

# Many-Electron Effects in the X-Ray Emission Spectra and the One-Particle Green's Function. Correspondence Theorem

Anatoly V. Kondratenko, Lev N. Mazalov, and Gennady F. Khudorozhko

Institute of Inorganic Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 90, USSR

Within the framework of reasonable approximation the intensity of spectral bands in the X-ray emission spectrum was shown to be proportional to the imaginary part of the one-particle Green's function. From this ensues a statement about a correspondence between the distribution of the intensity in the X-ray emission and photoelectron spectra – correspondence theorem.

**Key words:** X-ray spectra—many-electron effects—Green's function.

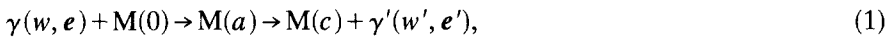
## 1. Introduction

The traditional methods of exciting X-ray emission (XE) spectra by radiation from an X-ray tube or by a high energy electron flow are such that the most intense lines in the spectra appear, as a rule, due to the transitions of electrons  $k \rightarrow x$  between the two orbitals  $k$  and  $x$ . The spectral emission lines connected with the one-electron transitions in the positive singly charged ion are usually referred to as the main or diagrammatic ones. They are fairly well treated in terms of different one-electron approximations, genealogically connected with the Hartree–Fock theory. As most of our ideas about chemical bonds lie within the framework of this theory, it is therefore clear why it is precisely one-electron transitions which are most actively used to investigate the electronic structure of substance [1, 2]. It is evident that the concept of pure one-electron transitions is an idealization. Many-electron effects influence the one-electron transitions over a certain range and, besides, cause many-electron ones. For instance, besides the diagrammatic lines such satellites as shake-up and shake-off may appear in X-ray emission spectra [3] after the analogy of photoelectron (PE) spectra [4].

For certain we shall speak about a molecule with completely occupied shells below. It is easy to see a close connection between the XE and the PE spectra of the molecule. In the XE spectra all transitions occur between many-electron states  $|s\rangle$  of the positive singly charged ion, the same states are terminating for the transitions from the ground state  $|0\rangle$  in the PE spectra (here we do not consider the so-called XE multiple ionization satellites) [5]. In practice this connection is effectively used to investigate the electronic structure of substance simultaneously by XE and PE spectroscopies [1, 2]. In the present paper the correspondence theorem will be proposed [6, 7] concerning the connection between the intensities of the bands in XE and PE spectra.

## 2. X-Ray Emission and the One-Particle Green's Function

XE radiation results from resonance fluorescence, in other words, from inelastic resonance scattering of the exciting X-ray photon by the molecule  $M$ . At the first stage of the fluorescence a transition of the molecule to a high-excited state  $|a\rangle$  occurs, the second stage is the disintegration of the intermediate state  $|a\rangle$  into the lower states  $|c\rangle$  with the emission of a new X-ray photon:



where  $\gamma(w, e)$  and  $\gamma'(w', e')$  are the exciting and emitted photons with the frequencies  $w$  and  $w'$ , and the polarization vectors  $e$  and  $e'$ , respectively;  $M(a)$ ,  $M(0)$ ,  $M(c)$  are the molecule  $M$  in the states  $|a\rangle$ ,  $|0\rangle$  and  $|c\rangle$  with the energies  $E_a$ ,  $E_0$ ,  $E_c$ , respectively. The cross section of the XE process (1) is described by the well-known Kramers–Heisenberg relation [8] (atomic units:  $\hbar = m = e = 1$ , are used in the paper):

$$d\sigma_{e_0}(w, w')/d\Omega' = \alpha^4 w w'^3 \left| \sum_a \frac{W'_{ca}{}^+ W_{a0}}{E_a - E_0 - w - i\gamma_a/2} \right|^2 \delta(E_0 + w - E_c - w'). \quad (2)$$

Here the summing-up is carried out over all states  $|a\rangle$  of the molecule including the continuous states;  $\alpha = 1/137.04$ ; the electromagnetic interaction operators

$$W = \mathbf{d} \cdot \mathbf{e} \quad \text{and} \quad W' = \mathbf{d} \cdot \mathbf{e}',$$

where  $\mathbf{d}$  is the dipole moment of the  $N$ -electron system of the molecule,  $d\Omega'$  is the spatial angle for the emitted photon  $\gamma'$ , and  $\gamma_a$  is the radiative width of the state  $|a\rangle$ . Furthermore let us use the second quantization where the above electromagnetic interaction operators are written as follows:

$$W = \sum_{nl} W_{nl} a_n^+ a_l, \quad \text{and} \quad W' = \sum_{nl} W'_{nl} a_n^+ a_l.$$

