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Interpretation of $3d^N$-ion photoemission spectra. II. A general formalism for the core levels*

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The object of this paper is to provide a formalism for the interpretation of the core-level photoemission spectra of $3d^N$ ions embedded in a cubic environment. The formalism is first developed in the general case of the photoemission of a $n'l'$ electron from an inner shell of a nl^N ion in arbitrary symmetry G. This general formalism may be thought of as a coherent combination of the theory of level splitting (for the determination of the position of the core photopeaks) and of the theory of the photoemission intensity (for the determination of the intensity of the core photopeaks). The interactions taken into consideration here are the Coulomb, the spin-orbit, and the crystal-field interactions both for the photoemission initial Hamiltonian and the photoemission final Hamiltonian. General formulas for the matrix elements of the involved interactions are given for the initial configuration nl^N and the final configuration $n'l'^{4l'+1}nl^N$ in a weak-field basis adapted to the group G. The determination of the photopeak position follows from the diagonalization of the final Hamiltonian within the entire $n'l'^{4l'+1}nl^N$ manifold. The determination of the photopeak intensity requires the knowledge of the ground-state eigenvector of the initial Hamiltonian and of (all) the eigenvectors of the final Hamiltonian. General formulas are given for the intensity of the transitions $nl^N \rightarrow n'l'^{4l'+1}nl^N$ in a weak-field basis adapted to the group G. Finally, the general formalism is particularized to the case of iron-group ions ($nl \equiv 3d$) in octahedral symmetry ($G \equiv O$). Only those particular points which are specific to the case of $3d^N$ ions in octahedral symmetry are examined. In particular, the ejection process may concern the shells $n'l' \equiv n'p$ or $n'l' \equiv n's$.

I. INTRODUCTION

In the recent years, a considerable amount of both experimental and theoretical effort has gone into a renewed investigation of the physical and chemical structure of the iron-group ions in complexes and/or solids. This undoubtedly is due to the important role played by numerous iron-group compounds in technological applications. The photoemission spectroscopies (using ultraviolet, x-ray, or synchrotron radiation sources) may provide interesting experimental results, especially in regard to the electronic properties[1] so that great emphasis is placed today on the development of theoretical models for the interpretation of photoemission spectra. The first theoretical model for determining the photoemission cross sections is due to Cox.[2] His model concerns the calculation of the position and intensity of photopeaks appearing in the photoionization of d^N and f^N configurations. This pioneering work gave way to further developments and to applications, particularly in the case of the valence band for $3d^N$ oxides.[3,4] For its part, the present paper (the second of a series) mainly deals with the photoemission of a $n'l'(\equiv n's$ or $n'p)$ electron from an inner shell of a $3d^N$ ion embedded in a cubical environment and thus turns out to be a complementary part of a recently published paper[5] (hereafter referred to as Part I) devoted to the valence band of such an ion.

There are several approaches to the problem of the photoemission of an electron from an inner shell. The most general one lies on the theory of level splitting for the determination of the position of the photopeaks coherently combined with a specific treatment (an extension of the earlier work by Cox[2]) for the corresponding intensities. In such an approach, the structures observed in the photoemission spectra are interpreted as being due to electric dipole transitions from the ground state of the initial (before photoemission) configuration $n'l'^{4l'+2}3d^N$ to all the states of the final (after photoemission) configuration $n'l'^{4l'+1}3d^N$. Therefore, in principle, one can obtain the profile of an inner shell photoemission spectrum from the knowledge of (i) the initial state, (ii) the level splitting of the final configuration, and (iii) the final states. As a matter of fact, the position of the photopeaks follow from (ii) while (i) and (iii) are needed to make the usual formula for dipole cross sections work. However, the actual calculations are not so straightforward to conduct as it might appear at first glance. Indeed, the calculated position and intensity of the photopeaks drastically depend on the choice of the Hamiltonian to be diagonalized and on the subspaces spanned by the state vectors of the initial and final configurations. One is thus confronted with the alternative: either to choose a simplified Hamiltonian which neglects important interactions but proves to be quite simple to handle or to choose a more sophisticated Hamiltonian which involves the most relevant interactions but requires many parameters to be adjusted, with the associated dramatic dependence of the calculated photoemission shape on their determination. With a view of getting around the difficulty inherent to this alternative, the aim of this paper is twofold: first, to develop a formalism for the inner shell photoemission of a nl^N ion in arbitrary G symmetry and, second, to apply it to the case $nl \equiv 3d$ and $G \equiv O$.

