I. ATOMIC AND MOLECULAR PHYSICS.

ATOMIC EFFECTS IN SOLIDS

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Résumé. — Cette revue concerne l'origine des structures présentées par le coefficient d'absorption, lors de mesures par plusieurs techniques, à partir d'échantillons solides. On met l'accent sur les modèles atomiques de photoionisation en raison de la ressemblance des spectres du solide et de la vapeur, dans ce domaine d'énergies (10 à 350 eV) ; mais même les modèles les plus sophistiqués qui introduisent des corrélations dans l'état initial comme dans l'état final ne permettent pas toujours un bon accord quantitatif avec l'expérience. La photoionisation de l'atome libre ne peut expliquer certaines structures fines près des seuils ni une modulation du spectre due à la non-localisation du trou et au fait que le photoélectron est soumis à un champ issu de plusieurs centres.

Abstract. — This review concerns the origin of the structures of the absorption coefficient measured for solid state samples by several techniques. Because of a close similarity between the solid and gaseous samples spectra, in this energy range (10 to 350 eV), atomic photoionization models are emphasized; but the most elaborated models introducing correlation effects in both initial and final states are not always sufficient to give a good quantitative agreement with experiment. Some fine structures near the thresholds and a modulation of the spectra fail to be understood in terms of free atom photoionization because of the non-localization of the core hole and the multicenter nature of the field experienced by the photoelectron.

1. Introduction. — Since 1960, Synchrotron radiation has been used extensively for systematic studies of the optical properties of atoms, molecules and solids in the vacuum ultraviolet and soft X-ray regions (10 to 350 eV). Because of its high intensity and the continuous spectrum extending from the infrared to beyond the extreme vacuum ultraviolet, Synchrotron radiation is certainly a precious tool for investigations concerning the depths of the valence bands and the electronic structure of core levels in solids. Several review papers [1, 2, 3] have been devoted to the investigations of the electronic states in solids (insulators, such as rare gases and alkali-halides, as well as metals) by means of Synchrotron radiation. Vacuum ultraviolet absorption spectroscopy is not the only technique dealing with excitation of deep valence and core levels: energy loss spectroscopy [4] which excites core electrons with fast electrons also allows to deduce optical constants and absorption coefficient over a large energy range (2 to 200 eV) from the energy loss function. In addition to reflection and absorption measurements, secondary and decay processes are investigated: in photoemission [5], interest is focused on the excited states and the escaping electrons. These electrons constitute current which contains information on the band structure as well as electron transport at energies well above the Fermi energy. Photoemission allows to unravel band structure by resolving many of the transitions which contribute to optical absorption at a particular photon energy. It determines the energy of the initial and final states, while optical measurements determine only differences in energy between states. Further Auger electrons and secondary electrons leave the solid and their observation can give information on the excitation process, through the measurement of the total photoelectric yield, indeed, yield spectroscopy [6] which involves the measurement of the secondary electrons in function of photon energy allows for studying the absorption structures, from compact samples, instead of thin films.

In this paper, we shall focus on these features of the absorption spectra which cannot be interpreted in terms of a band structure model. Most of them can be seen also in the vapor spectra and predicted in the framework of an atomic picture. So, we shall emphasize the atomic models which have been worked out up to now, and their validity in this low energy range (10 to 350 eV) when deep valence and core levels are excited.

2. General formulas. — Within the one electron approximation, the absorption of a photon is described by the excitation of one electron of the system from an occupied state to an empty one. The imagi-
nary part of the dielectric function, $\varepsilon_2(\omega)$ gives the absorbed energy, according to the formula:

$$
\varepsilon_2(\omega) = \frac{\hbar^2 e^2}{\pi m^2 c^2} \int |\mathbf{e} \cdot \mathbf{D}_{\mathbf{e}}|^2 \delta(E_c - E_e - \hbar\omega) \, d^3k
$$

(1)

where $E_c$ and $E_e$ are energies of occupied valence (or core) and empty conduction states, $\mathbf{k}$ is the Bloch wave vector, $\mathbf{e}$ the polarization vector of the incident photon, the integration being carried out over the first Brillouin zone. Formula (2) gives the dipole matrix element:

$$
\mathbf{e} \cdot \mathbf{D}_{\mathbf{e}} = \int dV \psi_e^*(k_e, r) \psi_e(k_e, r) \exp(i\mathbf{K} \cdot \mathbf{r})
$$

where $\mathbf{K}$ is the propagation vector of the photon, $\psi_e$ and $\psi_e$ are Bloch functions, the integration extending over unit volume. $\hbar\omega$ is the photon energy, $e$ and $m$ having their usual meaning.

