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Atoms as Many-Body Systems

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Abstract

Some Personal Recollections

It is my pleasure to present this article in the volume, dedicated to the 70th birthday of Academician S. T. Belyaev. I have known him personally since 1961 and admire his profound contributions to the theory of Bose-liquids, to the theory of superconductivity of atomic nuclei and some other important scientific works. He is well known also as an organizer of science and education. For years he was, and is still the Chairman of the Synchrotron Radiation Commission of the Russian Academy of Science, a body which was established long ago to promote construction of high intensity light sources, and technological as well as scientific research using this light. One of the important directions of this study is investigation of photoabsorption by multielectron atoms in order to obtain information about their structure.

S. T. Belyaev strongly supported this direction, which gives me the right to choose as a title of my contribution

"Atoms as Many-Body Systems".

MASTER

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1. Introduction: Specifics of Atoms as Many-body Systems

Atoms are exceptional many body systems. Indeed, the interaction of their constituents, electrons and nucleus, is known with very high accuracy, the number of them varying from two for hydrogen up to about two and a half hundred. The electron density in atoms is strongly inhomogeneous and interelectron interaction is not too strong. The principal feature of atomic structure, namely the existence of shells is almost completely determined by the presence of nucleus. So, for a number of atomic characteristics at least as zero serves the Coulomb or hydrogenic approximation which treats the atom as a group of noninteracting particles moving in the Coulomb field of the nucleus. The good knowledge of interparticle interaction and relatively small number of electrons in atoms as compared to that in other multiparticle systems, such as solid bodies, permits to prefer ab initio, although approximate, calculations instead of parameterizing models.

Considering hydrogenic approach as a reasonable initial step, one should have in mind that the corrections due to interelectron interaction can be very important. Indeed, the potential energy of an electron in the field of its shell neighbors can be estimated as

$$U_i \approx N_i \frac{1}{r_{12}^{(i)}} \quad (1)$$

where N_i is the number of electrons, and $r_{12}^{(i)}$ is the mean interelectron distance in the shell i .

The potential energy of the same electron in the field of the nucleus is

$$U_n \approx \frac{Z_i}{r_i}, \quad (2)$$

where Z_i is the effective nuclear charge and r_i is the radius of the i -shell. The word "effective" means that the screening of nuclear charge by atomic electrons inner to the shell i is taken into account. Because $r_{12}^{(i)}$ is by the order of magnitude equal to r_i , these potential energies are comparable if

$$N_i \sim Z_i \quad (3)$$

which is correct for outer and intermediate atomic electron shells. For them the interelectron interaction can be even as important as the nucleus field. Therefore, the hydrogenic picture will require considerable correction firstly by introducing a better common field, in which the electrons are moving in atoms.

The best of them was suggested by Hartree and Fock in the thirties and forms the fundament of so-called Hartree-Fock (HF) approximation [1].

2. Hartree-Fock Approximation

In this section we will briefly describe the main features of the Hartree-Fock (HF) approximation. It assumes, that atomic electrons are independent particles moving in a common so-called self-consistent field, created by all but the considered atomic electrons. This is the best approach compatible with the idea of independent motion of real particles. Each consistent improvement of the HF approximation leads to quasiparticles instead of particles as objects of independent motion. These are unstable so all the description becomes much more complex.

In HF the following formulae are used to determine the one-electron wave function $\varphi_i(\vec{r})$ and the energy of an atom ε :

$$\left(-\frac{\Delta}{2} - \frac{Z}{r} - \varepsilon_i\right)\varphi_i(\vec{r}) + \sum_{j=1}^n \int d\vec{r}' \frac{1}{|\vec{r} - \vec{r}'|} \varphi_j^*(\vec{r}') [\varphi_j(\vec{r}') \varphi_i(\vec{r}) - \varphi_i(\vec{r}') \varphi_j(\vec{r})] = 0 \quad (4)$$

$$\varepsilon = \sum_{i=1}^N \varepsilon_i + \frac{1}{2} \sum_{i,j=1}^N (ij|V|ij - ji) . \quad (5)$$

Here Z is the nuclear charge^{*/}, N is the number of electrons ($N=Z$ for neutral atoms), $V = |\vec{r}_1 - \vec{r}_2|^{-1}$ is the Coulomb interelectron potential. The wave functions $\varphi_k(\vec{r})$ for $k \leq F$, i.e. for occupied and $k > F$ - vacant states, including the continuous spectrum, form a complete set.

^{*/}Atomic system of units is used in this paper: electron charge e , its mass m and Planck constant $\hbar$ are equal to one, $e=m_e=\hbar=1$.

The HF approximation accounts for very important many-particle effects, namely formation of the self consistent field, acting upon any atomic electron, and its possible exchange with other electrons.