The pattern will be as follows. Section II deals with the general case nl^N in G. The level splitting theory of partly filled shell(s) ions in external fields is adapted to the determination of the photoemission initial state and the photoemission final states, in Secs. II A and II B, respectively. A general treatment of the photoemission intensities is given in Sec. II C. Section III is devoted to the case $3d^N$ in octahedral symmetry. Only those aspects relative to the initial state, final states, and intensities which are particular to $3d^N$ in O are discussed with some detail in Secs. III A, III B, and III C, respectively.

II. CASE OF nl^N IN G

Before entering the subject of nl^N ions in arbitrary G symmetry, a word about the notation is in order. To avoid confusion in a problem where both electrons and holes are involved, we shall denote by l the electron and by $\bar{l}$ the corresponding hole. In addition, it will prove convenient to use the abbreviated form $nl^N n'\bar{l}'$ for $n'l'^{4l'+1}nl^N$ since close relationships exist between the configurations denoted by $nl^N n'l'$, $n\bar{l}^N n'l'$, $nl^N n'\bar{l}'$, and $n\bar{l}^N n'\bar{l}'$. The completely closed ($nl^{4l+2} \equiv n\bar{l}^0$) or completely empty ($nl^0 \equiv n\bar{l}^{4l+2}$) configurations will be specified only when necessary. All other notations and/or symbols will have their usual meaning.

A. Initial state

We start with the determination of the photoemission initial state $|i\rangle$. It is to be noted that $|i\rangle$ coincides with the ground state of the initial configuration nl^N.

In the case where the nl^N ion remains a sufficiently localized system when embedded in the crystalline environment, the most important interactions to be considered are the Coulomb interelectronic interaction $H_C(nl^N)$, the spin-orbit interaction $H_{so}(nl^N)$, and the crystal-field interaction $H_{cf}(nl^N)$. So that a realistic approximation for the initial Hamiltonian $H_i(nl^N)$ is written

$$H_i(nl^N) = H_C(nl^N) + H_{so}(nl^N) + H_{cf}(nl^N) \quad . \tag{1}$$

The matrix of $H_i(nl^N)$ within the nl^N manifold can be easily built up by using irreducible tensor methods. Among the various irreducible tensor methods, those methods that concern a chain of groups starting from O_3, the three-dimensional rotation group, and ending with G, the point symmetry group of the nl^N ion site, greatly simplify both the construction and the diagonalization of the energy matrix of $H_i(nl^N)$.[6,7] Furthermore, as far as we want to fully take advantage of classical tabulations[8-10] for the coefficients of fractional parentage and the reduced matrix elements of the Racah unit tensors, a weak-field basis adapted to the chain $O_3 \supset G$ (or to the associated chain of double groups) is the most suitable one from a practical point of view. (It is to be noted that the use of a weak-field basis does not necessarily imply a physical situation where the strength of the crystal-field is weak.) A typical state belonging to a weak-field basis adapted to the chain $O_3 \supset G$ is written $|nl^N \alpha SLJa\Gamma\gamma\rangle$ where Γ stands for an irreducible representations class (IRC) of G (or of its double group G^*), γ denotes a row index for Γ, and a is a multiplicity label indispensable when Γ occurs several times in J. (The identity IRC of G is specified by the notation Γ_0.) Combining the symmetry-adapted weak-field approach developed in Refs. 6 and 7 with Racah's methods,[8] each term in Eq. (1) is first expressed in a tensorial form adapted to $O_3 \supset G$. Second, the geometrical part associated with the group G is extracted from the matrix element of each component of $H_i(nl^N)$ in the $|nl^N \alpha SLJa\Gamma\gamma\rangle$ basis owing to the $O_3 \supset G$ Wigner-Eckart theorem. Third, the remaining part is decomposed in turn into coefficients of fractional parentage, standard reduced-matrix elements, and purely radial parameters. Hence, we get (see Ref. 11) (a) for the Coulomb interaction $H_C(nl^N)$:

$$\langle nl^N\alpha'S'L'J'a'\Gamma'\gamma'|H_C(nl^N)|nl^N\alpha SLJa\Gamma\gamma\rangle$$