Most of the calculations of $\varepsilon_2(\omega)$ have only been concerned by the determination of the density of states $N(\omega)$, the matrix element being considered as a constant throughout the Brillouin zone. Let us recall that the density of states is proportional to $\sin^2 \frac{\pi}{a} (E_c - E_e - \hbar\omega)$.

Anyway, the attempts to compare experiment with theory, starting from $\varepsilon_2$ proportional to $N(\omega)$ failed, except for photoabsorption by electrons rather close to the Fermi level, because they did not take into account the variation of the matrix element with photon energy. Considering that core electrons are perturbed in a solid by a very small amount from the atomic character, an atomic picture should often be applicable. Figure 1 shows the absorption spectrum of solid [7] and gaseous [8] xenon in the range of 4d transitions, while we can see in figure 2 the corresponding curves for barium [9]. We remark that these spectra are different from those found in the X-Ray region and a close similarity between the spectra of free atoms and those of solid samples.

In Atomic Physics, one usually calculates the photoionization cross-section $\sigma$ related to the linear absorption coefficient $\mu$ by:

$$
\sigma = \mu N_a = \frac{\omega \varepsilon_2(\omega)}{N_a c n}
$$

(3)

$N_a$ being the number of atoms per unit volume, $n$ the refraction index and $c$ the light velocity. Before calculating the photoionization cross-section relative to an atom in state $i$, we recall that the process can be written schematically:

$$
\hbar\omega + A_i \rightarrow A_j^+ + e^- \quad \text{(4)}
$$

the residual positive ion being left in state $j$, and the photoelectron being ejected with kinetic energy $\varepsilon$ such as:

$$
\hbar\omega = I_{ij} + \varepsilon \quad \text{(5)}
$$

$I_{ij}$ is the energy to just remove an electron from $A_i$ (ionization threshold). For photoionization theory, we shall refer to general books, for instance Bethe and Salpeter [10], and we shall start from the cross-section of single ionization by an unpolarized photon beam with energy $\hbar\omega$, as given by Bates [11]:

$$
\sigma_{ij}(\varepsilon) = \frac{4 \pi^2}{3} \frac{a_0^3}{g_i} (I_{ij} + \varepsilon) |D_{ij}|^2 \quad \text{(6)}
$$

where $f$ indicates the final state of the system (ion $A_i^+$ plus photoelectron); $a_0$ is the fine structure constant, $a_0$ the Bohr radius and $g_i$ the statistical weight of the initial discrete state $A_i$. In [6], both $I_{ij}$ and $\varepsilon$ are expressed in Rydbergs. The matrix element $D_{ij}$ can be written:

$$
|D_{ij}|^2 = \frac{4}{(\varepsilon + I_{ij})^2} \times \sum_l \left| \left< f \left| \sum_n \exp(i\mathbf{K}_n \cdot \mathbf{r}_n) \mathbf{V}_n \right| i \right> \right|^2 \quad \text{(7)}
$$

FIG. 1. — Photoabsorption cross-section for solid (solid curve) and gaseous Xe (dashed curve) in 4d excitations region (from Haensel et al. [7]).