The HF equations and their solutions have some distinctive features which deserve to be mentioned. These are coming from the nonlocality and exchange character of the last, so called Fock's, term in the left hand side of (4). The radial dependence of the self consistent field or occupied and unoccupied states is different at the asymptotical distances. Indeed, according to (4) one has

$$U(r)|_{r \rightarrow \infty} = \begin{cases} -(Z-N+1)/r & \text{for } k \leq F \\ -(Z-N)/r & \text{for } k > F \end{cases} \quad (5)$$

Exchange term leads to peculiarities in the radial dependence for the bound state wave functions at $r \rightarrow \infty$. While for ordinary potential, without exchange it is determined by the eigenstate energy ϵ_i .

$$\varphi_i(r) \sim \exp(-\sqrt{|\epsilon_i|}r), \quad (6)$$

one has from (4) [2]

$$\varphi_i(r) \sim \exp(-\sqrt{|\epsilon_F|}r), \quad (7)$$

where ϵ_F is the smallest binding energy among all occupied states $i \leq F$. If the outer electron's principal quantum number is n , its wave function r -dependence at $r \rightarrow \infty$ is given by $\varphi_o(r) \sim r^{n-1} \exp(-\beta r)$, with $\beta = \sqrt{-\epsilon_o}$. Then due to exchange the inner electron wave function instead of being equal at $r \rightarrow \infty$ $\varphi_i(r) = \alpha^{3/2} \exp(-\alpha r)$ becomes

$$\varphi_i(r) = \alpha^{3/2} e^{-\alpha r} - \frac{\beta^{5/2}}{\alpha^2} r^{n-3} e^{-\beta r} \left(\int \varphi_n^*(\vec{r}') \vec{r}' \varphi_i(r') d\vec{r}' \right), \quad (8)$$

with $\alpha = \sqrt{-\epsilon_i}$.

The second term in (8) at large distances can easily become much bigger than the first. This can considerably affect the probabilities of processes which depends upon the asymptotical wave function, such for instance as sub barrier penetration.

Solutions of HF equations (4) for occupied states have another specific feature - the number of zeroes N_0 which they have as a function of r is not directly connected with their radial quantum numbers n_r , so that one has $N_0 \neq n_r - 1$ [3]. This feature is also a result of exchange, which according to (4) admixes states with higher n_r (or principal quantum number n) to the lower ones.

A specific consequence of HF equations nonlinearity is nonuniqueness of their solutions. It was demonstrated numerically [4] and in a model [5] that in some particular cases it can be two sets of solutions of (4) with almost the same total energy. A separate problem to decide, however how they correspond to the physical reality, in which a known linear Hamiltonian describes the system of N electrons moving in a Coulomb field of the nucleus and interacting by a pair Coulomb potential.

Due to nonlocality HF equations are gauge noninvariant [6]. As a result, two usually equivalent expressions for operator $\hat{W}$, describing the interaction between an electron and electromagnetic field becomes nonequivalent:

$$\vec{E}\vec{r} \neq \vec{p}\vec{A} . \quad (9)$$

Here $\vec{E}$ is the strength of electromagnetic field, $\vec{A}$ its vector potential, $\vec{r}$ is the radius-vector and $\vec{p}$ the momentum of an electron. Equation (9) is a consequence of the fact that for HF Hamiltonian $\hat{H}^{\text{HF}}$ the velocity $\vec{v}$ is not determined by the usual relation $\vec{v} = \dot{\vec{r}} = \vec{p}$ (in atomic system of units). Instead, one has

$$\vec{v} = \dot{\vec{r}} = [\hat{H}^{\text{HF}}\vec{r}] \neq \vec{p} \quad (10)$$

Because of (10) the well known dipole sum rule for oscillator strengths is violated in HF. The difference between so called "length" $\vec{E}\vec{r}$ and "velocity" $\vec{p}\vec{A}$ (or $i\vec{v}\vec{A}$) forms creates a question,

which of them is in principle preferential. For the real atom they are equivalent but in HF frame the length form should be preferred, because according to (10) it follows directly from the definition of the electron current $\vec{j} = \vec{v} = \dot{\vec{r}}$.

HF approximation is quite good in reproducing the ground state binding energy, intermediate and inner shells ionization potentials and electron density distribution. However this approximation is nonsatisfactorily for many other characteristics, such as position of excited levels, ionization cross sections and so on. Rather bad is HF in describing photoionization. Indeed, it fails to reproduce very important features of the corresponding cross sections: big maxima in continuous spectrum called giant resonances and rapid variations as function of the frequency, called autoionizational resonances.

To describe satisfactorily the cross section one must go beyond the HF independent electron approach by taking into account correlations of atomic electrons, caused by that part of the Coulomb interaction which is neglected in HF i.e. by the residual interaction. A comparatively simple step beyond HF is the so-called Random Phase Approximation with Exchange -RPAE.

3. Random Phase Approximation with Exchange - RPAE

The simplified version of RPAE - Random Phase Approximation (RPA) originates from the theory of electron gas in metals [7]. It is often and successfully applied to nuclei. The main idea of RPA is to take into account along with the direct electron-vacancy excitation by the external field also indirect processes, in which the atom is excited virtually by creating "one electron - one vacancy" virtually excited states. These due to interelectron interaction transfer their energy to the real electron-vacancy excitation. In RPA as one-electron the Hartree wave functions are used.

Exchange or Fock terms are very important in HF theory for atoms. If HF function are used, RPA must be complemented by consistent account of exchange, which leads to RPA with

Exchange or RPAE. In the language of many-body theory diagrams RPAE accounts for infinite sequence, which for photoionization look in the following way:

$$(11)$$

Here a line with an arrow to the right (left) denotes an electron (vacancy), the wavy line is the Coulomb interaction and the dashed line is a photon.

