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**THURSDAY, JULY 26**



## **RELATED THEORY**



# Polarization and relaxation effects in photodetachment from $\text{Si}^-$ , $\text{Ge}^-$ and $\text{Sn}^-$ negative ions

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The results of the renewed calculations of photodetachment cross section of the negative ions with outer  $np^3$  subshells are presented. The study of resonance features in photodetachment from negative ions with open  $np$  subshell has attracted much attention in recent years [1] because of a variety of resonance structures. The aim of the present work is to study the near-threshold features, which are related to inner-electron transitions into vacant states in the outer  $np$  subshell. The many-body theory method combining the Random Phase Approximation with Exchange (RPAE) and the Dyson Equation Method (DEM) has been recently developed [1-2]. It enables us to improve (relative to the starting spin-polarized Hartree-Fock (SPHF) approximation) the description of ground states and to calculate the cross sections with intra- and interchannel interaction, dynamic polarization and relaxation (screening).

The calculations performed for  $\text{Si}^-$ ,  $\text{Ge}^-$  and  $\text{Sn}^-$  negative ions have confirmed the presence of window resonances in  $np^3$  subshell photodetachment cross section in the vicinity of the  $ns^2$  subshell threshold predicted earlier in [3]. This minimum is due to the interference between the direct transition  $np$  electron to continuum and the transition of  $ns$  electrons into the vacant states of  $np$  subshell. It is shown that the influence of dynamic polarization and relaxation changes significantly the resonance shapes and the values of maxima below and above the minimum in photodetachment cross section.

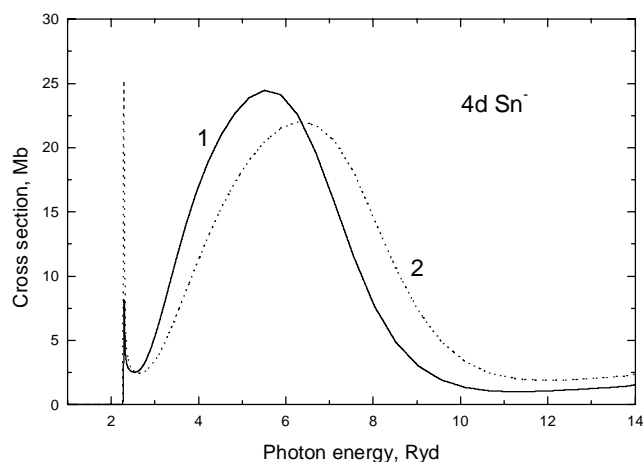


Figure 1. Photodetachment cross section of the  $\text{Sn}^-$  4d subshell. 1 – the RPAE, 2 – the GRPAE.

The relaxation effects are rather important for the electron photodetachment from inner shells. The 3d and 4d cross sections have been calculated for the photodetachment of  $\text{Ge}^-$  and  $\text{Sn}^-$ , respectively. Figure 1 shows the 4d-electron photodetachment cross section of  $\text{Sn}^-$  obtained within the RPAE and the GRPAE, which takes the rearrangement effects into account. The near-threshold maximum is associated with the  $4d \rightarrow \epsilon p$  transitions into “ $5p^4$ ” quasi-bound state.

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# Photodetachment from negative ions with outer $np^2$ subshells

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The aim of the present work is to study the interference features in photodetachment from negative ions with outer  $np^2$  electrons. These resonance features in photodetachment from negative ions with open  $np$  subshell attract much attention in recent years because of a variety of resonance structures ([1] and references therein). The results of calculations for the photodetachment cross section and photoelectron angular distribution of outer  $s$ -,  $p$ -,  $d$ - subshells in  $\text{In}^-$  and  $\text{Tl}^-$  negative ions are presented. The calculations have been completed within the relativistic version of the Random Phase Approximation with Exchange (RRPAE).

The ground state wavefunctions of negative ions,  $\text{In}^- \dots 4d_{5/2}^6 5s_{1/2}^2 5p_{1/2}^2 \ ^3P_0$  and  $\text{Tl}^- \dots 5d_{3/2}^6 6s_{1/2}^2 6p_{1/2}^2 \ ^3P_0$ , are determined using the Dirac-Fock (DF) approximation. The DF single-electron energies of the outer subshells are rather close to the experimental electron affinities which are about 0.3 eV. The wave functions of excited states in the continuum are calculated within the frozen-core DF approximation. Considering the outer shell photodetachment we have included 4 interacting channels describing dipole transitions from the outer  $np_{1/2}$  and  $ns_{1/2}$  subshells:

$$np_{1/2} \rightarrow \epsilon d_{3/2}, \epsilon s_{1/2}$$

$$ns_{1/2} \rightarrow \epsilon p_{1/2}, \epsilon p_{3/2}$$

and neglect the influence of the  $4d$  electron transitions because the DF ionisation potential of the  $4d_{5/2}$  subshell is significantly higher (22.36 eV for  $\text{In}^-$ ) than the energy range under consideration.

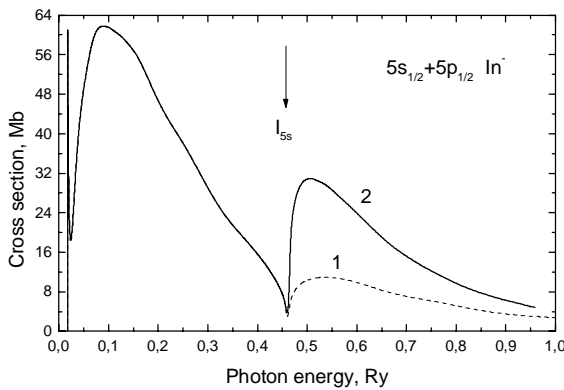


Fig. 1. Photodetachment cross section of  $\text{In}^-$  within the RRPAAE: partial  $5p_{1/2}$  (1) and total (2) cross sections.

of  $\text{Tl}^-$  reveal the similar behaviour in the vicinity of the  $6s$  threshold.

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Figure 1 presents the results of the RRPAAE calculations of photodetachment cross section from  $5p$  and  $5s$  outer subshells in  $\text{In}^-$ . One can see the window-type resonance in the  $5p$  partial cross section near the  $5s$  threshold, which appear due to the interference between  $5p_{1/2} \rightarrow \epsilon d_{3/2}$  and  $5s_{1/2} \rightarrow \epsilon p_{3/2}$  transitions. The main contribution to the total cross section comes from  $5p_{1/2} \rightarrow \epsilon d_{3/2}$  transition. Above  $5s$  threshold the partial  $5s_{1/2} \rightarrow \epsilon p_{3/2}$  is responsible for the shape resonance. The resonance feature appears also in the angular distribution of  $5p$  photoelectrons. The partial  $6p$  and total photodetachment cross sections

# MULTI-CENTRED THEORY OF MOLECULAR PHOTOIONIZATION

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A new theory of near-threshold photoionization of electrons from atoms confined in multi-centred atomic formations, e.g., molecules, clusters, or fullerenes, is developed. The theory is based on a zero-range-potential model where the interaction of a photoelectron from the ionized atom with other atoms of the formations is replaced by suitable boundary conditions imposed on the photoelectron wave function at locations of these atoms. General formulae for differential photoionization cross sections of such multi-centered formations are obtained. These formulae reduce to relatively simple formulae in case of a diatomic molecule whose differential photoionization cross section  $d\sigma/d\Omega$  turns out to be separable, i.e.,  $d\sigma/d\Omega = \sigma_a S(\mathbf{e}, \mathbf{k}, \mathbf{R})$ , in terms of the angle-integrated photoionization cross section of the *isolated* atom,  $\sigma_a$ , and what we call the “modulation function”  $S(\mathbf{e}, \mathbf{k}, \mathbf{R})$ . The latter depends on the relative orientations of the photon polarization vector  $\mathbf{e}$ , the photoelectron momentum vector  $\mathbf{k}$  and the molecular axis vector  $\mathbf{R}$ , along with some other *purely atomic parameters*, e.g., electron-atom elastic scattering phase shifts. Hence, to understand angular distributions of low energy photoelectrons in near-threshold photoionization of inner electrons from atoms confined in diatomic molecules, it is enough to calculate the modulation function. As an example, Figure 1 shows  $S(\mathbf{e}, \mathbf{k}, \mathbf{R})$  calculated in the framework of our theory for near-threshold electron photodetachment from the  $\text{C}^-\text{O}$  molecule where a resonance behaviour in dependence on  $k$  is clearly seen. This is due to diffraction of the detached photoelectron (from  $\text{C}^-$ ) on the neighboring atom O.