$$\begin{aligned}
&=\delta(S'S)\delta(L'L)\delta(J'J)\delta(a'a)\delta(\Gamma'\Gamma)\delta(\gamma'\gamma)\frac{N(N-1)}{2}(2l+1)^2\\
&\times\sum_{\substack{k\alpha_1S_1L_1S_3L_3\\ \alpha_2S_2L_2\alpha_2'S_2'L_2'}}\langle l^{N-2}\alpha_1S_1L_1|\}l^{N-1}\alpha_2S_2L_2\rangle\langle l^{N-1}\alpha_2S_2L_2|\}l^N\alpha SL\rangle\\
&\qquad\times\langle l^{N-2}\alpha_1S_1L_1|\}l^{N-1}\alpha_2'S_2'L_2'\rangle\langle l^{N-1}\alpha_2'S_2'L_2'|\}l^N\alpha'SL\rangle(-1)^{L_3}\\
&\qquad\times(2S_3+1)(2L_3+1)[(2S_2+1)(2L_2+1)(2S_2'+1)(2L_2'+1)]^{1/2}\\
&\qquad\times\begin{Bmatrix}\frac{1}{2} & S & S_2\\ S_1 & \frac{1}{2} & S_3\end{Bmatrix}\begin{Bmatrix}\frac{1}{2} & S & S_2'\\ S_1 & \frac{1}{2} & S_3\end{Bmatrix}\begin{Bmatrix}l & L & L_2\\ L_1 & l & L_3\end{Bmatrix}\begin{Bmatrix}l & L & L_2'\\ L_1 & l & L_3\end{Bmatrix}\begin{Bmatrix}l & l & k\\ l & l & L_3\end{Bmatrix}\begin{pmatrix}l & k & l\\ 0 & 0 & 0\end{pmatrix}^2F^k(nl,nl)\ ,
\end{aligned}\tag{2}$$

(b) for the spin-orbit interaction $H_{\text{so}}(nl^N)$:

$$\langle nl^N\alpha'S'L'J'a'\Gamma'\gamma'|H_{\text{so}}(nl^N)|nl^N\alpha SLJa\Gamma\gamma\rangle$$

$$=\delta(J'J)\delta(a'a)\delta(\Gamma'\Gamma)\delta(\gamma'\gamma)(-1)^{S+L'+J}[l(l+1)(2l+1)]^{1/2}\begin{Bmatrix}S' & S & 1\\ L & L' & J\end{Bmatrix}(l^N\alpha'S'L'\|V^{11}\|l^N\alpha SL)\zeta_{nl}\ ,\tag{3}$$

(c) for the crystal-field interaction $H_{\text{cf}}(nl^N)$:

$$\langle nl^N\alpha'S'L'J'a'\Gamma'\gamma'|H_{\text{cf}}(nl^N)|nl^N\alpha SLJa\Gamma\gamma\rangle$$

$$\begin{aligned}
&=\delta(S'S)\delta(\Gamma'\Gamma)\delta(\gamma'\gamma)(-1)^{S+L+J'}[(2J+1)(2J'+1)]^{1/2}\sum_{ka_0}\begin{Bmatrix}J' & J & k\\ L & L' & S\end{Bmatrix}(l^N\alpha'S'L'\|U^k\|l^N\alpha SL)\\
&\qquad\times f\begin{pmatrix}J' & J & k\\ a'\Gamma\gamma & a\Gamma\gamma & a_0\Gamma_0\gamma_0\end{pmatrix}D[ka_0]_{nl}\ .
\end{aligned}\tag{4}$$

Equations (2)–(4) involve the Slater-Condon-Shortley parameters $F^k(nl,nl)$, the spin-orbit parameter ζ_{nl}, and the crystal-field parameters $D[ka_0]_{nl}$. All these parameters must be determined from *ab initio* calculations or fitting procedures. Equations (2)–(4) also involve standard reduced matrix elements $(\|U^k\|)$ and $(\|V^{11}\|)$ of the Racah unit tensors U^k and V^{11}, respectively, as well as coefficients of fractional parentage $\langle|\}\rangle$. For $l\equiv p$, d, and f, both the reduced matrix elements and the coefficients of fractional parentage may be taken from the tabulation by Nielson and Koster.[9] The coefficients ( ) and { } in Eqs. (2)–(4) are $3-jm$ and $6-j$ coefficients, respectively. There exist in current standard programs, in addition to the tables by Rotenberg *et al.*,[10] the means for calculating numerical values of $3-jm$ and $6-j$ symbols. Finally, the coefficient $f(\ )$ in Eq. (4) is a coupling coefficient adapted to the chain $O_3\supset G$ (or the associated chain of double groups), as defined in Ref. 7. Values of the f symbols in compact and/or table form are available for numerous groups G (or double groups G^*).[7,12]