Analytically, the RPAE photoionization amplitude $(\epsilon|D(\omega)|i)$ is determined by the equation:

$$(\epsilon|D(\omega)|i) = (\epsilon|d|i) + \sum_{\substack{\epsilon' > F \\ i' \leq F}} [(\epsilon'|D(\omega)|i')(\omega - \epsilon' - I_i - i\delta)^{-1} \times \\ \times (\epsilon' i|u|i' \epsilon) + (i'|D(\omega)|\epsilon')(\omega + \epsilon' + I_{i'})^{-1}(i' i|u|\epsilon' \epsilon)] \quad (12)$$

with

$$(\epsilon' i|u|i' \epsilon) = \int d\vec{r} d\vec{r}' \varphi_{\epsilon'}^*(\vec{r}') \varphi_i(\vec{r}) |\vec{r}' - \vec{r}|^{-1} (\varphi_{i'}^*(\vec{r}') \varphi_{\epsilon}(\vec{r}) - \varphi_{i'}^*(\vec{r}) \varphi_{\epsilon'}(\vec{r}')) \quad (13)$$

Here one electron wave function $\varphi_k(\vec{r})$ are determined by solving (4). Summation in (12) is performed over occupied ($\leq F$) and vacant states. In the latter case it includes also integration over the continuum.

It is important to have in mind, that a big fraction of RPAE diagrams may be taken into account by a proper choice of a one-electron approximation, thus making the border between one-electron and correlational effects to some extent conditional. Indeed, all "time forward"

RPAE diagrams with vacancy states having the same energy can be taken into account by choosing properly the continuous spectrum one electron wave function $\tilde{\varphi}_\varepsilon$:

$$\begin{aligned}
 & \left[\text{Diagram with } \tilde{D}, \varepsilon, i, L=1, S=0 \right] = \left[\text{Diagram with } d, \varepsilon, i, L=1, S=0 \right] + \left[\text{Diagram with } \tilde{D}, \varepsilon', i', L=1, S=0 \right] \\
 & + \left[\text{Diagram with } \tilde{D}, \varepsilon, i, L=1, S=0 \right] \equiv \left[\text{Diagram with } d, \tilde{\varepsilon}, i, L=1, S=0 \right]
 \end{aligned} \quad (14)$$

The equation for $\tilde{\varphi}_\varepsilon(r)$ is similar to (4) but in the sum over j one term, namely that with $j=i$ is excluded. If one-electron states $\tilde{\varphi}_\varepsilon(r)$ are used in order to escape double count, equation (12) must be modified by introducing in front of the sum over $\varepsilon' > F$, $i' \leq F$ a projection operator P which eliminates terms with $i'=i$. Direct calculations have demonstrated, that double count, as well as other violation of consistency in the choice of one-electron wave function and RPAE-type corrections lead to considerable errors [6].

The RPAE has important features similar to that of a precise equation. For instance, cross sections in length (r) and velocity (v) forms are the same and the Golden sum rule is fulfilled:

$$\sigma_r^{\text{RPAE}}(\omega) = \sigma_v^{\text{RPAE}}(\omega), \quad (15)$$

$$S_r^{\text{RPAE}} = S_v^{\text{RPAE}} = N.$$

Extensive calculations were performed applying RPAE to a number of atoms, mainly with closed shells. Reasonably good quantitative agreement with experiment was achieved [6]. It appeared, that for the absolute cross sections of multielectron shells in the sum over i' in (12) it is sufficient to include only the states, belonging to the same shell, thus taking into account *intrashell* correlations. The multielectron nature of atomic giant resonances was disclosed by demonstrating that the agreement with experiment can be reached only if RPAE electron

correlations are taken into account. This is illustrated by the example of the Xe 4d cross section - Fig. 1. The width of the giant resonances is coming entirely from the nonlocality of the one-electron potential in (4). The RPAE actually decreases the width, which is too big in HF if the $\tilde{\varphi}_\varepsilon$ function determined by (14) are used.

Very important proved to be the *intershell* correlations, completely modifying the cross sections even of multielectron shells, however far from their thresholds. As to the few electron shells, they are entirely compulsorily collectivized by their neighbors, so that almost nothing is left of their individual photoionization cross section. This is illustrated in Fig. 2 by the case of $4s^2$ Xe subshell, which two electrons are sandwiched between neighboring multielectron shells - $5p^6$ and $4d^{10}$.

While comparing RPAE results with experimental data, it is necessary to understand what in fact is calculated. At first glance, it is the one-electron photoionization cross section. Below the threshold of Auger decaying vacancy formation it is the cross section of a single charged ion A^+ production. However, if the photoelectron's energy is enough to ionize the outer shell, a real two-step process can take place: an emission of a photoelectron, described by RPAE, and its inelastic scattering leading to elimination of the second electron. This results in A^{+2} formation [8]. Thus, RPAE calculation must be compared with the experimentally measured absorption rather than A^+ formation cross sections.

4. Beyond RPAE: Account of Rearrangement and Construction of GRPAE

Results of RPAE calculations in near threshold region for intermediate and inner shells are far from experiment. The positions of thresholds have also a noticeable inaccuracy - they are unperturbed HF energies ε_i from (4). These shortcomings of RPAE are results of neglecting two important physical mechanisms, connected with electron shell rearrangement after the vacancy is created. Sometimes *statical* and *dynamical* rearrangement are specified. When an inner vacancy is formed outer atomic electrons experience a stronger attraction to the nucleus.