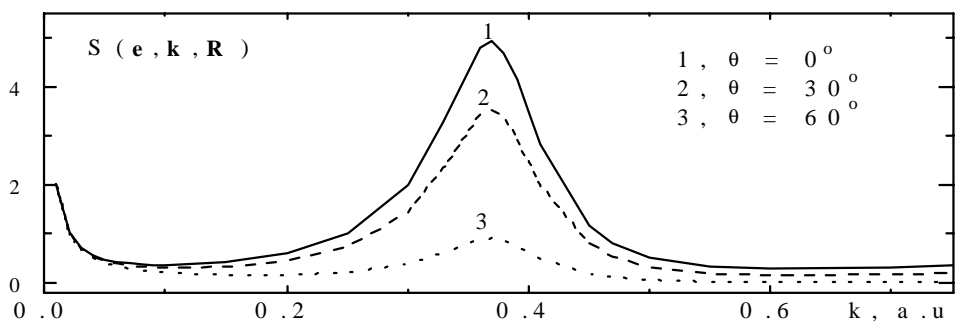


Figure 1: Function  $S(\mathbf{e}, \mathbf{k}, \mathbf{R})$  for photodetachment from  $\text{C}^-\text{O}$  as function of the photoelectron momentum  $k$  (in atomic units, a.u.) for two different angles  $\theta = 0, 30$  and  $60^\circ$  between  $\mathbf{k}$  and the molecular axis  $\mathbf{R}$  that parallels the polarization vector  $\mathbf{e}$ .

Our next step will be application of the theory to photoionization of atoms confined in  $\text{C}_{60}$ .

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# MBPT calculations of autoionizing resonances in Kr isoelectronic sequence

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We present the preliminary results of a many-body theory study of the  $4p$ -subshell photoionisation cross sections and  $4s \rightarrow np$  autoionizing resonances in the photoabsorption spectrum along the Kr-like isoelectronic sequence. The method of calculations combines the Random Phase Approximation with Exchange (RPAE), the Dyson Equation Method (DEM) and the Many Body Perturbation Theory (MBPT) to obtain the parameters of the autoionizing resonances. The Hartree-Fock (HF) approximation is used as a zero one.

Earlier it has been shown a very important role of many-electron effects in describing the partial photoionisation cross sections of  $ns$  electrons in noble-gas atoms [1]. The experimental study of photoionisation of  $3p^6$  subshell in the vicinity of autoionizing resonances in the Ar-like isoelectronic sequence [3] revealed the dramatic changes in profiles of the  $3s \rightarrow np$  resonances. Newly investigated many-electron correlations, in particular double-electron processes, are shown to play a crucial role in the interpretation of the resonance structure. The changes of the resonance shapes along the series and sequence reveal a very interesting physics in interference interaction between electrons and result from their position relative to the Cooper minimum in the  $3s$  and  $3p$  photoabsorption. Present study of the  $4p$  partial cross section and autoionizing  $4s \rightarrow np$  resonances in Kr,  $Rb^+$  and  $Sr^{++}$  is initiated by the effects found in Ar-like sequence.

The concrete calculations have been performed taking into consideration many-electron correlations step by step. At first we have completed the RPAE calculations of the outer  $4p$  electron photoionisation cross sections and the parameters of Fano formula for Kr,  $Rb^+$  and  $Sr^{++}$ . The total  $4p$  cross section becomes smaller along the sequence, and Cooper minimum moves closer to the  $4p$  threshold. The precise positions of the  $4s \rightarrow np$  transitions is very important to obtain appropriate resonance parameters. Therefore at the second step, we apply the DEM to correct the energies and wavefunctions of ground and excited states and then use the new wavefunctions in RPAE calculations. Fano parameters of these resonances have completely changed. However, it is not enough to get well-known window profile for  $4s \rightarrow np$  resonances in neutral Kr. Only inclusion of the double-electron excitations [3] within the MBPT have been permitted to get the correct resonance shapes in Kr. As well as for the Ar-like isoelectronic sequence [2] the double-electron processes play a crucial role in description of the autoionizing  $4s \rightarrow np$  profiles. It is shown that the profiles change their shapes (and corresponding Fano parameters) from window-type resonances to ordinary resonance along the sequence Kr,  $Rb^+$  and  $Sr^{++}$ . At the final stage of our calculations we take into account the spin-orbit splitting of the excited discrete states  $4s \rightarrow np_{1/2}, np_{3/2}$ . These calculations are in progress and the results will be presented at the conference.

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# Electronically nonadiabatic transitions after Auger decay of resonant core-excited H<sub>2</sub>O

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Auger decay is one of the well-known processes subsequent to core-electron excitation of molecules. After the Auger decay, energetically unstable cationic states might dissociate into smaller fragments (i.e., ion dissociation). So far, a number of studies have discussed the mechanisms of ion dissociation after the Auger decay [1]. However, most of these analyses implicitly assume that the ion dissociation occurs on only one adiabatic potential energy surface, and thus take no account of electronically nonadiabatic transitions during the ion dissociation. In this study, we demonstrate that electronically nonadiabatic transitions play a very important role in the dynamical processes subsequent to the Auger decay. The ion dissociation of H<sub>2</sub>O<sup>+</sup> following resonant core-electron excitations (O 1s → 4a<sub>1</sub> and 2b<sub>2</sub>) is chosen.

To describe the ion dissociation dynamics, we calculate global adiabatic potential energy curves for various Auger final states of H<sub>2</sub>O<sup>+</sup>. The calculations are carried out at the MR-SDCI level of theory with use of the full-valence CASSCF wave functions as references. The aug-cc-pVTZ basis set is used. To simplify the ion dissociation dynamics and make it easy to analyze the electronically nonadiabatic transitions, we assume C<sub>2v</sub> molecular symmetry.

Figures 1 show the adiabatic potential energy curves of the low-lying (a,b) <sup>2</sup>A<sub>1</sub> and (c,d) <sup>2</sup>B<sub>2</sub> Auger final states as a function of the H–O–H bending angle. The former (<sup>2</sup>A<sub>1</sub>) corresponds to the Auger final state subsequent to O 1s → 4a<sub>1</sub> excitation and the latter (<sup>2</sup>B<sub>2</sub>) to O 1s → 2b<sub>2</sub> excitation. The OH internuclear distance *r* is fixed at some representative values. As is clearly seen from the figures, the adiabatic potential energy curves have several avoided crossings and at some of which the electronically nonadiabatic transitions seem to occur. To quantitatively estimate the nonadiabatic transition at each avoided crossing, we employ a semi-classical method [2]. According to the analysis, it is found that the electronically nonadiabatic transitions dominate the ion dissociation and the present theoretical results are in good accord with the experimental observations [3]. The detailed mechanisms of the ion dissociation will be discussed.

