining explicit expressions for mean characteristics of spectra, their line or level groups were elaborated and applied to obtain main global characteristics of spectra and many-body effects in them, new wavefunction bases were suggested, efficient theoretical methods for the analysis of X-ray and Auger spectra were elaborated and applied for their interpretation. Some of these results and developed methods are also applicable in the optical spectra and nuclear shell theory.

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REZIUMĖ

Habilitaciniame darbe išplėtota sudėtingų atomų su vakansijomis vidiniuose elektronų sluoksniuose ir Rentgeno bei Ožė spektrų, atitinkančių radiacinius ar neradiacinius šuolius tokiuose atomuose, teorija. Įrodyta netikėta konfigūracijų su vakansijomis savybė: lygmenų parcialinių bei pilnų natūralių pločių, apspręstų Ožė ir radiacinių šuolių, o taip pat fluorescencijos našumo apytikris invariantiškumas. Tai leidžia žymiai supaprastinti šių dydžių skaičiavimą. Nustatyta, jog konfigūracijose su dviem atvirais sluoksniais gali susidaryti lygmenų grupės, apspręstos elektrostatinės pamaininės saveikos tarp elektronų, kas atskleidžia įdomius sąryšius tarp energijos lygmenų ir Rentgeno spektrų struktūros, o taip pat įgalina įvesti naujas tikslesnes banginių funkcijų bazes. Gautos daugiaelektronių šuolių (staigios perturbacijos artutinume) ir Ožė šuolių tikimybių išraiškos atomams su atvirais sluoksniais. Jos panaudotos pirmiems Rentgeno spektrų tyrimams, atsižvelgiant į kaskadą procesų, lemiančių spektro struktūrą. Parodyta, jog kelių stipriai susimaišančių konfigūracijų modelis gana gerai paaiškina intensyvių satelitinių linijų atsiradimą Rengeno ir Ožė spektruose.

Darbe suformuluotas bendras diagraminis sumavimo metodas, įgalinantis gauti energijos lygmenų, emisijos ir Ožė spektrų vidutinių charekteristikų algebrines išraiškas vienkonfigūraciniame ir konfigūracijų sumaišymo artutinumuose. Jis pritaikytas šių spektrų pagrindinėms charakteristikoms rasti. Tai išplečia sudėtingų spektrų, kuriuos spinduliuoja plazma ar laisvieji atomai, teorinio aprašymo galimybes, o taip pat įgalina numatyti ir tirti bendrus spektrų dėsningumus. Naudojantis antrinio kvantavimo atvaizdavimu išplėtoti būdai lygmenų bei linijų grupių, o taip pat spektrų, atitinkančių šuolius iš vieno lygmens į visus kitos konfigūracijos lygmenis, vidutinėms charakteristikoms rasti. Minėtieji metodai taip pat pritaikyti koreliciniams efektams atomuose tirti.

Kai kurie gauti teoriniai rezultatai pritaikomi ir optinėje spektroskopijoje bei branduolio sluoksnių teorijoje.

Daugelis gautų teorinių rezultatų galioja ir optinėje spektroskopijoje, o kai kurie- taip pat atomo branduolio sluoksnių teorijoje.

The author was born in Subačius, North Lithuania, in 1942. He graduated from Vilnius University in 1964. During 1965-1967 he was a post-graduated student on theoretical and mathematical physics under prof. A. Jucys at the Institute of Physics and Mathematics and in 1968 defended the Ph. D. thesis (Cand. Sc., Phys. and. Math.) "Some Questions on the Calculation of Energy Operator Matrix Elements for Complex Atoms". Since 1970 he has been working at this Institute as a senior scientific worker. In 1972-79 he also was a scientific secretary of the Lithuanian Physical Society. R. Karazija is the author of two monographs and about 65 papers on the theory of X-ray and electronic spectra of free atoms, many-electron atomic theory. He also published 5 popular books on physics.

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