Here  $W_{nl} = \langle n | \mathbf{r} e | l \rangle$  and  $W'_{nl} = \langle n | \mathbf{r} e' | l \rangle$ ,  $a_n^+$  and  $a_n$  are the creation and annihilation operators for an electron in the Hartree–Fock one-particle states  $|n\rangle$ , obtained when calculating the ground state of the molecule. Now the full cross

section looks like this:

$$d\sigma(w, w')/d\Omega' = \alpha^4 w w'^3 \times \sum_c \left| \sum_a \frac{\langle c | \sum_{kl} W'_{ik} a_k^+ a_l | a \rangle \langle a | \sum_{op} W_{op} a_o^+ a_p | 0 \rangle}{E_a - E_0 - w - i\gamma_a/2} \right|^2 \delta(E_0 + w - E_c - w'). \quad (3)$$

By means of numerous transformations one is convinced that the cross section is expressed through the many-particle Green's function which is very difficult to deal with. Therefore, we shall make a number of simplifying assumptions:

Let us use the following known assumption for all high-excited states of the molecule involved in (5) [9, 10]:

$$\begin{aligned} |a\rangle &\cong A |e_a\rangle |r\rangle, \\ |c\rangle &\cong A |e_c\rangle |s\rangle, \end{aligned} \quad (4)$$

where  $|e_a\rangle$  and  $|e_c\rangle$  are the Hartree-Fock one-particle states of the photoelectron in continuum, and  $|r\rangle$  and  $|s\rangle$  are the exact states of the  $N-1$ -electron positive molecular ion,  $A$  is the antisymmetrization operator which we shall further omit for brevity. This approximation is valid in the high energy limits, i.e. in the case the photoelectron energy being rather high. Here we shall only be interested in such processes where there occurs the decay of such a state of the ion to which the state with a hole on the core (X-ray) orbital  $x$  corresponds within the framework of the Hartree-Fock theory. We shall mark such states as  $|x^{-1}\rangle$ . From the above there naturally ensues the validity of the following relations for the energies of the excited states:

$$E_a = E_0 + I_x + \varepsilon_a; \quad E_c = E_0 + I_s + \varepsilon_c, \quad (5)$$

where  $\varepsilon_a$  and  $\varepsilon_c$  are the PE energies in the continuum states  $|e_a\rangle$  and  $|e_c\rangle$ , and  $I_x, I_s$  are the ionization potentials of the states  $|x^{-1}\rangle$  and  $|s\rangle$ :

$$I_x \equiv E_{x^{-1}} - E_0; \quad I_s \equiv E_s - E_0.$$

In the high energy limits the following relations are approximately fulfilled as well:

$$\langle 0 | a_j^+ a_i | e_a \rangle | x^{-1} \rangle \cong \langle 0 | a_j^+ | x^{-1} \rangle \delta_{ie_a}. \quad (6)$$

Let us also assume that the following relations are rather well satisfied:

$$\begin{aligned} \sum_{kl} \langle c | a_k^+ a_l | a \rangle &\cong \sum_{kl} \langle s | \langle e_c | a_k^+ a_l | e_a \rangle | x^{-1} \rangle \\ &\cong \sum_{kl} \langle e_c | e_a \rangle \langle s | a_k^+ a_l | x^{-1} \rangle = \delta(\varepsilon_c - \varepsilon_a) \sum_{kl} \langle s | a_k^+ a_l | x^{-1} \rangle. \end{aligned} \quad (7)$$

Now with the help of the assumptions made the following chain of formulas for the cross-section of X-ray photon scattering naturally results:

$$d\sigma(w, w')/d\Omega' = \alpha^4 w w'^3 \sum_{se} \frac{\left| \sum_{klp} W'_{lk}{}^* W_{ep} \langle x^{-1} | a_p | 0 \rangle \langle s | a_k^+ a_l | x^{-1} \rangle \right|}{(I_x + \varepsilon - w)^2 + \Gamma^2/4} \times \delta(w - I_s - \varepsilon - w'), \quad (8)$$

where  $\Gamma$  stands for the full natural width of the state  $|x^{-1}\rangle$ . Let us introduce some rather more evident approximations:

$$\langle x^{-1} | a_p | 0 \rangle \cong \langle x^{-1} | a_x | 0 \rangle \delta_{px},$$

and

$$\begin{aligned} \langle x^{-1} | a_n^+ a_m | s \rangle &= \langle x^{-1} | \delta_{nm} - a_m a_n^+ | s \rangle \\ &\cong -\langle x^{-1} | a_m a_n^+ | s \rangle \cong \langle x^{-1} | a_x a_n^+ | s \rangle \delta_{mx} \text{ etc.} \end{aligned} \quad (9)$$