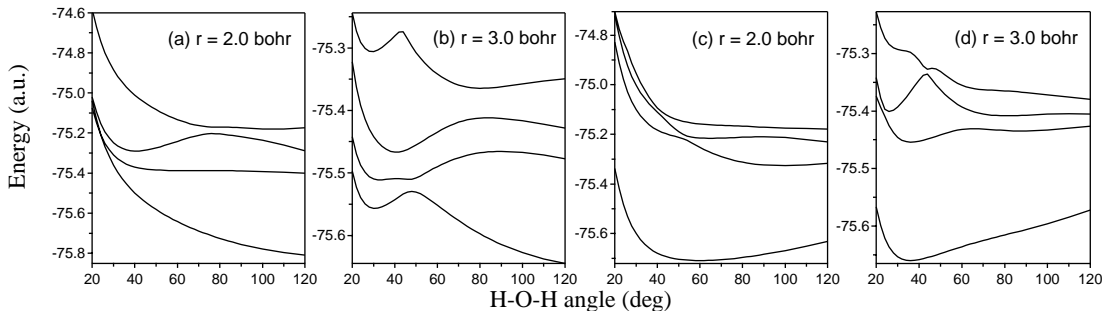


Figure 1: Adiabatic potential energy curves of the low-lying <sup>2</sup>A<sub>1</sub> and <sup>2</sup>B<sub>2</sub> Auger final states.

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# Theory of Polarization Dependence in Resonant X-Ray Emission Spectra of Uranium Compounds

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X-ray emission spectrum (XES) has become quite a powerful tool to investigate the electronic state of strongly correlated materials. When the incident X-ray energy is tuned to some characteristic peaks of X-ray absorption spectrum (XAS), the XES is denoted by resonant XES (RXES), and the incident and emitted X-rays are strongly related. Therefore, it is expected that RXES using the polarized incident X-rays shows strong polarization dependence [1].

Actinide elements have a partially filled  $5f$  shell, which shows the intermediate nature between localized (the  $4f$  shell of rare earth) and itinerant (the  $3d$  shell of transition metal) states. They exhibit a rich variety of properties due to the  $5f$  states, and have attracted much interest.

In some Uranium compounds, such as  $\text{UO}_3$ , the effect of solid state hybridization is very important. Therefore, we apply the impurity Anderson model taking into account full multiplet effects to the analysis of XAS and RXES. The incident X-ray is assumed to be linearly polarized, and the scattering angle is  $90^\circ$ . The calculated results of  $3d_{5/2}$  XAS and  $5f \rightarrow 3d_{5/2}$  RXES of U in  $\text{UO}_3$  are shown in Fig.1, in which both polarized (the polarization vector of the incident X-ray is perpendicular to the scattering plane) and depolarized (the polarization vector is parallel to the scattering plane) spectra are plotted. The inelastic structures in the energy loss region around 5eV are present for both configurations, while the structure at energy loss about 10eV is enhanced only in the polarized configuration. This behavior is similar to that of  $4f \rightarrow 3d$  RXES of  $\text{CeO}_2$  [1].

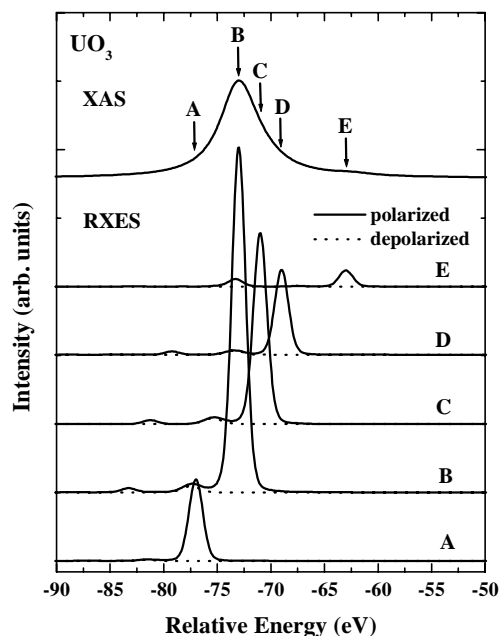


Figure 1: Calculated results of  $5f \rightarrow 3d_{5/2}$  RXES of  $\text{UO}_3$ . Excitation energies are indicated by arrows on the XAS.

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# ROLE OF MANY-ELECTRON CORRELATIONS IN COMPTON SCATTERING UPON MEDIUM AND HEAVY ATOMS

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We present calculated photon inelastic scattering cross sections for the outer and intermediate subshells of Kr and Xe atoms. The cross sections are obtained both in the one electron Hartree-Fock method and with account of many-electron correlations using the Random Phase Approximation with Exchange (RPAE). We find that electron correlations affect the cross sections very strongly, leading to new maxima and minima of totally collective nature. The calculated results call for experimental verifications that are possible through using currently existing beams of high-energy photons.

The results are obtained over the range of transferred energies  $I < E < 20Ry$  and momenta  $0 < q < 4 a.u.$ , respectively, where  $I$  is the ionization potential of the target atom. We considered dipole, monopole and quadrupole channels of one-electron ionization from the subshells  $4p^6$ ,  $4s^2$ ,  $3d^{10}$  in Kr and  $5p^6$ ,  $5s^2$ ,  $4d^{10}$  in Xe. Note, that the investigated domains of  $E$  and  $q$  coincide mainly with the values of incoming photon frequencies  $\omega$ 's and scattering angles  $\theta$ 's for which classical Compton scattering on a free electron is permitted:  $1 < \omega\theta/c < 4$ , where  $c$  is the speed of light.

The Compton scattering cross section of an atom or multi-atomic formation for sufficiently high  $\omega$  can be expressed in the HF approximation via matrix elements of the operator  $exp(i\mathbf{q} \cdot \mathbf{r})$ , calculated with one-electron HF wave functions describing occupied and vacant continuous spectrum atomic states. In order to take into account the many-electron correlations in RPAE, the operator  $exp(i\mathbf{q} \cdot \mathbf{r})$  must be replaced by the effective one  $\hat{A}_{RPAE}(E, q)$  [1]. The Compton cross section is expressed via  $\hat{A}_{RPAE}(E, q)$  as

$$\frac{d\sigma_{i,f}(\omega, \omega')}{d\Omega'} = \left(\frac{d\sigma}{d\Omega'}\right)_0 \frac{\omega'}{\omega} | \langle f | \hat{A}_{RPAE}(E, q) | i \rangle |^2,$$

where  $\Omega'$  is the photon solid angle corresponding to  $\omega'$ ,  $(d\sigma/d\Omega')_0$  is the Thompson classical cross section of light scattering and  $E = \omega - \omega'$ .

The Compton scattering results presented here are closely connected to the recent Generalized Oscillator Strengths of fast electron collisions with atoms [2].

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# HIGH FREQUENCY LIMITS OF TWO-ELECTRON IONIZATION CROSS SECTION

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In this presentation we consider several different characteristics of the two-electron ionization process at high but non-relativistic photon frequencies  $\omega$ . Those of them were studied that are expressed solely via the initial state wave function of the ionized two-electron object. The new high precision and locally correct non-variational wave functions describing the ground and several lowest excited states of  $H^-$ , He and Helium-like ions [1] are used in calculations of the corresponding cross sections and a number of the cross section ratios  $R(\omega)$ , which at high  $\omega$  are constant values. The calculated ratios are that of “ionization with excitation-to-total ionization”, “double-to-total” and “double-to-single” photoionization cross sections in pure dipole approximation as well as correction  $f$  to these ratios that are of the order of  $\omega/c^2$  [2]. The dependencies of all these quantities upon the nuclear charge  $Z$  and the principal quantum number  $n$  of the initial state excitation are studied. Excited initial state with  $1 < n < 5$  are considered.

High-energy two electron ionization and ionization with excitation cross sections are obtained. We showed that using highly accurate initial state wave functions is very important for all considered characteristics. It is demonstrated that excitation of one of the electrons increases the relative probability of double ionization considerably, increasing the probability of ionization with excitation dramatically. The  $Z$ -dependence of the ratios changes considerably with the  $n$  growth: already for  $n \geq 2$  they reach the asymptotic  $Z^{-2}$  behavior much slower than for  $n = 1$ . The  $f$  corrections to  $R$  are obtained for excited states  $n \geq 2$  demonstrating their slow increase with  $Z$  growth. The asymptotic values of  $f$  in  $Z$  are also found [3].