FIG. 2. — Photoabsorption cross-section for solid (dashed curve) and gaseous Ba (solid curve) in 4d excitations region (from Rabe et al. [9]).
with a summation over all the initial and final states, \( \mathbf{r}_n \) being the position vector of the \( n \)th electron. Because we are dealing with rather low energy range, \( \exp(\mathbf{K} \cdot \mathbf{r}) \) can be well approximated by 1 (dipolar approximation) so that:

\[
|D_{if}|^2 = \frac{4}{(l_i + \ell_f)^2} \times \sum_{i,f} \left( \sum_{n} \left| \left\langle f \left| \sum_{n} \mathbf{V}_n \right| i \right\rangle \right|^2 \right)^2 \quad (8)
\]

These two expressions in (8) are formally equivalent and are usually referred to as dipole-velocity and dipole-length formulations respectively. However, they may give quite different results, since exact wave functions to describe the initial and final states are available only for hydrogen. We shall come back to this point further on.

3. Various models to calculate photoionization cross-sections. — To start with we shall describe briefly the simplest models, in the framework of the one electron picture.

3.1 Central potential models. — The basic idea consists in replacing the exact Hamiltonian \( \mathcal{H} \) by an approximate central field Hamiltonian \( \mathcal{H}^0 \), whose solutions will be used to describe the atom, before and after the photoionization process:

\[
\mathcal{H}^0 = \sum_n [p^2/2m + V(r_n)].
\]

These solutions are antisymmetric products of single electron wave functions \( P_{nl}(r) r^{-1} Y^m_l(\theta, \varphi) \), \( P_{nl} \) being replaced by \( P_{nl} \) for electrons ejected to the continuum. We must solve the same following equation to get both \( P_{nl} \) and \( P_{nl} \):

\[
\left[ \frac{d^2}{dr^2} + E - V(r) - \frac{l(l + 1)}{r^2} \right] P_{nl}^{n_l}(r) = 0. \quad (10)
\]

Such a central potential model is a single electron model, since core relaxation effects are excluded. It has been described extensively and used by Manson and Cooper [12], Combet Farnoux [13], McGuire [14]; these authors used the Herman and Skillman [15] potential, which we shall refer to as HS potential. Their calculations have allowed to point out the existence of characteristic features in the spectra of many elements, over a relatively wide energy range; among them:

1) The cross-section relative to a subshell with at least one node shows a Cooper minimum due to the dipole matrix element \( D_{nl, n_l+1} \) going through zero. In comparison, the 2p, 3d, 4f cross-sections show a single broad maximum shifted from the threshold.

2) The first maximum in the cross-section \( \sigma_{nl} \) is shifted from the threshold, because of the existence of a potential barrier due to the centrifugal repulsion term \( l'(l' + 1)/r^2 \); this potential barrier keeps far out the core the low energy continuum states \( \ell' = l + 1 \). It is at the origin of the broad maximum in the 4d spectrum of xenon (Fig. 1) mentioned above and interpreted by Cooper [16] first, using the HS potential. Other examples of a potential barrier were pointed out by Combet Farnoux [17] and Cooper [16], and Combet Farnoux [19] in the case of xenon, from different central potentials. But they may predict the main structures of the spectra when ionization takes place in \( nl \) subshells of atoms such as no \( (n, l + 1) \) electron is bound in the ground state: in this case, the transitions to the continuum \( (nl \rightarrow e, l + 1) \) are major, compared to the discrete transitions \( (nl \rightarrow n, l + 1) \) and their maximum is delayed as long as the potential barrier \( \ell' \geq 2 \) is not reached. So, some general studies, as those of Manson and Cooper [12] for 3p and 3d subshells, or Combet Farnoux [13] for heavy elements can be very useful to experimentalists in both Atomic and Solid State Physics. The comparison of theoretical and experimental results for the spectrum of iridium [20] (30 to 500 eV) was an extra proof of these conclusions. Anyway, an improvement of the quantitative agreement is possible in so far as the exchange effects between the residual ion and the photoelectron are approximated by the same local averaged exchange potential as used to determine the wave functions of the initial ground state (Slater approximation to exchange). More realistic exchange effects have been introduced in the framework of independent particle models, by means of the Hartree-Fock (HF) approximation applied to the continuum. Before showing the dramatic improvements brought by this HF treatment, let us notice that, with central potential models, dipole-length and dipole-velocity formulations must give the same results: this property is a good way of checking the numerical accuracy of calculations, without being a guarantee for a good agreement with experiment.