Thus the cross-section formula is simplified remarkably:

$$d\sigma(w, w')/d\Omega' = \frac{\alpha^4 w w'^3}{\pi} g_x(x^{-1}) \sum_e |W_{ex}|^2 \frac{1}{(I_x + \varepsilon - w)^2 + \Gamma^2/4} \times \sum_{ln} W'_{lx}{}^* W'_{nx} \text{Im } \tilde{G}_{ln}^A(-w + \varepsilon + w'), \quad (10)$$

where the notations  $g_k(s)$  are employed for so-called Feynman–Dyson amplitudes [11]

$$g_k(s) = |\langle s | a_k | 0 \rangle|^2.$$

Here  $\tilde{G}_{ln}^A$  is the approximate advanced one-particle Green's function

$$\tilde{G}_{ln}^A(y) \equiv \sum_s \frac{\langle \tilde{0} | a_n^+ | s \rangle \langle s | a_l | \tilde{0} \rangle}{y + I_s - i\eta}, \quad (11)$$

where  $|\tilde{0}\rangle$  is the approximate ground state of the molecule:

$$|\tilde{0}\rangle = a_x^+ |x^{-1}\rangle. \quad (12)$$

When deducing formula (10) the formal identity

$$\delta(y) = \frac{1}{\pi} \text{Im} \left( \frac{1}{-y - i\eta} \right),$$

was used, where  $\eta$  is the positive infinitesimal quantity.

Let us assume further that the function  $\text{Im } \tilde{G}_{ln}^A$  is equal approximately to the imaginary part of the respective advanced one-particle Green's function  $G_{ln}^A$  [10–13],

$$G_{ln}^A(y) \equiv \sum_s \frac{\langle 0 | a_n^+ | s \rangle \langle s | a_l | 0 \rangle}{y + I_s - i\eta}.$$

Thus we have shown that within the framework of reasonable assumptions made the XE cross-section is proportional to the imaginary part of the one-particle Green's function  $G_{ln}$  so long as  $\text{Im } G_{ln}^A(\varepsilon + w' - w) = \text{Im } G_{ln}(\varepsilon + w' - w)$  (since  $(\varepsilon + w' - w) < 0$ ,  $\text{Im } G_{ln}^R(\varepsilon + w' - w) = 0$  [10–12])

$$d\sigma(w, w')/d\Omega' = \frac{\alpha^4 w w'^3}{\pi} g_x(x^{-1}) \sum_e |W_{ex}|^2 \frac{1}{(I_x + \varepsilon - w)^2 + \Gamma^2/4} \times \sum_{ln} W_{lx}^* W'_{nx} \text{Im } G_{ln}(-w + \varepsilon + w'), \quad (13)$$

where

$$G_{ln}(y) \equiv G_{ln}^A(y) + G_{ln}^R(y) \equiv \sum_s \frac{\langle 0|a_n^+|s\rangle\langle s|a_l|0\rangle}{y + I_s - i\eta} + \sum_r \frac{\langle 0|a_k|r\rangle\langle r|a_l^+|0\rangle}{y + A_r + i\eta}, \quad (14)$$

where  $|r\rangle$  is the exact state of the negative  $N+1$ -electron ion and  $A_r$  is the electron affinity of this state:  $A_r \equiv E_0 - E_r$ . Eq. (13) has an advantage over more exact Eq. (10) thanks to the fact that there are rather well developed methods for calculating the Green's function  $G_{ln}$  in literature [10–13]. Moreover, Eq. (13) throws additional light on the connection between the XE and PE spectra. Really, in [9, 10] it was found that the photoionization cross-section is also proportional to the imaginary part of the one-particle Green's function:

$$d\sigma(w, \varepsilon)/d\varepsilon = 4\pi^2 \alpha^2 w \sum_{ent} W'^* W_{el} \text{Im } G_{ln}(\varepsilon - w) \delta(\varepsilon - \varepsilon_e), \quad (15)$$

where  $\varepsilon_e = w - I_s$  (it is Einstein's equation for photoeffect). Since in (13) and (15) the smooth functions of  $w'$  and  $\varepsilon$  precede the Green's functions, it is not difficult to make the important conclusion about the correspondence of the intensity distributions in the PE and XE spectra. This correspondence becomes particularly clear in the diagonal approximation for the Green's function ( $G_{ln} \equiv G_{ll}\delta_{ln}$ ):