The results obtained are compared, where it is possible, to previous calculations, including those in which the inter-electron interaction is taken into account in the lowest order. The strict limitations of this approach are clarified. The numerical results obtained proved to be very sensitive to the details of the initial state wave function.

The results for the ratio “double-to-single” of Compton Ionization cross sections are also presented and the values and the  $Z$ -dependence for this ratio is obtained by studying the same objects as in the two-electron photoionization. We plan also to discuss the high-energy limits for two-electron recombination processes with emission of a single photon.

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# Orbital Ordering in $\text{LaMnO}_3$ : Cluster Model Calculation in Resonant X-ray Scattering and X-ray Absorption at the Mn $L_{2,3}$ edge

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We present results of cluster model calculations in resonant x-ray scattering (RXS) and x-ray absorption spectra (XAS) at Mn  $L_{2,3}$  edge in  $\text{LaMnO}_3$  with special attention to the observation of orbital ordering. As it is well known,  $\text{LaMnO}_3$  is of fundamental interest as a mother compound of colossal magnetoresistance (CMR) materials. The charge, spin and orbital degrees of freedom in manganites are known to play important roles in understanding CMR phenomena. However, the interaction and interdependence of the spin, orbital and Jahn-Teller (JT) ordering is complex, and the detailed mechanism is not yet fully understood. Recently, Murakami *et al.* carried out RXS at the Mn K-edge in CMR compounds, claiming a direct observation of orbital ordering possible [1]. However since JT distortion also contributes to the RXS intensity, this K-edge experiment so far performed failed to distinguish between orbital and JT ordering. In order to approach a better understanding it would be very helpful to be able to observe the JT and orbital ordering independently of one another. In this connection, RXS and linear dichroism in XAS at Mn  $L_{2,3}$  edge have recently been proposed theoretically by different authors [2,3]. However both these predictions are presented based on a single-ion model in a  $D_{4h}$  crystal field and they are not enough to describe more detailed electronic structure. An interesting question is of course how the cluster model in  $D_{4h}$  symmetry change their predictions.

For this purpose, we adopt the  $(\text{MnO}_6)^{10-}$  cluster model including the intraatomic 3d-3d and 2p-3d multipole Coulomb interactions in the Mn ion. In the present model the anisotropic effect due to six oxygen ions surrounding the Mn ion is also taken into account through the anisotropic Mn 3d - O 2p hybridization and the crystal field for Mn 3d states, where the local symmetry around the Mn ion is approximately treated as  $D_{4h}$  symmetry instead of  $D_{2h}$  in actual crystals. Our system is composed of Mn 2p and 3d core and O 2p states. We describe the ground state of these systems by a linear combination of two-configurations,  $3d^4$  and  $3d^5\bar{L}$ . The intermediate states in RXS (the final state in XAS) are thus described by linear combinations of  $2p^53d^5$  and  $2p^53d^6\bar{L}$ . The final state in RXS contains  $3d^4$  and  $3d^5\bar{L}$ . We show that the results of cluster calculation with  $D_{4h}$  symmetry are qualitatively same as that of previous atomic calculation, but are rather different quantitatively. Cluster calculation can reproduce the experimental results of XAS at the Mn  $L_{2,3}$  edge better than the atomic model analysis. We also demonstrate how it should be possible to make direct observations of orbital ordering as well as JT ordering using RXS and XAS at the Mn  $L_{2,3}$  edge.

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# DISTORTION OF SHAPE RESONANCES OF X-RAY ABSORPTION AND IONIZATION IN SMALL AND MACRO MOLECULES

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Identification of a feature in X-ray absorption (XA) with a shape resonance is questioned if double excitations and changes in nuclear motion accompany essentially promotion of a core-electron into an unoccupied molecular orbital. Single-hole ionization (SHI) is considered as a basic probe to check this identification [1]. However this probing encounters difficulties when applied to large polyatomic systems because of depressing of the photoelectron main line. To understand to what extent shape resonance (one-particle) phenomena are resident in XA of macromolecules, polymers and clusters, intramolecular interference of the photoelectron waves is examined in respect with spatial localization of the interference region, their damping inside the absorber and its local deformation (polarization) in the photoelectron field. A straightforward way based on distortion of a shape resonance due to assistance of valence electrons and local vibrations in its creation, is discussed to bridge the interferential phenomena in small and large systems. A quasibond state localized inside a molecule (fragment) deformed in the photoelectron field is defined as a *distorted-shape-resonance* (DSR) [2]. In contrast to a simple shape resonance a DSR is a collective excitation that demonstrates

- 1) Resonance variations of both the photoelectron main line and the satellite intensities,
- 2) Divergence of the single-hole creation (SHC,  $\sigma^-$ ) and the SHI ( $\sigma^+$ ) cross sections, their irregular behavior at the inelastic photoelectron thresholds, and energy shift of a resonance position upward of a few electron-Volts,
- 3) Anisotropy in decay of intermediate core-excited states dependent on direction of the photoelectron emission in the molecular frame

XA cross section is decomposed into three terms  $\sigma^{\text{abs}}(\omega) \approx \sigma^+(\omega, \kappa) + \kappa\sigma^-(\omega, \kappa) + X(\omega)$  where both the first and the second terms depend on interference of the photoelectron waves and the photoelectron – photoion coupling. In the framework of the quasi-atomic and optical potential approaches [2] the photoelectron – photoion coupling  $\kappa$  constants and intramolecular interference pictures are computed for series of small and large molecules in respect to the inelastic channels in the photoelectron emission. We show that the shape resonances are found substantially distorted even for small molecular species such as CO and CO<sub>2</sub> for which the  $\kappa$  reaches 0.17 and 0.31 respectively. Dominance of collective properties (as  $\kappa \approx 1$ ) is predicted for the broad resonance features of XA spectra of large organic molecules. Relations between DSRs and giant resonance phenomena and applicability of one-particle descriptions are discussed.

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# Spin-Orbit Interaction in the 2p Ionization and Excitation of Second-Row Elements in Some Simple Molecules. Theory and Experiment

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Molecular field effects and core-valence exchange interactions are significant in the soft X-ray photoelectron and photoabsorption spectroscopy. Molecular field and core-valence exchange splittings have been discussed in recent photoelectron and photoabsorption spectra of the spin-orbit-split 2p ionized and excited states of second-row elements (for example, refs.[1-4]). Now theoretical development has been essential for their detailed analysis and discussion. The most accurate approach to take into account the spin-orbit interaction is a four-component method based on the Dirac-Fock configuration interaction calculations, but this is very complicated in the molecular case and is not generally used. To simplify the four-component scheme, a two-component spin-orbit Hamiltonian is practically used[5]. In the present work, an ab initio Breit-Pauli (BP) approach as a two-component spin-orbit Hamiltonian is applied to evaluate the molecular field, core-valence exchange, and spin-orbit splittings for some typical molecules containing sulfur and phosphor. The BP Hamiltonian is expanded with electron configurations using non-relativistic orbital functions; then, we can discuss character of the spin-orbit wavefunction with the molecular field effect and core-valence exchange interaction. The simplest approach based on the BP Hamiltonian is to expand the Hamiltonian matrix with a minimum number of configurations. Furthermore, within the framework of the minimum BP Hamiltonian matrix, we introduce correlation correction into the diagonal and some off-diagonal elements. The correction due to the molecular field effect and core-valence exchange interaction is evaluated with non-relativistic configuration interaction (CI) calculations of core hole (ionized/excited) states.

The present calculations are compared with high-resolution and angle-resolved photoion yield spectra successfully measured at a new beamline in the UVSOR facility. We will discuss mixing between the perpendicular and parallel transitions, 2p hole dependence of the core-valence exchange interaction, and bond-length dependence of the spin-orbit interaction.