The use of an $O_3\supset G$ symmetry-adapted basis allows us to arrange the matrix of $H_i(nl^N)$ into the direct sum of submatrices, each submatrix being associated with an IRC Γ of G (or G^*). Thus, we may classify the eigenvectors of $H_i(nl^N)$ (in addition to the associated eigenvalues W) with IRC's of G (or

G^*). The initial photoemission state $|i\rangle \equiv |nl^N W_i \Gamma_i \gamma_i\rangle$ we are looking for is then given by specializing ($W \equiv W_i$, $\Gamma \equiv \Gamma_i$, $\gamma \equiv \gamma_i$) the relation

$$|nl^N W\Gamma\gamma\rangle = \sum_{\alpha SLJa} \langle nl^N \alpha SLJa\Gamma\gamma | nl^N W\Gamma\gamma\rangle \times |nl^N \alpha SLJa\Gamma\gamma\rangle \ , \tag{5}$$

where the coefficients $\langle|\rangle$ are nothing but the matrix elements of the unitary transformation between the symmetry adapted weak-field state vectors $|nl^N\alpha SLJa\Gamma\gamma\rangle$ and the eigenvectors $|nl^N W\Gamma\gamma\rangle$.

B. Final states

When a hole $n'\overline{l'}$ is created by the photoemission of a $n'l'$ electron from an inner shell of the nl^N ion under consideration, three new interactions need to be added to the previously introduced ones, namely, the Coulomb interaction $H_C(nl^N,n'\overline{l'})$ between the N electrons nl and the hole $n'\overline{l'}$, the spin-orbit interaction $H_{\text{so}}(n'\overline{l'})$ for the hole $n'\overline{l'}$, and the crystal-field interaction $H_{\text{cf}}(n'\overline{l'})$ between the hole $n'\overline{l'}$ and the surrounding. We are thus left with the (more complex) final Hamiltonian

$$H_f(nl^N,n'\overline{l'}) = H_C(nl^N) + H_{\text{so}}(nl^N) + H_{\text{cf}}(nl^N) + H_C(nl^N,n'\overline{l'}) + H_{\text{so}}(n'\overline{l'}) + H_{\text{cf}}(n'\overline{l'}) \ , \tag{6}$$

the matrix of which has to be constructed within the (more complex) $nl^N n'\overline{l'}$ manifold. By making use of the complementary nature of electrons and holes, the matrix elements of $H_f(nl^N,n'\overline{l'})$ between the state vectors of the configuration $nl^N n'\overline{l'}$ can be related to the corresponding matrix elements of $H_f(nl^N,n'l')$, $H_f(n\overline{l}^N,n'l')$, and $H_f(n\overline{l}^N,n'\overline{l'})$ between the state vectors of the configurations $nl^N n'l'$, $n\overline{l}^N n'l'$, and $n\overline{l}^N n'\overline{l'}$, respectively. Especially, the matrices of $H_f(nl^N,n'\overline{l'})$ and $H_f(n\overline{l}^N,n'l')$ within the $nl^N n'\overline{l'}$ and $n\overline{l}^N n'l'$ manifold, respectively, are very similar[13,14]: The matrices for the Coulomb interaction appear to be the same apart from a constant term on the diagonals, while the matrices for the spin-orbit and the crystal-field interactions have opposite signs, viz.,

$$\begin{aligned}
&\langle nl^N(\alpha'S'L'),n'\overline{l'}(\tfrac{1}{2}l')S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_f(nl^N,n'\overline{l'})|nl^N(\alpha SL),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\quad = \langle n\overline{l}^N(\alpha'S'L'),n'l'(\tfrac{1}{2}l')S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_C(n\overline{l}^N) - H_{\text{so}}(n\overline{l}^N) - H_{\text{cf}}(n\overline{l}^N) \\
&\qquad + H_C(n\overline{l}^N,n'l') - H_{\text{so}}(nl') - H_{\text{cf}}(n'l')|n\overline{l}^N(\alpha SL),n'l'(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\qquad + \delta(\alpha'\alpha)\delta(S'S)\delta(L'L)\delta(S_1'S_1)\delta(L_1'L_1)\delta(J_1'J_1)\delta(a_1'a_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1) \\
&\qquad \times \Bigg[[2(2l'+1)(N-2l-1)+4l'(2l+1)]F^0(nl,n'l') \\
&\qquad + \sum_k (2l+1)^2(N-2l-1)[2\delta(k0)-(2l+1)^{-1}]\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 F^k(nl,nl) \\
&\qquad + \sum_k 2l'(2l'+1)^2[2\delta(k0)-(2l'+1)^{-1}]\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 F^k(n'l',n'l') \\
&\qquad + \sum_k [(2l'+1)(2l+1-N)-2l'(2l+1)]\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 G^k(nl,n'l') \Bigg] \ .
\end{aligned} \tag{7}$$