3.2 Hartree-Fock approximation (single configuration). — It is well known and often used in the discrete spectra calculations, at least in first order calculations. Its extension to many electron continuum wave functions is more delicate, in so far as the variation principle is not applicable anymore. Then it is necessary to isolate the electron ejected into the continuum and calculate its wave function in the field determined through a HF calculation for the residual ion core. This way yields a single integro-differential equation, which Kennedy and Manson [21] solved for \( np \) outer shells of rare gases, and Combet Farnoux [22] for \( nd \) subshells in heavy elements.
The solution $P_{\alpha}(r)$ was used to calculate the dipole matrix elements to be introduced in the cross-section formula (6). In HF calculations, core relaxation may be included or not, whether we use the same discrete orbitals for initial and final states. Combet Farnoux [23] used the frozen core HS orbitals in the calculation of $\sigma_{5d}$ for gold and bismuth. Figure 3 shows the results for bismuth, compared to two experimental curves, one obtained by Dhez and Jaegle [24], the other by Haensel et al. [25]. The agreement with experiment is pretty good, except in the region of the threshold, although the theoretical curve is not able to reproduce the modulation of the maximum (Kronig structure). In figure 4, we see the comparison of oscillator strength curves for 5d excitations in gold; the theoretical curve is deduced from Combet Farnoux [23] results and the experimental one is calculated from the fast electron energy loss spectrum obtained by Wehenkel and Gauthe [26].

Taking into account that at lower energies, the refraction index $n$ may vary strongly (oscillator strength is proportional to $n^4$) and make appear strong fluctuations in the experimental curve, an atomic calculation of oscillator strength should give an envelope of these fluctuations if the threshold value took into account both the atomic and extra-atomic relaxation effects [27].

Other comparisons to HF calculations concerning the photoemission results obtained by Lindau et al. [28] for 3d excitations in gallium and arsenic, 4d excitations in indium and antimony were promising, in a broad energy range (20 to 350 eV). They seem to show that for these nd excitations in atoms such as no nf electron is bound in the ground state configuration, the HF approximation could give an acceptable agreement with experiment. However, we must note that this agreement concerns essentially the dipole-length formulation of the cross-section, while a discrepancy of nearly 50% is often observed between the results of the two formulations. Indeed, in this section, the major improvement, compared with a central potential model, concerns the description of the final state, since solving a HF continuum equation is equivalent to diagonalizing an intrachannel interaction matrix, according to Brillouin's theorem. So, we have to go beyond the HF approximation when it fails, because of neglecting the ground state correlations or some important interchannel effects, as it is the case for $\sigma_{3s}$ of argon. Let us notice also that HF models allow to take into account multiplet structure for open shell systems, but for atoms in solids, the valence shell structure may be very different from free atoms and we cannot be sure that is a real improvement.

3.3 Beyond the single configuration HF approximation. — A correct agreement between the results of the two formulations has only been obtained with elaborated models introducing correlation effects in both initial and final states. They have been reviewed recently, for instance, by Burke [29], Manson [30], Combet Farnoux [31] and few details will be given here. We will emphasize only the basic ideas of the three most important methods proposed up to now:

3.3.1 Configuration interaction methods. — The method developed by Fano [32] to deal with autoionization resonances was the first approach introducing configuration interaction into continuum wave functions. It is equivalent to diagonalizing directly the interchannel matrix, starting from an approximate HF Hamiltonian in each channel, so that the intrachannel interactions are already diagonalized. A multichannel extension of the continuum HF calculations (close-coupling approximation) has often been preferred to it and the recent application of the $R$ matrix theory [33] to this close-coupling formalism has allowed to introduce consistently pseudo-orbitals and configuration interaction in both initial discrete
and final continuum wave functions. Seaton's method [34] has the same advantages but uses different numerical techniques. Up to now, the corresponding codes have been essentially used for light elements and outer subshells.