$$d\sigma(w, w')/d\Omega' = \alpha^4 w w'^3 P_x(x^{-1}) \sum_{ks} \frac{|\langle w - I_s - w' | re | x \rangle|^2}{(w' + I_s - I_x)^2 + \Gamma^2/4} |\langle x | re' | k \rangle|^2 P_k(s), \quad (16)$$

$$d\sigma(w, \varepsilon)/d\varepsilon = 4\pi^2 \alpha^2 w \sum_{ks} |\langle w - I_s | re | k \rangle|^2 P_k(s) \delta(\varepsilon + I_s - w), \quad (17)$$

where the values  $P_k(s)$  are the pole strengths or the residues in the discrete poles  $z_s$  of the complex matrix Green's function  $G_{ln}(z)$  eigenvalues  $D_k(z)$  [10, 14]. In the diagonal approximation they are equal to Feynman–Dyson amplitudes  $g_k(s)$ . It should be noted that when obtaining Eqs. (16), (17) the one-particle continuous states  $|e\rangle$  were not for simplicity taken into account, in other words, we restricted ourselves to the summing-up only over the approximate bound ionic states  $|s\rangle$  in calculating the Green's function (14) ( $\text{Im } P_k(s) \equiv 0$  [14]). The influence of the continuum on the intermediate X-ray excited state  $|x^{-1}\rangle$  (Auger effect) was taken into account only by using in all the equations the full natural width  $\Gamma$  instead of the radiative width  $\gamma$  for this state. It is easy to understand that in

case  $k \notin F$ , where  $F$  is the set of occupied orbitals in the ground Hartree–Fock state,  $P_k(s) \equiv 0$ , and if  $k \in F$ , the following sum rule [10] is fair:

$$\sum_s P_k(s) = 1, \quad (18)$$

where the summing-up is carried out over all the states of the molecular positive ion. From Eqs. (16)–(18) one can readily make the following statements which we shall refer to the correspondence theorem [6, 7]:

1. In the XE spectrum, in the region where in the Hartree–Fock frozen orbital approximation only one main or diagrammatic line due to the one-electron transition  $k \rightarrow x$  is found, a whole band appears owing to all the possible many-electron transitions in the ion  $|x^{-1}\rangle \rightarrow |s\rangle$ .
2. The intensity distribution in this band coincides with that in the PE spectrum of the orbital  $k$ , the first being independent of the X-ray hole location or the orbital  $x$ , i.e. it is the same for the XE spectra of all the atoms and series (K, L, M etc.).
3. The total intensity of this band is equal to the intensity of the one-electron transition  $|k\rangle \rightarrow |x\rangle$  calculated in the Hartree–Fock frozen approximation. Figuratively, the many-electron transitions borrow their intensity from the one-electron one.

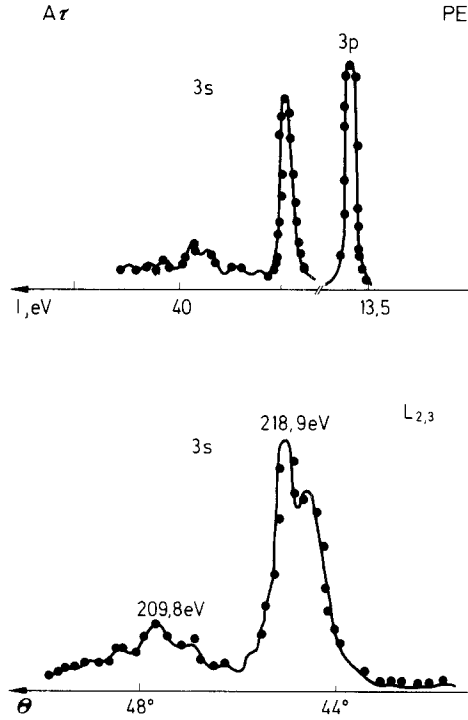
Note that it is an open question whether we may divide the XE band into a diagrammatic line corresponding to the one-electron transition and in to satellites such as shake-up or shake-off accompanying this line. For example, for the transitions from the upper valence orbitals with the ionization potentials 10–15 eV such a division can be made. But for the transitions from the innermost valence orbitals with the ionization potentials 15–50 eV it does not work because here all the transitions are substantially of a many-electron nature [15–21]. It is highly important that according to [10], the diagonal approximation for the matrix  $G_{in}$  is to a marked degree valid for the molecules consisting of the atoms of elements belonging to Periods I–III.