They change their states, increasing the screening of the vacancy, the field of which acts upon the outgoing photoelectron. This is static rearrangement (SR). It results in decrease of the strength of the field acting upon photoelectron thus decreasing the photoionization cross section. The other effect of SR is the ionization potential shift off its HF value. Indeed, in HF approximation the energy, required to eliminate an electron off the level i is equal to the difference between the energies of the atom and the ion with vacancy i , which is not equal to HF energy ϵ_i (see (4)). Diagrammatically, in lowest order in interelectron interaction SR is exemplified by two diagrams

Here the dashed circle denotes the RPAE photon absorption amplitude. The diagram (16a) accounts for the screening of the photoelectron-vacancy interaction (see 11)) due to virtual excitation of other atomic electrons - j . The diagram (16b) presents the alteration of the ionizational potential i due to the same virtual excitations, as in (16a).

Entirely, rearrangement is a very complicated process. It is time dependent because it starts only *after* the vacancy is created. To take into account diagrams (16) and the similar in higher orders is difficult. As essential simplification is to assume, that along the final state vacancy line only the same state i appear, as is noted in (16). In this approximation the photoionization cross section at threshold becomes smaller than in RPAE and smaller is the ionization potential. This is in qualitative agreement with the experimental results for intermediate and inner shells. The static rearrangement in this approximation can be taken into account by calculating the photoelectron wave function in the self-consistent field of a totally relaxed ion with a vacancy i instead of that of the atom in its initial state.

If these same wave functions are used also in the intermediate virtually excited states in (12) with experimental values for the ionization potential I_i , the Generalized RPAE, or GRPAE is constructed. It gives good results for intermediate multielectron shells, like $4d^{10}$ in Ba and La and equalities (15) are fulfilled in its frame with reasonable accuracy.

Another rearrangement effect is caused by the inner vacancy Auger-decay. It affects the photoelectron moving through the ionizing atom. As a result of the decay the photoelectron finds itself in the two- instead of one vacancy field. This is again a complicated time-dependent process, the accurate account of which is difficult to achieve. However the problem becomes much simpler if the Auger-decay can be considered as instant for the photoelectron.

Diagrammatically, this process can be presented in the following way:

Here the doubled circle denotes the GRPAE photoionization amplitude and the doubled line denotes the photoelectron moving after the Auger-decay in the field of two (i_1 and i_2) instead of one (i) vacancy. The transition from a single to a double line in (17) represents the overlap integral $(\epsilon' | \tilde{\epsilon})$ of one-electron functions ϵ' and ϵ , calculated in the atomic self-consistent field with vacancies i and $i_1 i_2$, respectively. The dynamical rearrangement (DR), described by (17) leads to the growth of the potential acting upon photoelectron, thus increasing the ionization cross section at threshold.

The simplified diagrams (17) are still quite complicated to calculate. It appeared however, that good results are obtained in a modified one-electron approach in which the RPAE matrix element is calculated with vacancy wave functions given by (4) and with photoelectron

wave function calculated in the HF self-consistent field of an ion with two vacancies i_1 and i_2 (or even more), which approximately accounts for DR.

The inclusion of rearrangement effects considerable improves the agreement with experiment by taking into account SR for intermediate shells and DR for inner shells which is illustrated in Fig. 3 (4d shell in La) and in Fig. 4 (1s-shell in Ar), respectively.

These effects are powerful and important, but even after their inclusion in remains a number of open problems. At first, the final state is still effectively one electron, and other than with the vacancy i states are not included in (16) or (17). If the diagrams (16) and (17) would be calculated accurately, an open question would remain about the role of other higher order corrections, which include the interaction of two continuous spectrum electrons, namely ϵ'' and ϵ' in (16a). To take them into account at first a three body problem must be solved, describing the motion of two interacting electrons in the HF field of an ion with one vacancy. Corresponding theory is far from being developed, but there are some essential achievements in this direction which will be discussed in the next section.

5. Creation of "Two Electron - Two Vacancy" States

In this section some particular cases, where the final state is of "two electron-two vacancy" structure will be discussed.

Let us start with a process, described by (17). If photon energies close to the i -shell threshold are considered, the instant change of the field acting upon the slow photoelectron must be taken into account. It leads to the alteration of the photo- and Auger-electron energies and the probability of the decay process. This phenomenon is called Post-Collision Interaction - PCI [9]. Its semiclassical theory gives a formula for the decrease of the photoelectron energy $\Delta\epsilon$.

Assuming that the Auger-electron is fast, one has for $\Delta\epsilon$:

$$\Delta\epsilon = \Gamma_i / v, \quad (18)$$

$$v = \sqrt{2\epsilon},$$

where Γ_i is the vacancy i Auger width. At large distances r from the nucleus the increase of the potential acting upon photoelectron after Auger-decay is $(-1/r)$. Thus, the expression (18) presents the extra potential energy of the photoelectron at $r = v / \Gamma_i$, acquired at the moment of the Auger-decay.

In the quasiclassical approximation but taking into account finite speed of Auger electron, an expression is obtained:

$$\Delta\epsilon \approx \frac{\Gamma_i}{v} \left(1 + \frac{v}{|\vec{v} - \vec{v}_A|}\right), \quad (19)$$

v_A being the Auger-electron's speed. This shift essentially depends upon the angle between $\vec{v}$ and $\vec{v}_A$.