3.3.2 Many Body Perturbation Theory (MBPT). — It consists in taking a zeroth order Hartree-Fock basis set and considering the total Hamiltonian including the interaction with the external field. It has been essentially developed in Atomic Physics and in photoionization by Kelly [35] and coworkers. Through the relationship between the photoabsorption cross section \( \sigma(\omega) \) and the frequency dependent polarizability \( \alpha(\omega) \), as also the diagrammatic perturbation expansion of \( \text{Im} \ \alpha(\omega) \), they were able to calculate the corrections to the dipole matrix element from the zeroth order value determined by the basis set. In addition to many calculations involving outer subshells and not much concerned by our study, we shall mention the rather successful calculations of \( \sigma_{4d} \) for barium [36]. They reproduce with fair agreement the experimental data of Connerade and Mansfield [37] (vapor spectrum).

3.3.3 Random Phase Approximation with Exchange (RPAE). — It has been used extensively in photoionization by Amusia [38] and coworkers, and Wendin [39]. It allows to introduce both the initial ground state and final excited state correlations, in so far as it assumes that the atom is excited, not only by creating particle-hole pairs, but also by destroying particle-hole pairs already present in the ground state. An important property of the RPAE approximation for closed shells atoms is that the results with the length and velocity operators are identical. The equations of RPAE may be formulated in several ways : starting from the time-dependent Hartree-Fock equations, or the equations of motion, or the Green's functions formalism, but this is out of the scope of our study, and we send back to the review papers mentioned above and references therein. In all cases, the results do not lead directly to a very clear physical picture of the interactions included in the calculation or to an identification of the dominant excitations. Even the traditional interpretation, according to which sums to all orders of the contributions from pairs of excited electrons (including simultaneous excitation of several pairs) are introduced, has been challenged by Chang and Fano [40]. Anyway, RPAE has been the most used model for getting theoretical curves to be compared with solid samples spectra in the V.U.V. region. As an example, figure 5 shows the comparison of Desy spectrum for cesium [41] with Amusia [38] RPAE curves in the 4d excitations region. While the small structures at the onset, may be due to 4d-6p transitions (like for Xe) the peak at 85.5 eV is ascribed to a localized f state. The broad peak at 105 eV is due to 4d \( \rightarrow \) f transitions strongly influenced by correlation effects whose major part is taken into account by RPAE. However, the remaining discrepancy seen in figure 5 cannot be due to solid state effects only, since the comparison with Cs vapor spectrum also shows a deviation which atomic outer shells rearrangement accounts for, according to recent calculations by Amusia et al. [42]. For barium, Wendin [43] had already taken into account these relaxation effects through introduction (on the same level of approximation) of all diagrams representing the hole self-energy, the screening of the electron-hole interaction and the self-induced potential seen by the photoelectron. Figure 6 shows the improvement of these results if compared to those obtained with usual Tamm-Damcoff Approximation with Exchange (TDAE) and RPAE [31]. Both Amusia's [42] and Wendin's [43] calculations emphasize cases where
RPAE method with HF frozen core assumption fails. They are those cases when the continuum resonance peaks are too sharp and shifted from their experimental position. Everything happens as if the core hole was not localized and a consequence of its fluctuations was a shift toward lower energies and a broadening of the continuum resonance, related to a less narrow and shifted potential well. Let us notice also that for Ba, $4d \rightarrow 4f$ transitions dominate the spectrum near the threshold where small structures are no longer ascribed to $4d \rightarrow 6p$ transitions.

4. Validity of atomic models. — Even with as elaborated models as RPAE and MBPT, in some cases, the agreement of theory with experiment is bad; it would be interesting to know whether the atomic model involved does not take into account the major correlation effects or the main features of the spectrum are not relevant to an atomic picture. With this purpose, we shall consider first the cases where the above models cannot interpret even the vapor spectra and secondly, these features of solid spectra which the atomic picture fails to reproduce.