The correspondence theorem is visually interpreted [7] in terms of the set of standard statements of the sudden perturbation theory [3, 4, 7, 22–26]. The terminating states of the molecular ion  $|k^{-1}\rangle$  in the processes of photoionization  $k \rightarrow \varepsilon$  and resonance fluorescence  $x \rightarrow \varepsilon$ ,  $k \rightarrow x$  are the same. If we now consider these two processes to be sufficiently rapid ( $1/(2\varepsilon)^{1/2} \ll 1/I_s$  and  $1/(I_x - I_s) \ll 1/I_s$  [22]) then the probabilities of the subsequent exciting of all the possible ion states in the PE and XE spectra are identical and equal to  $\langle s | k_0^{-1} \rangle^2$ , where  $|k_0^{-1}\rangle$  is the “frozen” state with the hole on the orbital  $k$ :

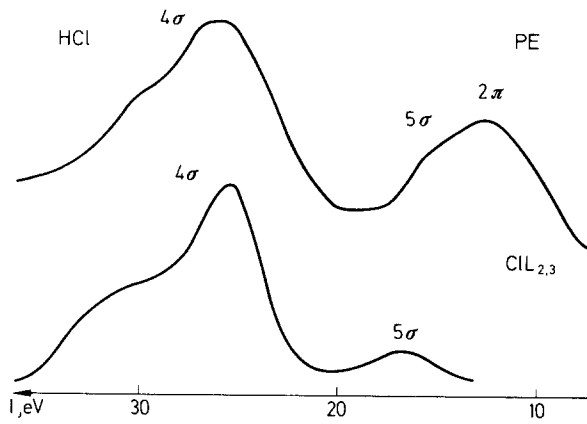
$$|k_0^{-1}\rangle = a_k |0\rangle.$$

### 3. Discussion

The experimental PE and XE  $L_{2,3}$  (the bands  $k \rightarrow \varepsilon$  and  $k \rightarrow 2p$  respectively) spectra of the atom Ar and the molecule HCl are presented in Figs. 1, 2. When



**Fig. 1.** Photoelectron [27] and X-ray emission  $L_{2,3}$  [28] spectra of the atom Ar;  $\theta$  is the Bragg's angle



**Fig. 2.** Photoelectron and X-ray emission Cl  $L_{2,3}$  [1] spectra of the molecule HCl

comparing the PE spectra with the XE ones it is necessary to bear in mind that all the lines in XE  $L_{2,3}$  spectra split into two components  $k \rightarrow 2p_{1/2}$  and  $k \rightarrow 2p_{3/2}$  due to the spin-orbital interaction, just what we can see in the case of the atom Ar  $L_{2,3}$  spectrum in Fig. 1. A comparison of the atom Ar (molecule HCl) PE band  $3s \rightarrow \epsilon$  ( $4\sigma \rightarrow \epsilon$ ) and the respective XE band  $3s \rightarrow 2p$  ( $4\sigma \rightarrow 2p$ ) intensity distribution shows them to be in semiquantitative agreement in accordance with the correspondence theorem.

The correspondence theorem may be of considerable practical significance. Thus, it enables one to calculate the total intensities in the one-electron model of even such bands which are many-electron ones by origin. As an example, the XE inner-most valence orbital spectra can be pointed out [20, 21]. Besides, by comparing the PE spectrum with the XE ones or XE spectra of different series among themselves one can by means of correspondence theorem, readily identify the multiple ionization satellites in the XE spectrum under discussion: there is no corresponding line in the PE or in any other XE spectrum.

Here it should be noted that the XE multiple ionization satellites can be removed from the experimental XE spectra using the photoelectron  $e(\varepsilon)$ -X-ray emitted photon  $\gamma'(w, e')$  coincidence technique [14, 29].

Interestingly, from formula (16) it immediately ensues that many-electron effects (relaxation and correlation), within the framework of the assumption made, reduce the intensity of the diagrammatic line  $k \rightarrow x$ . Moreover,  $P_k(k^{-1})$  is known to be approximately equal to 0,9 for the upper valence orbitals. Hence the many-electron effects do practically not influence the relative intensities of diagrammatic lines  $k \rightarrow x$  in XE spectra. This conclusion is confirmed by, e.g., the results of calculating the molecule HCl XE spectra [30] by Hartree-Fock method taking into account electron relaxation, i.e. the orbital reorganization under the action of the hole on one of the orbitals.

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