If the Auger-decay proceeds in several steps, which means that one of the vacancies i_1 or i_2 or both of them undergo in their turn an Auger decay, the expression for the slow electron energy shift $\Delta\epsilon$ is modified. For a two-step decay instead of (18) one has

$$\Delta\epsilon = \frac{\Gamma_i}{v} \left(1 + \frac{\Gamma_k}{\Gamma_i + \Gamma_k}\right), \quad (20)$$

where Γ_k is the second step Auger width. In deriving (20), it is assumed that the second step of the decay also adds to the potential acting upon the photoelectron $(-1/r)$ at big distances.

On its way out of the atom photoelectron collides with other electrons, mainly of the outer shells. They can be excited or ionized if the photoelectrons energy is sufficient. The simplest diagram describing such a process, which is called direct knock out look in the following way

For a deep vacancy i the cross section of double ionization $\sigma_i^{++}(\omega)$ and ionization with

excitation $\sigma_i^{+*}(\omega)$ is given by an expression [8]:

$$\sigma_i^{++}(\omega) + \sigma_i^{+*}(\omega) = \sum_{\ell=\ell\pm1} \sigma_{i\ell}^{\text{RPAE}}(\omega) [1 - \exp(-2\text{Im}\delta_\ell(\epsilon'))], \quad (22)$$

where $\sigma_{i\ell}^{\text{RPAE}}(\omega)$ is the RPAE photoionization cross section of the i -subshell with photoelectron having the angular momentum ℓ' , its elastic scattering phase shift being $\delta_\ell(\epsilon')$. Of course, $\sigma_i^+(\omega)$ is also modified due to photoelectron's inelastic scattering. It is given by the expression

$$\sigma_i^+(\omega) = \sum_{\ell'=\ell\pm1} \sigma_{i\ell'}^{\text{RPAE}}(\omega) \exp[-2\text{Im}\delta_{\ell'}(\epsilon')]. \quad (23)$$

Of course, one can substitute the RPAE cross sections in (22) and (23) by that calculated in GRPAE. Direct calculations using either (21) or its simplified expressions (22) and (23) demonstrate that the direct knock-out is an important effect, which is illustrated by the case of $4d^{10}$ shell of Ba in Fig. 5 [10].

One of the electrons in (17) or (21) (or both) can be excited to discrete level, thus forming correlational excitations of atoms. Some of them are very intensive, particularly those which include an inner vacancy and low energy outer shell excitation.

6. Multielectron Ionization by a Single Photon

Multielectron ionization by a single photon can take place only as a consequence of interelectron interaction. While a photon interacts only with a single electron, more than one of them can leave the atom via such processes as Auger-decay, shake off, direct knock-out as well as due to interelectron interaction in the ground state of the atom. Multiple ionization, up to A^{+8} and even higher was observed experimentally [11]. If step-by-step Auger-decay is allowed, it forms the most probable way of multiple ionization. The calculation of such multistep chains is not an easy task, because of rapidly increasing number of possible Auger-channels. As a function of photon frequency, the cross section $\sigma_{A+n}(\omega)$ of A^{+n} ion formation via Auger-decays

is determined by the first step, i.e. by the inner or intermediate shell vacancy creation process. All resonances in it, simple or giant, as well as its other peculiarities are reflected in $\sigma_{A+n}(\omega)$.

For He with its two electrons the double ionization cross section became a subject of numerous calculation [6,12]. The ratio R of double-to-single ionization cross section at high frequencies ω proved to be ω independent and equal, according to different theoretical papers, to $1.6 \div 2.3\%$ [12]. The relative smallness of double ionization cross section permits to perform calculations in the lowest order of perturbation theory in interelectron interaction. The same approximation is applied to other atoms, where R is considerably bigger. However, it is clear that in general lowest order perturbation theory is not sufficient and the photon-electron interaction must be modified by taking into account RPAE (or GRPAE) type corrections. The direct Coulomb interelectron interaction which causes the elimination of the second electron must be also modified by taking into account the screening due to virtual excitation of other electrons (see (16a)). The interaction between photoelectron can be also of importance.

Of interest as a multielectron effects is the production of ions with charges different from that what should be obtained via Auger-decay chains. A good example is the A^+ formation far above outer shell ionization threshold. In this case the final state is known, being a vacancy in the outer shell and a photoelectron, which carry away almost all photon energy. The amplitude of this process is expressed via intermediate or inner shell polarizability.

In general, the yields of differently charged ions are complicated function of photon energy ω which is hard to calculate. However one characteristics of multiionization process, namely the mean ion charge's $N(\omega)$ qualitative behavior can be easily explained. It was observed [11] that the function $N(\omega)$ is increasing while ω approaches from below the $1s$ threshold in Ar. This behavior of $N(\omega)$ was attributed [13] to the contribution of a diagram

and others, presenting different channels of the 1s-vacancy decay. The contribution of (24) is increasing as $(I_{1s}-\omega)^{-1}$ while ω is approaching I_{1s} . This leads to an expression

$$N(\omega) = N_- + \frac{1}{[1 + 2\pi(I_i - \omega)\sigma_{i+1}(I_i) / \Gamma_i \sigma_i(I_i)]} \quad (25)$$

where $\sigma_{i+1}(I_i)$, $\sigma_i(I_i)$ are the photoionization cross sections below and above the threshold I_i , respectively; Γ_i is the vacancy i width and N_- is the mean ion charge well below the threshold I_i .