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# **INFLUENCE OF REFRACTION AND REFLECTION OF LIGHT ON PHOTOELECTRON DIFFRACTION EFFECTS**

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Photoelectron diffraction effects are very sensitive to the atomic and magnetic structure of surfaces, interfaces and adsorbate systems. The success of the method is based on the great variety of parameters which may be changed in the experiment. Among them are the incidence angle and polarization state of the exciting light. Presently only weak attention has been paid to the change of light polarization due to refraction and reflection at the vacuum-solid surface and as a result the influence on photoelectron diffraction.

We present analytical and numerical results of photoelectron intensity for light of general state of polarization incident at general polar and azimuthal angles taking into account the optical properties of the solid. In a first step the radiation field inside the solid is approximated macroscopically according to classical electrodynamics. Analytical expressions are derived within a real-angle representation of Fresnel equations to reveal the influence of refraction and reflection of light on the transition matrix elements of photoemission directly. It is shown, that the refracted light in an absorbing material may be decomposed into three components, the usual s- and p-components of polarization and a third component caused due to absorption effects of the solid.

Spin polarization and dichroism in core-level photoemission are discussed in dependence on the incidence angle and the state of polarization of light. It is shown that due to absorption effects and the change of light polarization caused thereby a strong symmetry breaking in the photoemission intensity may be caused at surfaces and interfaces.



# LDA MODEL : APPLICATION TO SPHERICAL JELLIUM CLUSTERS.

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In this work we have developed a simple self-consistent spherical model for the treatment of the outer shell electron structure in the fullerene  $C_{60}$  and  $C_{20}$  molecules, starting from the self-consistent solution of the Kohn-Sham equation in the local-density approximation (LDA) for the exchange-correlation functional  $E_{xc}[\rho]$ . Our model is applicable for the many-body description of various collision processes involving the fullerene  $C_{60}$  and  $C_{20}$ , in which only valence electrons are important.

We have calculated the photoionization cross sections of  $C_{20}$  and  $C_{60}$ , using the wavefunctions of the ground and excited states of the outer shell electrons obtained in our model. This calculation is performed in the length and velocity forms for the dipole electron-photon interaction within the framework of the local density approximation[1] and random phase approximation.

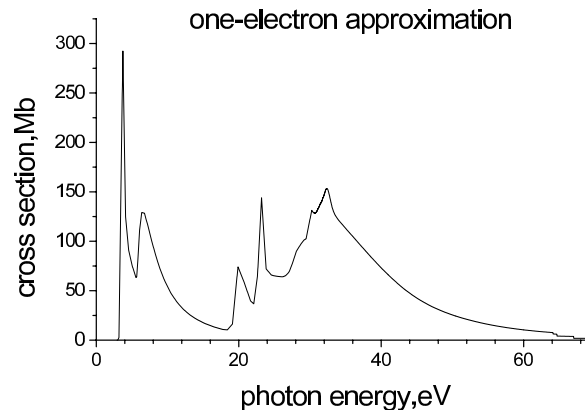


Figure 1: Photoionization cross section of the fullerene  $C_{60}$  molecule.

Our calculation demonstrates strong plasmon resonance enhancement of the photoionisation cross sections, which is in the good agreement of the experimental observations and the results of other calculations[2,3,4].

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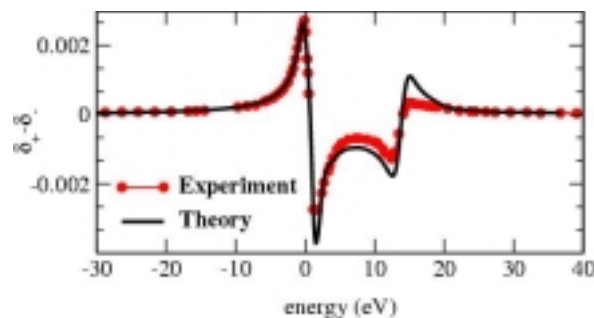
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# Resonant magneto-optical properties of disordered alloys in the X-ray regime

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A version of the Kubo–formula is presented, that allows to calculate the resonant magneto–optical properties in the X–ray regime for arbitrary materials. This is achieved by representing the underlying electronic structure in terms of the electronic Green’s function. Calculating the Green’s function in the framework of spin–polarized relativistic multiple scattering theory in particular gives access to spin–orbit induced resonant magneto–optical properties. An example for these are the circular dichroic parts of the complex refractive index  $n=1-\delta+i\beta$ . This is demonstrated in the figure by corresponding results for the circular dichroism  $\delta_+-\delta_-$  at the  $L_{2,3}$ –edge of pure bcc–Fe, that are compared with recent experimental results of Kortright and Kim [1]. Obviously, the calculations are able to reproduce the highly–resolved experimental data in a quantitative way.



Using the Green’s function formalism allows in a straightforward way to deal with systems without three–dimensional translational symmetry. Two important examples for these are surfaces and disordered alloys. To deal with the later case the Coherent Potential Approximation (CPA) alloy theory has been adopted here. Corresponding results to be presented for the  $L_{2,3}$ –edge of Fe and Ni in the disordered alloy  $Fe_{0.5}Ni_{0.5}$  were found in very good agreement with recent experimental results of Mertins et al. [2]. For the disordered alloy system  $Co_xPt_{1-x}$  the magnetic dichroism at the  $L_{2,3}$ –edge of Pt, that is due to the induced magnetic moment of the Pt–atoms, has been investigated throughout the whole concentration range. Using these results, in particular the relationship of the amplitude of the dichroic signals  $\delta_+-\delta_-$  and  $\beta_+-\beta_-$  with the magnetic moment of the probed atom will be discussed in some detail.

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# HARTREE-FOCK APPROACH FOR DEFORMED MANY-ELECTRON SYSTEMS: METAL CLUSTERS AND CONFINED ATOMS.

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The Hartree-Fock (HF) method is developed for deformed many-electron systems, such as a deformed metal clusters and atoms confined inside a deformed endohedral environment [1,2]. This approach extends the spherical HF method by using the partial-wave expansion of the electron wave functions in spheroidal coordinates ( $\xi, \eta, \varphi$ ) and can be applied to a various types of many-electron systems which do not have a spherical symmetry. This method serves as a basis for *ab initio* development of many-body theory of deformed many-electron systems.

We present the results of calculation of the electronic structure and a shape deformation parameters for a series of sodium clusters with the number of atoms in a cluster ranging from 4 to 40. Our model explains, on the basis of *ab initio* principles, the complex size dependence of the total energy, ionization potentials and other characteristics of the metal clusters as a consequence of non-spherical cluster's shapes. The cluster deformations are in a reasonable agreement with the available experimental data and the results of other theories.

We have also studied the electronic properties of atoms encapsulated endohedrally inside deformed fullerene molecule. The deformed fullerene cage has been modeled by an attractive-shell potential sandwiched between two ellipsoids of revolution, which define the geometry of the fullerene. This approach allows the treatment of the endohedral metallofullerene as a quasi-atom and uses simple atomic concepts rather than more elaborate molecular tools. We have applied our method to the hydrogen atom confined inside a deformed C<sub>60</sub> molecule and studied the electronic structure of the encapsulated atom as a function of the deformation parameter. Experimentally, the shape of the C<sub>60</sub> cage can be altered by the external field or by exciting one or more valence electrons belonging to the carbon skeleton. This study is also relevant to other trapping fullerene cages, like the egg-shaped C<sub>82</sub>, which are naturally not spherical.

This work is supported in part by the Royal Society of London, NATO, INTAS, the Volkswagen Foundation and RFBR (grant 99-02-18294a).

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# OPTICAL CONSTANTS: METHODS OF CALCULATION ON THE BASIS OF EXPERIMENTAL DATA, ACCURACY

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The purpose of the paper is to analyze the different ways of the calculations of the optical constants of materials. SiO<sub>2</sub> layers on a Si substrate with different thickness of the dioxide (2,0 nm, 10 nm, 120 nm) were investigated. The samples were prepared by a dry oxidation method. Spectral and angular dependencies of reflection coefficients were measured by using s-polarized synchrotron radiation in a broad spectral range.