4.1 Rare-Earths and Transition Metals. — Most of the calculations performed up to now with atomic models mentioned above concern these $nl$ subshells of atoms such as no $(n, l+1)$ electron is bound in the ground state configuration. However, as we have just discussed, they can be extended to those elements such as one $(n, l+1)$ electron is nearly bound, as it was the case for a $4f$ electron in Cs and Ba; it would be also the case for an $nl$ electron in these elements between the rare gases and the transition elements, i.e. just before the filling of an $nd$ subshell. This incomplete $4f$ subshell is at the origin of the failure of available atomic models to interpret the rare-earths spectra [44, 45, 46] in the $4d$ excitations region. However, there is a close similarity between these metal and vapor spectra, as shown recently for Ce by Wolff et al. [47], for Eu by Mansfield and Connerade [48]. These results support the earlier assumption of Dehmer et al. [49], resumed in calculations by Sugar [50] : $4d^{10} 4f^N \rightarrow 4d^9 4f^{N+1}$ transitions in solid rare-earths take place deep in ion cores, screened from their metallic surroundings. It is interesting to remark that nearly all the rare-earths spectra show a giant resonance like Cs, Ba, La, although the minor structures before this big peak are more numerous and spread over a larger energy range. Sugar [50] has calculated (intermediate coupling scheme) the multiplet splitting and relative oscillator strength for the $3p^6 3d^N \rightarrow 3p^5 3d^{N+1}$ in several neutral atoms of the first series transition elements. Unlike the $4d$-$4f$ transitions in rare-earths, few lines are intense but their positions correspond to the broad maximum shown by the experimental spectra, as we can see in figure 8 for manganese. This result supports the same interpretation as for rare-earths. i.e. the possibility of broadening of these discrete lines by autoionization of these excited states $3p^5 3d^{N+1}$ into the continuum $3p^5 3d^6$ $\alpha$d. But for nickel, Dietz et al. [57] have suggested the possibility
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4.2 Failure of the Atomic Picture. — As already mentioned, an atomic picture is not applicable to outer electrons which are very different in a solid, compared to an atom, since they are involved in the binding of the aggregate of atoms. For inner electrons, although the wave functions remain atomic in a solid, we must isolate the region just above the core level ionization threshold, when the photoelectron energy is small. Then, the core hole can be filled very fast in a solid, especially a metal: the photoelectron will be strongly perturbed, since it will be in a rather different field as compared to the free atom where the hole fills only after the photoelectron has left the atom. Such relaxation effects, related to the non-localization of the hole, give rise to some edge singularities which were discussed extensively, for instance by Nozieres and De Dominicis [59]. They remind us of those core relaxation and outer shells rearrangement effects mentioned above for the free atom; but the complexity of the solid requires other models, such as those based on semi-phenomenological model Hamiltonians.

Still near the threshold (but up to 20 eV above) some differences with the free atoms may occur, since the description of the outgoing photoelectron far from the nucleus is very different according to the boundary conditions used to normalize the continuum wave functions. For a free atom, these boundary conditions depend on a long range Coulomb field and for a solid, on a periodic field. Such deviations lead to a failure of the atomic picture to describe some strong shape resonances near the thresholds; they could be interpreted quantitatively only by taking into account the multiconfiguration behavior of the field experienced by the photoelectron at low energies. This is a point which could be cleared up with the recent results derived from molecular photoionization. Such new models could also help to interpret the modulation of the spectra with weak fine structure extending hundreds of volts above threshold and called EXAFS (extended X-Ray absorption fine structure); this effect was first explained by Kronig [60] as an interference between the outgoing wave of the photoelectron and the backscattered electron waves from the neighbours surrounding the excited atom.

5. Conclusions. — To summarize this review, we shall emphasize the success of atomic models to interpret the main features of absorption spectra in the low energy range: 10 to 350 eV. But we shall keep being cautious for interpretation of fine structures (near the thresholds) whose origin may be very different according to the spectrum: either atomic transitions broadened by autoionization as well as band structure effects, or excitonic structures (in insulators and semi-conductors) due to electron-hole interactions but whose starting point is often an atomic excitation, or edge singularities (in metals) which require the study of influence of the Fermi gas of conduction electrons in a metal on relaxation effects resulting when a core electron is excited. Getting both solid state and vapor spectra and using molecular photoionization models will certainly be of great help for the interpretation, in the near future.

References