Note that singularities in the cross sections of the production of $(+n)$ ions are almost completely eliminated from $N(\omega)$, because the corresponding cross sections enter both the nominator and denominator of (25).

7. Decay of Vacancies and Configuration Mixing

Multielectron structure is essential in the vacancies decay. Let us start with one-vacancy radiative and Auger decay [6]. The radiative decay amplitude consists of a one-body contribution and its correlational correction, which is exemplified by the diagrams

Correction (26b) is noticeable for any intermediate or outer shell decay. There are cases, where (26b) almost completely compensates (26a), reducing considerably the radiative decay probability. A good example is the decay of 4p vacancy in Xe, where the account of virtual excitation of 4d-subshell suppresses the one-electron probability by a factor of ten.

The same phenomena took place also in Auger decay. Most important are the corrections due to virtual excitations of multielectron shells, particularly if their excitation energy is close to that released in the transition.

Due to the interelectron interaction *correlative decay* processes became possible [14], such as simultaneous emission of two Auger-electrons which share the total transition energy.

Far from having high probability, such processes are of special interest, because they are able in principle to give information about the effective interelectron interaction in atoms as a continuous function of the transferred energy.

Having good separated shells, atoms are giving the possibility to observe two-vacancy decays in which either a single electron or single photon is emitted. These processes can take place only because of interelectron residual interaction. They are exemplified by diagrams:

If $i_1 i_2$ are inner vacancies, the decay described by (27) and more complicated diagrams with the same initial and final states can be distinguished by a specifically high energy emitted - ω or ϵ . For instance, if $i_1 = i_2 = 1s$, the energy either of the decay photon ω or of the electron ϵ is about twice the $1s$ -binding energy.

The theory of these transitions is almost at its beginning. Most of the calculations are performed in the lowest order of perturbation theory. The accuracy of these calculations is considerably improved, if real energies of states instead of sums of their one-particle HF values are used, and the electron wave functions are calculated for configurations with several vacancies, thus being different for different intermediate states. In the language of many-body theory this method includes a number of infinite series summation. For example, by using the experimental energies $\epsilon_{i_1 i_2}^{\text{exp}}$ of states the following sequence of diagonal parts of diagrams are taken into account:

$$\begin{array}{c} i_1 \longrightarrow \\ i_2 \longrightarrow \end{array} + \begin{array}{c} i_1 \longrightarrow \\ i_2 \longrightarrow \end{array} \begin{array}{|c|} \hline \text{diagonal part} \\ \hline \end{array} \begin{array}{c} i_1 \longrightarrow \\ i_2 \longrightarrow \end{array} + \begin{array}{c} i_1 \longrightarrow \\ i_2 \longrightarrow \end{array} \begin{array}{|c|} \hline \text{diagonal part} \\ \hline \end{array} \begin{array}{c} i_1 \longrightarrow \\ i_2 \longrightarrow \end{array} + \dots + \text{EXCHANGE} \quad (28)$$

Here the dashed square represents the effective vacancy-vacancy interaction, which in the lowest order is reduced to the Coulomb one. By choosing a two vacancy state $i_1 i_2$ with a given term, i.e. with total angular momentum L and spin S , a summation is performed in (28) over all intermediate states with the same vacancy energies but with different spin s_{i_1} and s_{i_2} and angular momentum (m_{i_1} and m_{i_2}) projections.

To calculate a one-electron wave function in the field of vacancies means to include infinite sums of time forward diagrams with all intermediate state vacancies belonging to same subshells, i.e. with same energy but any angular momentum and spin projections. As an example, in (29) the corresponding sequence of diagrams is presented:

$$\begin{array}{c} \varepsilon \\ i_1 \\ i_2 \end{array} \leftarrow \leftarrow \leftarrow + \begin{array}{c} \varepsilon \\ i_1 \\ i_2 \end{array} \leftarrow \leftarrow \leftarrow \begin{array}{c} \varepsilon' \\ i_2 \end{array} \leftarrow \leftarrow \leftarrow + \begin{array}{c} \varepsilon \\ i_1 \\ i_2 \end{array} \leftarrow \leftarrow \leftarrow \begin{array}{c} \varepsilon'' \\ i_1 \\ i_2 \end{array} \leftarrow \leftarrow \leftarrow \begin{array}{c} \varepsilon' \\ i_1 \\ i_2 \end{array} \leftarrow \leftarrow \leftarrow + \dots \quad (29)$$

Note, that the specific feature of (28) and (29) is that the interaction is not changing the energy of vacancies i_1 and i_2 . Thus, for the intermediate states the summation is performed over angular momentum and spin projection, as well as the integration over electron's energies ε .

The described methods of calculations permit to include a big fraction of many-electron correlational corrections into a simple matrix element (27). But this matrix elements is hard to calculate, because there are many different terms to which a multivacancy state can belong. Note, that each of them have also different wavefunctions.

Many-electron atomic nature transparently manifests itself in so-called configuration mixing, i.e. in interaction of a simple and a more complicated states. An example is the interaction of a one-vacancy and a "two vacancy-one electron" states. The configuration mixing can considerably reduce the intensity of pure one-vacancy state. This reduction, or *spectroscopic factor*, can in atoms be as small as 0.3, thus spreading the rest of intensity of a line over multitude of more complicated configurations. Each of them, if their energy is sufficient, can

decay by emitting electrons. If these widths are big enough, any trace of a pure one-vacancy state disappear.