The optical constants of amorphous SiO<sub>2</sub> and Si have been calculated from angular dependent reflectivity spectra and from reflection spectra. The data were derived: 1) by means of Fresnel formulas neglecting the substrate; 2) using a recursion equation; 3) using Kramers-Kronig analysis. The least squares fits were carried out by varying of the following parameters: the dielectric constants  $\epsilon_f = \epsilon_{1,f} + i\epsilon_{2,f}$ , the rms roughness height  $\sigma_f$  and thickness  $d$  of the SiO<sub>2</sub> film, the dielectric constants  $\epsilon_s = \epsilon_{1,s} + i\epsilon_{2,s}$  of the substrate and the rms roughness height  $\sigma_i$  at the interface between the substrate and film. The influence of the extrapolation outside the spectra range of the experiment in a high energy region on the accuracy of the values of optical constants was examined.

For all samples a good agreement between the measurements and the calculations was obtained. The thickness of the films and surface and interface roughness were determined quite accurately. The results for the optical constants agree better than 5% with the values obtained for the all samples. Especially in the energy region above the OK edge the results are very consistent.

However, in the regions of anomalous dispersion where the photon energy is closed to the SiL<sub>2,3</sub>- and OK-absorption edges some inconsistencies are observed. Because the x-ray absorption fine structure is strongly influenced to the nearest surrounding of the atoms that participate in the absorption process one can suggest the existence of intermediate layer characterized by an atomic composition distinguishable from SiO<sub>2</sub>. Analysis of the calculated optical data points to the fact the values derived from angular dependencies of reflection by neglecting the substrate and by a recursion equation shows a significant disparity near absorption edges, too. There is good reason to believe that the interface between the substrate and the film is not well described by recursion equation.

# RELATIVISTIC CALCULATION OF THE TWO-PHOTON BREMSSTRAHLUNG PROCESS

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We report new results from the relativistic theory of free-free transitions, and propose [1] an approximation for effective quantitative analysis of the processes the amplitude of which contains, as a constituent part, the radiative free-free matrix elements between intermediate (virtual) states.

The transitions of this type are encountered in a number of physical processes in which the collision of a projectile with a target (either structural or without internal degrees of freedom) is accompanied by emission/absorption of a photon (photons) (see e.g. recent reviews [2]). The list of such processes includes, in particular, (i) the bremsstrahlung-type phenomena in an external field, (ii) inelastic bremsstrahlung, when the emission/absorption of the photon is accompanied by simultaneous ionization of the target (these include also the  $e \rightarrow 2e + \gamma$  processes), (iii) the Compton scattering from many-electron atoms, (iv) many-photon ionization of atoms and ions.

The *exact* relativistic treatment of the free-free transitions encountered in these processes is extremely cumbersome, and for many processes (e.g. many-photon free-free transitions) such a problem has not been solved so far. The approach we propose [1], although being approximate, allows, nevertheless, to evaluate effectively the principal parts of the free-free matrix element with much less analytical and computational efforts. It is based on the accurate treatment of the diagonal singularities in the one-photon relativistic matrix elements, which appear in the compound matrix element.

We illustrate the applicability of the method [1] by presenting, for the first time, the numerical results of calculations of spectral and angular distributions for two-photon bremsstrahlung process of relativistic electron and their comparison with available experimental data and more simpler approximations. The calculations are performed on the basis of combination of developed formalism within Furry-Sommerfeld-Maue approximation. The results of the present research are the relativistic extension of the method introduced recently [3] for a non-relativistic projectile.

The work was supported by the RFBR grant 99-02-18294a.

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# RELATIVISTIC CALCULATION OF POLARIZATIONAL BREMSSTRAHLUNG SPECTRA

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The fully relativistic formalism for the description of bremsstrahlung formed in a charged particle–atom collision was developed recently [1]. It accounts for both leading mechanisms of the radiation formation, the ordinary (OBrS) and the polarizational (PBrS) bremsstrahlung. The well-known process of OBrS, i.e. the process of photon emission by a charged projectile accelerated in the static field of a target, has been intensively studied previously in a wide range of the parameters. The situation is the opposite with the PBrS, which is a result of dynamic polarization of the internal structure of particles involved in the collision process. So far there were no numerical calculations of the PBrS cross section in the relativistic domain. In this report we present the results of such computation based on the developed formalism [1] aiming to illustrate the importance of the relativistic and higher-multipole effects in the PBrS formed in the collision of a relativistic projectile with a high- $Z$  target. The presented results refer to a collision of 3 GeV proton with an ion  $\text{Ag}^{+46}$ . The OBrS can be neglected in a wide range of the photon energy. In Figure 1a the results of calculation of the PBrS spectra is presented. Figure 1b presents the dependencies  $\omega d\sigma/d\omega$  calculated for  $\hbar\omega$  equal to 100 and 200 keV as functions of the relativistic factor  $\gamma = \varepsilon/mc^2$  of the incident proton.

The work was supported by the RFBR grant 99-02-18294a.

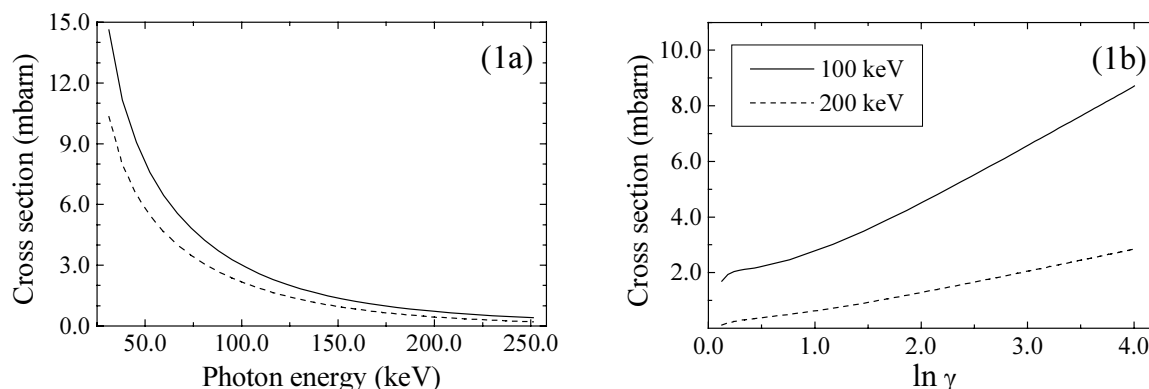


Figure 1: Spectral (fig.1a) distributions of PBrS for 3 GeV proton (thick solid line represents the relativistic cross section, the dashed line corresponds to the result of the non-relativistic dipole-photon theory). In figure 1b the cross section  $\omega d\sigma/d\omega$  versus  $\ln \gamma$  is plotted for two values of the photon energy as indicated.

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# THE LOCAL GEOMETRICAL STRUCTURE OF AL-TRANSFERRIN PROBED BY XANES SPECTROSCOPY

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Transferrin is a metalloprotein found in the plasma of vertebrates. It's role in the transport of many metal ions has biomedical relevance; of particular interest is the transport of aluminum. Knowledge of the high resolution aluminum site structure is of major benefit for understanding the mechanism of the protein- metal binding.

We have applied multiple scattering theory to simulate the Al K-XANES of serum transferrin. The method is based on the comparison between experimental data [1] and many theoretical calculations performing by varying structural parameters. Starting from geometrical configurations around the absorber 1a8e, 1a8f and 1b3e, chosen from Protein Data Bank (PDB) [2],[3], we have generated series of models which have different first coordination shell distances. The best agreement between theoretical and experimental results is reached using 1a8e model. Although the hexacoordinated ionic radius of Al<sup>3+</sup> is smaller with respect to the ionic radius of Fe<sup>3+</sup> (0.54 versus 0.65 Angstrom) average Me-O and Me-N bond length have been found to be very similar when Me atom is Al and Fe. Coordination of the Al ion by the water molecule has been examined. The comparison of theoretical spectra calculated with different Al-H<sub>2</sub>O distances with experimental data shows the Al-H<sub>2</sub>O bond length is 2.05 Angstrom.