This clearly indicates that one can obtain with ease the matrix of $H_f(nl^N,n'\overline{l'})$ from that of $H_f(nl^{4l+2-N},n'l')$. The latter remark allows us to focus our attention on the configuration $nl^N n'l'$ and then to only consider $H_f(nl^N,n'l')$. Moreover, it proves convenient to use a basis for the final configuration $nl^N n'l'$ which resembles the one for the initial configuration nl^N with the aim of yielding as easy a calculation as possible of the photoemission transition intensities. In this respect, an $O_3 \supset G$ symmetry adapted weak-field basis with state vectors of the type $|nl^N(\alpha SL),n'l'(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle$ is the most suitable. The matrix elements of $H_f(nl^N,n'l')$ are therefore obtainable in a straightforward fashion by combining Racah's methods[8] with the $O_3 \supset G$ weak-field approach.[6,7] Hence, we get (see Ref. 11) (a) for the

Coulomb interaction $H_C(nl^N)$:

$$\langle nl^N(\alpha'S'L'),n'l'(\tfrac{1}{2}l')S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_C(nl^N)|nl^N(\alpha SL),n'l'(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle$$

$$=\delta(S'S)\delta(L'L)\delta(S_1'S_1)\delta(L_1'L_1)\delta(J_1'J_1)\delta(a_1'a_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1)\frac{N(N-1)}{2}(2l+1)^2$$

$$\times\sum_{\substack{k\alpha_2S_2L_2S_4L_4\\ \alpha_3S_3L_3\alpha_3'S_3'L_3'}}\langle l^{N-2}\alpha_2S_2L_2|\}l^{N-1}\alpha_3S_3L_3\rangle\langle l^{N-1}\alpha_3S_3L_3|\}l^N\alpha SL\rangle$$

$$\times\langle l^{N-2}\alpha_2S_2L_2|\}l^{N-1}\alpha_3'S_3'L_3'\rangle\langle l^{N-1}\alpha_3'S_3'L_3'|\}l^N\alpha'SL\rangle(-1)^{L_4}$$

$$\times(2S_4+1)(2L_4+1)[(2S_3+1)(2L_3+1)(2S_3'+1)(2L_3'+1)]^{1/2}$$

$$\times\left\{\begin{matrix}\frac{1}{2} & S & S_3\\ S_2 & \frac{1}{2} & S_4\end{matrix}\right\}\left\{\begin{matrix}\frac{1}{2} & S & S_3'\\ S_2 & \frac{1}{2} & S_4\end{matrix}\right\}\begin{Bmatrix}l & L & L_3\\ L_2 & l & L_4\end{Bmatrix}\begin{Bmatrix}l & L & L_3'\\ L_2 & l & L_4\end{Bmatrix}\begin{Bmatrix}l & l & k\\ l & l & L_4\end{Bmatrix}\begin{pmatrix}l & k & l\\ 0 & 0 & 0\end{pmatrix}^2F^k(nl,nl)\ , \qquad (8)$$

(b) for the spin-orbit interaction $H_{\text{so}}(nl^N)$:

$$\langle nl^N(\alpha'S'L'),n'l'(\tfrac{1}{2}l')\,S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{so}}(nl^N)|nl^N(\alpha SL),n'l'(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle$$

$$=\delta(J_1'J_1)\delta(a_1'a_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1)(-1)^{S'+L'+l'+1/2+2S_1+L_1+L_1'+J_1}$$

$$\times[l(l+1)(2l+1)(2S_1+1)(2L_1+1)(2S_1'+1)(2L_1'+1)]^{1/2}$$

$$\times\begin{Bmatrix}L_1 & L_1' & 1\\ S_1' & S_1 & J_1\end{Bmatrix}\left\{\begin{matrix}S_1 & S_1' & 1\\ S' & S & \frac{1}{2}\end{matrix}\right\}\begin{Bmatrix}L_1 & L_1' & 1\\ L' & L & l'\end{Bmatrix}(l^N\alpha'S'L'\|V^{11}\|l^N\alpha SL)\zeta_{nl}\ , \qquad (9)$$