The simplest diagram, representing configuration mixing is the same as that for Auger-decay:

(30)

but with the difference that ϵ can be also a discrete excited state and the energy conservation $\epsilon + \epsilon_{i_1} + \epsilon_{i_2} = \epsilon_i$ is not fulfilled. If (30) is big similar higher order terms must be iterated, for example in the following way:

(31)

The account of (30) and other corrections of this type modifies the probability of the decay with emission of an electron. Entirely, the interelectron interaction is very important determining the structure and lifetime of vacancies.

8. Emission of Photons in Collision Processes

Generally it is accepted that ordinary bremsstrahlung (OB), i.e. deceleration of incoming particles by the statical atomic field is responsible for continuous spectrum photon emission. It was demonstrated however, that for frequencies of the order and higher than the atoms ionizational potential, another mechanism, called Atomic (or Polarizational) bremsstrahlung (AB) is at least of the same importance [14]. Indeed, a charged projectile polarizes the target atom pushing and pulling its electrons and nucleus in opposite direction thus inducing a dipole moment. This dipole moment being time-dependent in magnitude and orientation becomes a source of continuous spectrum radiation. The same effect takes place if both target and projectile

are neutral atoms or ions. Consider for simplicity a fast incoming particle of the charge e_p and mass M , for which the bremsstrahlung amplitude is given by three diagrams:

(a) (b) (c)

(32)

The two first represents OB, while the third describes AB. The cross denotes statical atomic field.

The OB amplitude is proportional [15] to e_p^2 , nuclear charge Z and M^{-1} while for AB it is proportional to e_p and the dynamical dipole polarizability $\alpha_d(\omega)$ of the target atom and is independent upon the projectile's mass. As functions of ω and e_p these amplitudes are quite different. Originating from different space regions, namely AB from long and OB from short distances, these two amplitudes do not interfere and the total bremsstrahlung spectrum is simply a sum of two contributions, namely that of OB and AB:

$$\omega \frac{d\sigma}{d\omega} = \frac{16}{3} \frac{Z^2 e_p^4}{c^3 v^2 M^2} \ln(2pR_a) + \frac{16}{3} \frac{e_p^2}{c^3 v^2} \omega^4 |\alpha_d(\omega)|^2 \ln(v / \omega R_a), \quad (33)$$

where R_a is the atomic radius. In deriving (33) it was assumed that $\ln(2pR_a) \gg 1$. For heavy projectiles with $M \gg 1$ the main contribution to (33) is given by the second term, it is by AB. But even for an incoming electron, with $M = 1$, the AB contribution is considerable. Indeed, for $\omega \rightarrow \infty$ the polarizability is equal to $(-N/\omega^2)$. Thus a neutral atom with $N = Z$ has almost equal contributions of OB and AB, which add up to

$$\omega \frac{d\sigma}{d\omega} = \frac{16}{3} \frac{Z^2}{c^3 v^2} \ln \frac{2p^2}{\omega} \quad (34)$$

This is bremsstrahlung of an electron in the field of a bare nucleus instead of a neutral atom. The descreening is a result of accounting for AB.

AB is essential even for hydrogen, but is particularly important for atoms with giant resonances in photoionization cross section, for which $\alpha_d(\omega)$ is big.

Almost all radiation is coming as AB in relativistic electron-and positron-atom collision. AB is the most important mechanism of continuous spectrum radiation in ion atom-collisions. The radiation cross section is expressed via polarizabilities and form-factors of colliding partners. Its intensity is even higher than that achieved in electron-atom collisions.

Emitting a sufficiently high frequency photon, the projectile can become slow. Its state is then essentially affected by the interaction with the target. The latter for an electron is presented at first by the HF field. The multiparticle nature of the target may be also essential. The corresponding correction is illustrated by the following diagram:

(35)

Here the doubled line represents the projectile, which is not necessarily an electron. Higher order corrections particularly of the RPAE type (11) must be taken into account. If a target system has strong collective excitations, for instance of the giant resonance type, it is reflected in emission of photons cross section.

9. Elastic Scattering and Negative Ions Formation

Elastic electron-atom scattering is a process, in which the multielectron nature of the target is reflected. Particularly important it is for low-energy collisions. The simplest diagram, which takes into account the possibility of the target internal excitation is given by (35). This diagram, together with higher order corrections accounting for interaction between atomic constituents only, leads at big distances from the atom to so-called polarizational potential $U_{pol}(r)$:

$$U_{pol} \rightarrow -\alpha_d / 2r^4, \quad (36)$$

Here α_d is the target's dipole polarizability. This characteristic is considerably affected, just as is $U_{pol}(r)$ at any r , by electron correlations in the target atom. Important could be also the interaction between the projectile E' and atomic electrons k in the intermediate state $E'kj$, which makes the calculation of the intermediate state at least as complex as solving a three-body problem. However reasonably good results were obtained in a number of calculations in which the polarizational projectile-target interaction was represented by (35), with higher order terms accounting for RPAE (GRPAE) interaction between atomic electrons and vacancies. The polarizational interaction described by (35) is not enough to take into account perturbatively. On the contrary, it is usually necessary to solve the Dyson equation with (35) as its self-energy part:

$$\begin{array}{c} \varepsilon \\ \hline \hline \end{array} \rightarrow \begin{array}{c} \varepsilon \\ \hline \hline \end{array} = \begin{array}{c} \varepsilon \\ \rightarrow \bullet \end{array} + \begin{array}{c} \varepsilon \\ \rightarrow \end{array} \begin{array}{c} \hline \hline \end{array} \begin{array}{c} \varepsilon' \\ \hline \hline \end{array} \quad (37)$$

The equation (37) can be transformed into that for an elastic scattering phase shift. The corresponding calculations give good agreement with the experiment, which is illustrated in Fig. 4, where the results for electron elastic scattering on Xe are presented [16,17].