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# ON THE STRIPPING APPROXIMATION IN THE BREMSSTRAHLUNG PROCESS.

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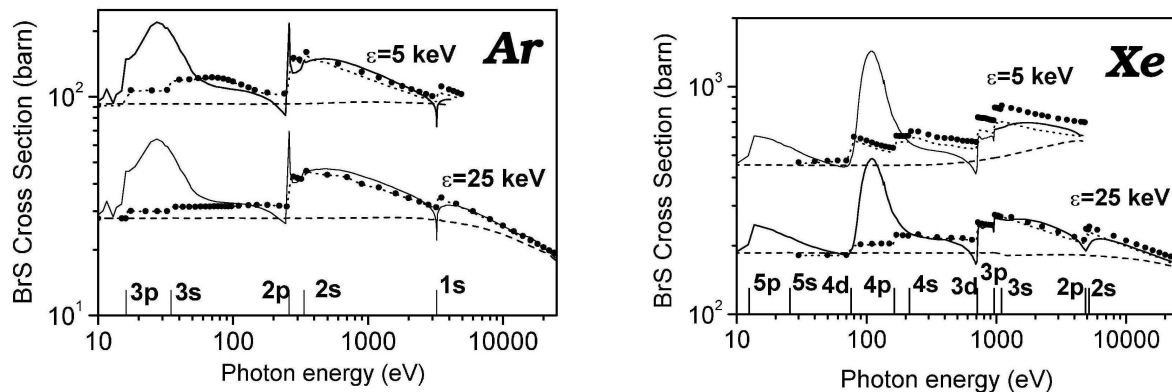
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We discuss two different approaches [1,2] for the approximate treatment of the bremsstrahlung (BrS) process of non-relativistic electrons on many-electron atomic/ionic targets, described by a total amplitude which is a sum of ordinary and polarizational BrS amplitudes. The approaches are based on the so called "stripping" effect [3] and are useful for the calculation of the BrS spectra for photon energies  $\omega$  greater than the ionization thresholds of the outer atomic shells.



**Figure 1:** BrS cross section of 5 and 25 keV electrons on *Ar* and *Xe* atoms. Dashed lines and solid lines represent the exactly calculated ordinary and total BrS respectively. Chain lines correspond to the stripping approximation of Ref. [1], full circles to the corresponding approximation of Ref. [2].

This work is supported in part by NSF grant 9970293 and RFBR grant 99-02-18294-a.

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# ATOMIC ORIGIN OF CORE-LEVEL SHIFTS BY PHOTOELECTRON DIFFRACTION

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Surface core-level shifts of photoemission peaks enrich adequately the wealth of information available to a photoemission investigation. In fact the intensity and resolution presently available at new synchrotron radiation sources makes surface core-level photoemission able to solve chemistry and structure of surfaces and interfaces with a sensitivity which is not commonly reachable by other surface science techniques. In spite of these many assets to exploit, only seldom an indisputable approach to photoemission core-level shifts data is reported, mainly because of the unknown atomic origin of such core level shifts. To this aim the use of methods to assign atomic origins to surface core-level peaks is necessary and hopefully leading to great advantages in the study of surface properties. A method to cope with such a challenging task is the photoelectron diffraction from surface shifted core-levels (SCLS-PD) [1-3]. We shall present the rationale of the analyses of SCLS –PD for several semiconductors (Si(001)-2x1, As/Si(111), As(Sb)/Si(001)-2x1, Ge(001)-c(4x2)) [1-7] and metal surfaces systems (0/Ag(100)) [8] and the status of the evolution of photoelectron diffraction analyses from both sides of deconvolution of raw data and the calculations of photoemission angular cross-section by means of full multiple scattering approach [2-3] with complex potential. Results will be compared with final state calculations present in literature.

The quantitative analyses of several SCLS's will be compared with the semi-classical analyses of core level intensities and escape depth attenuation. In particular some conclusions will be drawn about the limits of application of the semi-classical approach to the analyses of core level shifts. The question of branching ratio variations (mainly in d core levels) [9] will be addressed and the applications of a spin dependent multiple scattering calculations will be shown to the aim of increasing the level of completeness of the investigation.

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# Resonant X-Ray Scattering on $\text{YTiO}_3$ and $\text{YVO}_3$

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We investigate the effect of the crystal structure to the resonant X-ray scattering (RXS) intensities on the Ti  $K$  edge region of  $\text{YTiO}_3$  and V  $K$  edge region of  $\text{YVO}_3$  using the band structure calculation combined with the local density approximation.

The resonant X-ray scattering spectroscopy has attracted much attention because this experimental method is considered as one of the most powerful tools which can directly observe the orbital order in the strongly correlated systems. Despite much effort so far, how and to what extent the RXS spectra reflect the orbital order are still controversial, especially on the perovskite compounds, because the Jahn–Teller distortion and the  $\text{GdFeO}_3$  type distortion, which can also give rise to the RXS intensity, are present.

In this study we exclude the effect of the orbitally polarized  $3d$  state. The calculated spectra consist of several peaks as a function of photon energy in agreement with the recent experiments[1,2]. It is also found that the spectra for the (100) reflection are strongly affected by the Jahn–Teller distortion (see Fig. 1), although the spectra for the (001) and (011) reflections are not so affected. This result is consistent with the experiment on  $\text{YVO}_3$  [1]. Because the effects of the orbitally polarized  $3d$  state are excluded in our calculation, our results show that the RXS intensity arises due to the distorted crystal structure, *i.e.*, the tilt of the  $\text{TiO}_6$  or  $\text{VO}_6$  octahedra and the Jahn-Teller distortion, which considerably modifies the  $4p$  states in the intermediate states of the dipolar process. This casts doubt on a simple interpretation that the resonant x-ray scattering is a direct observation of the orbital order.

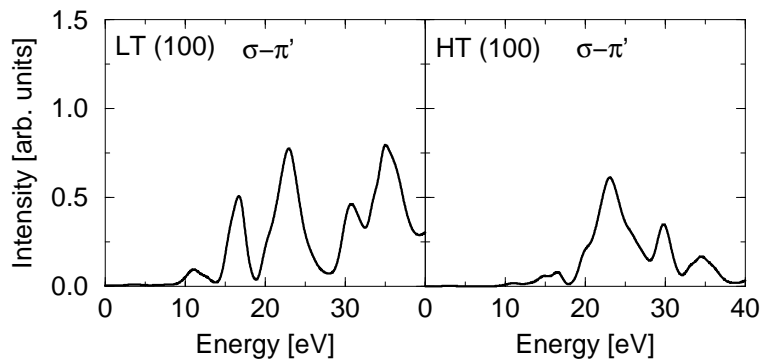


Fig. 1 Calculated RXS spectra as a function of photon energy for the  $\sigma\text{-}\pi'$  (100) reflection on  $\text{YVO}_3$ . In the left panel the crystal structure in the low temperature phase is assumed and the right panel that in the high temperature phase is assumed. The Jahn-Teller distortion almost vanishes in the high temperature phase. The origin of energy corresponds to the energy of photon which excites an electron from the  $1s$  state to the Fermi level.

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# Resonant x-ray scattering from the quadrupole ordered phase of rare-earth compounds

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We report the calculated results of the resonant x-ray scattering (RXS) spectra for the superlattice spots near Ce  $L_{III}$  absorption edge in the quadrupolar ordered phase of  $CeB_6$ . We treat the  $5d$  states of Ce as a band and the  $4f$  states as localized states. We obtain a large intensity in the dipolar process, which arises mainly from the  $5d$  states modulated by the quadrupole order of the  $4f$  states through the intra-atomic Coulomb interaction. This contrasts with the RXS spectra near the Mn  $K$  edge in  $LaMnO_3$ [1], where the  $4p$  states are so extended that they are mainly modulated by the Jahn-Teller distortion through neighboring oxygen potentials[2,3,4]. As shown in Fig. 1, the temperature dependence of the RXS intensity is found to resemble closely to the variation of the order parameter of the quadrupole order[5], in agreement with the recent experiment. The magnetic field dependence indicates that the induced dipolar and octapolar order have little influence on the RXS intensity. We also discuss the azimuthal angle dependence of the intensity.

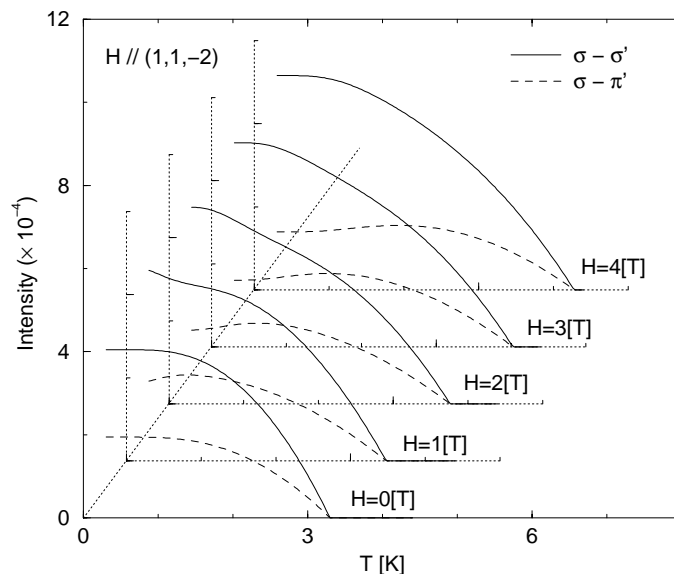


Figure 1: Temperature dependence of the RIXS intensities. The fields are applied in  $(1, 1, -2)$  direction. Solid and broken lines are the intensities for the  $\sigma - \sigma'$  and  $\sigma - \pi'$  polarizations, respectively.

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# **THEORETICAL STUDY OF PHOTOIONIZATION PROCESSES IN ORGANOMETALLIC COMPOUNDS**

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Density Functional calculations have been carried out to determine the photoionization cross sections and the asymmetry parameter profiles of organometallic compounds, using an explicit treatment of the continuum wave-function. An accurate numerical treatment is employed to ensure convergence of the calculated photoemission profiles without further potential approximation. All valence and carbon and metal core ionizations are investigated over a wide energy range. A very satisfactory agreement is obtained with the many experimental data available for this molecule, indicating that the present LDA level of theory is generally adequate to interpret the complete photoemission spectra in organometallic compounds, with the only exception of autoionization resonances, allowing to extract from the spectra chemically relevant information and to resolve uncertain assignment. The analysis of the calculated cross sections allows to definitely uphold the experimental assignment of the first four outer valence ionizations and furthermore suggests that characteristic behaviours can be recognized also in the core metal cross section profiles.

# CALCULATIONS OF PHOTOEMISSION PROFILES OF C<sub>60</sub> AND ENDOHEDRAL COMPOUNDS

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Extensive calculations of cross section and asymmetry parameter of C<sub>60</sub> and M@C<sub>60</sub> (M = alkaline or alkaline-earth metal) have been carried out employing a local density approach and a convergent one center expansion. Good agreement with available experimental data is obtained for C<sub>60</sub>, and new resonances predicted in M@C<sub>60</sub>.

In particular results for total cross section and HOMO/HOMO-1 oscillations up to high energy will be presented. Resonances in M@C<sub>60</sub> are interpreted by analysing the final dipole projected continuum wavefunction.

## The Shapes of Photoelectron Satellite Spectra

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The correlation satellite  $1s^{-1} 2s^{-1} ({}^3S)3s({}^2S)$  of Ne  $1s$  photoionization [1] was the first example of a Fano-type lineshape in photoelectron spectra. The asymmetry of the satellite lineshapes comes from two different effects : from interference between direct shake-off excitation [1,2] and excitation via resonance and from strong depression of the low-binding energy side of a satellite line [2]. The first effect is similar to that taking place in resonant photoabsorbtion, while the second is a consequence of the correlation nature of photoelectron satellite resonances [2]. In the present work the lineshape of the satellite  $1s^{-1} 2s^{-1} ({}^3S)3s({}^2S)$  is calculated making use of perturbation expansion up to the 3<sup>rd</sup> order and limited number of the 4<sup>th</sup> order diagrams is also taken into account. Theoretical results are in excellent agreement with the experiment. (see Figure). Theory is applied to other photoelectron satellites also. The work is supported by International Science and Technology Center (grant 1358).

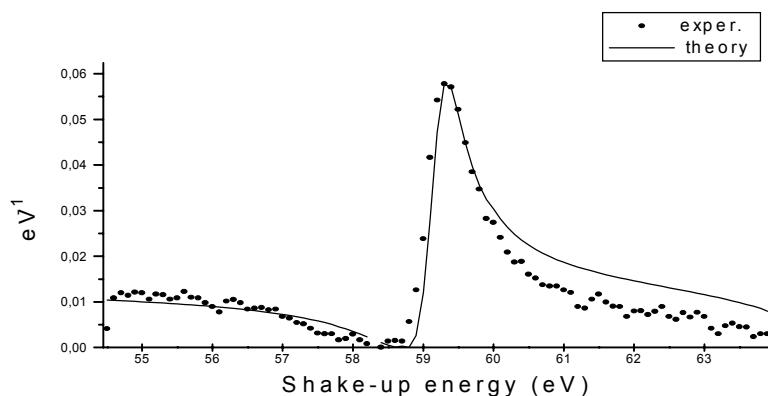


Figure. Theoretical and experimental [1] (points) satellite lineshape .

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# Energies and autoionization widths in the lithium iso-electronic sequence

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Energies and autoionization widths are presented for autoionizing states in Li I, Be II and B III lying between the  $1s^2$  and the  $1s2s\ ^3S$  ionization limits. A configuration interaction expansion combined with a *B*-spline basis set has been used to compute the properties of the lowest  $^2S^e$ ,  $^2P^o$  and  $^2D^e$  states which are, in the LS approximation, the only terms allowed to autoionize. The comparison with theoretical and experimental data shows the high accuracy of the *B*-spline approach applied to singly core-excited states. The error on the energies is found, in the case of Li I, to be well below 10 meV in general, while for Be II and B III, for which much less is known, the theoretical results points to the need for more accurate measurements. Several new identifications have been made and some identifications revised in the experimental data.

# MULTIPLE SCATTERING THEORY OF PHOTOELECTRON ANGULAR DISTRIBUTIONS FROM ORIENTED DIATOMIC MOLECULES

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Angular distributions of electrons photoemitted from oriented molecules have become an exciting new tool for studying electronic structure and dynamics [1-3]. We use multiple scattering photoelectron diffraction (MSPD) theory to calculate the final-state wavefunction of the electron leaving the molecule, and then subsequently its angular distribution. For low ( $E < 50$  eV) kinetic energies of the photoemitted electron, the electron scattering cannot be adequately represented by spherically-symmetric potentials. We thus include non-spherical scattering potentials in our formalism through non-diagonal scattering matrices.

As examples, we calculate the angular distributions of photoelectrons emitted from the K shell of oriented gas-phase CO and N<sub>2</sub> molecules, as recently measured by several groups [1-3]. We show that intramolecular scattering and interference are responsible for the experimentally measured patterns. Particularly important are the energies for which shape resonances appear in the continuum, with the angular distributions showing radical changes over such resonances. We calculate the final photoelectron angular patterns for different polarizations of the light (linear and circular), and discuss the issue of coherence in the photoemission from equivalent centers of homonuclear molecules (such as N<sub>2</sub>). This MSPD approach represents a more accurate and versatile method for dealing with such angular distributions as compared to prior calculations of these effects [4].

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