In principle, the same approach as for electron can be applied to positron-atom scattering also. The essential difference is that in intermediate state the virtually excited electron is strongly attracted by the positron, forming a positronium-like "(Ps)" state:

$$\begin{array}{c} E \\ \hline \hline \end{array} \rightarrow \begin{array}{c} \bullet \\ \hline \hline \end{array} \begin{array}{c} \text{Ps} \\ \hline \hline \end{array} \begin{array}{c} \bullet \\ \hline \hline \end{array} \rightarrow \begin{array}{c} E \\ \hline \hline \end{array} \quad (38)$$

i

Here the triple line denotes this state. The $e^+ e^-$ attraction considerably softens the target, increasing its effective polarizability and the phase shift determined by the target atom polarizational potential. This is at least in qualitative agreement with experiment for noble gas atoms.

Just as scattering the binding can be treated. Thus, solving equation (39) permits to study whether negative ions can be formed by the target atom either in its ground or excited states. Using (37), a number of negative ions affinities were calculated [18].

10. Conclusion

It was demonstrated, that the atoms response to external field and their inner structure is determined to a large extent by the interelectron interaction. Their many-body nature can be accounted for to a large extent in the framework of RPAE or GRPAE. It is essential, however, that single-electron potential's nonlocality must be taken into account rigorously, by solving HF equation for each atom. The variation of HF self-consistent potential when going from a given atom to its nearest neighbor proved to be big and important.

The HF and RPAE must be treated consistently in order to escape double count, which leads to big errors. As a result, a projection operator precedes the interaction in RPAE equations. This operator is different for different choices of HF versions, which are used in describing excited electrons.

Not only pure estimations, but also existing experimental material gives evidences that a next step in the theory beyond RPAE or GRPAE frame is desirable. This step must be done self-consistently, by improving simultaneously the one-electron and one-vacancy wave functions, the interelectron interaction and the photon-electron interaction operator by taking into account virtual excitation. Making this next step it is necessary to preserve that RPAE features which are characteristics of a precise theory, e.g. the equivalence of "length" and "velocity" operators in photoionization calculations.

To make this next step is not easy for any multiparticle inhomogeneous systems even if the interaction between constituents is of short range. But for Coulomb long range interaction this is particularly difficult, because each order of the electron-vacancy interaction includes a logarithmically divergent matrix element $\langle \epsilon i | V | \epsilon' i \rangle \sim \ln(\epsilon - \epsilon')$. For "two electron-two vacancy" states the electron-electron interaction matrix elements are also divergent and at least their

divergent parts must be taken into account nonperturbatively, which makes the corresponding problem very complicated.

While it is far from having this next step in theory made, some essential features of it are already included in calculations, namely the influence of electron shell rearrangement after inner or intermediate shell vacancy creation and decay. Rather elaborate is the theory of PCI, i.e. of effects caused by instant alteration of the field, acting upon photoelectron due to vacancy Auger-decay.

Of great interest for future research it is the role of electron correlations in formation and possible stabilization of highly excited atomic states. An example can be a state with all electron spins having the same projection. Even very simple calculations are giving microseconds for the lifetime of these states, if the nuclear charge is less than ten. But correlations can lead to much longer lifetimes and to other electron structures of the excited state. For instance, it can be a state with vacant inner and occupied outer shells. The stabilization of these states can be due to high symmetry of electron distribution. In any case the relative role of the nucleus in such states is much weaker than in the ground state of an ordinary atom, so the correlations become even more important.

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Figure Captions

- Fig. 1. Photoabsorption in $4d^{10}$ threshold region in Xe [6]
solid line - RPAE, dashed line - experiment.
- Fig. 2. Photoionization of $5s^2$ electrons in [6]
RPAE: solid line, with action of $5p^6$ and $4d^{10}$ included, dashed line - $5s^2$ electrons only, dash-dotted line - with effect of $5p^6$ electrons, dash-double dotted line - with action of $4d^{10}$ electrons. Chain line - experiment.
- Fig. 3. Photoionization of $4d^{10}$ shell in La [6]
solid line - GRPAE, dashed line - RPAE, dash-dotted line - experiment.
- Fig. 4. Photoionization of $1s^2$ - shell in Ar [6]
solid line - GRPAE, with account of Dynamical Rearrangement, dashed line - experiment, dotted line - GRPAE only, dash-dotted line - RPAE.
- Fig. 5. Photoionization of $4d^{10}$ - subshell in Ba [10]
solid line - GRPAE with account of direct knock-out, dashed line - RPAE, long dash line - RPAE with direct knock-out. Dots - experiment.
- Fig. 6. Bremsstrahlung cross section in collision of an electron e , α - particle and He atom on Xe as a function of photon frequency ω [14]. Projectile speed is 5 at. un.
- Fig. 7. Electron - Xe atom elastic scattering cross section [17]
solid line - with account of Xe polarizability, dashed line - HF, dash-dotted line - experiment.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7