(c) for the crystal-field interaction $H_{\text{cf}}(nl^N)$:

$$\langle nl^N(\alpha'S'L'),n'l'(\tfrac{1}{2}l')S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{cf}}(nl^N)|nl^N(\alpha SL),n'l'(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle$$

$$=\delta(S'S)\delta(S_1'S_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1)(-1)^{L'+l'+S_1+J_1'}[(2L_1+1)(2L_1'+1)(2J_1+1)(2J_1'+1)]^{1/2}$$

$$\times\sum_{ka_0}\begin{Bmatrix}L_1' & L_1 & k\\ L & L' & l'\end{Bmatrix}\begin{Bmatrix}J_1' & J_1 & k\\ L_1 & L_1' & S_1\end{Bmatrix}(l^N\alpha'S'L'\|U^k\|l^N\alpha SL)f\begin{pmatrix}J_1' & J_1 & k\\ a_1'\Gamma_1\gamma_1 & a_1\Gamma_1\gamma_1 & a_0\Gamma_0\gamma_0\end{pmatrix}D[ka_0]_{nl}\ , \qquad (10)$$

(a′) for the Coulomb interaction $H_C(nl^N,n'l')$:

$$\langle nl^N(\alpha'S'L'),n'l'(\tfrac{1}{2}l')S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_C(nl^N,n'l')|nl^N(\alpha SL),n'l'(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle$$

$$=\delta(S_1'S_1)\delta(L_1'L_1)\delta(J_1'J_1)\delta(a_1'a_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1)N(2l+1)(2l'+1)[(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2}$$

$$\times\sum_{\substack{k\alpha_2S_2L_2\\ S_3L_3}}(2S_3+1)(2L_3+1)\langle l^{N-1}\alpha_2S_2L_2|\}l^N\alpha SL\rangle\langle l^{N-1}\alpha_2S_2L_2|\}l^N\alpha'S'L'\rangle$$

$$\times\left\{\begin{matrix}\frac{1}{2} & S_1 & S\\ S_2 & \frac{1}{2} & S_3\end{matrix}\right\}\left\{\begin{matrix}\frac{1}{2} & S_1 & S'\\ S_2 & \frac{1}{2} & S_3\end{matrix}\right\}\begin{Bmatrix}l' & L_1 & L\\ L_2 & l & L_3\end{Bmatrix}\begin{Bmatrix}l' & L_1 & L'\\ L_2 & l & L_3\end{Bmatrix}$$

$$\times\left[(-1)^{L_3}\begin{Bmatrix}l & l' & L_3\\ l' & l & k\end{Bmatrix}\begin{pmatrix}l & k & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l' & k & l'\\ 0 & 0 & 0\end{pmatrix}F^k(nl,n'l')+(-1)^{S_3}\begin{Bmatrix}l & l' & L_3\\ l & l' & k\end{Bmatrix}\begin{pmatrix}l & k & l'\\ 0 & 0 & 0\end{pmatrix}^2G^k(nl,n'l')\right]\ , \qquad (11)$$

(b′) for the spin-orbit interaction $H_{\mathrm{so}}(n'l')$:

$$\langle nl^N(\alpha'S'L'),n'l'(\tfrac{1}{2}l')S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\mathrm{so}}(n'l')|nl^N(\alpha SL),n'l'(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle$$

$$= \delta(\alpha'\alpha)\delta(S'S)\delta(L'L)\delta(J_1'J_1)\delta(a_1'a_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1)(-1)^{S+L+l'+1/2+S_1+S_1'+J_1}$$

$$\times[l'(l'+1)(2l'+1)(2S_1+1)(2L_1+1)(2S_1'+1)(2L_1'+1)]^{1/2}$$

$$\times\begin{Bmatrix} L_1' & L_1 & 1 \\ S_1 & S_1' & J_1 \end{Bmatrix}\begin{Bmatrix} S_1' & S_1 & 1 \\ \frac{1}{2} & \frac{1}{2} & S \end{Bmatrix}\begin{Bmatrix} L_1' & L_1 & 1 \\ l' & l' & L \end{Bmatrix}(\tfrac{1}{2}l'\|v^{11}\|\tfrac{1}{2}l')\zeta_{n'l'}\ , \qquad (12)$$

(c′) for the crystal-field interaction $H_{\mathrm{cf}}(nl')$:

$$\langle nl^N(\alpha'S'L'),n'l'(\tfrac{1}{2}l')S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\mathrm{cf}}(n'l')|nl^N(\alpha SL),n'l'(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle$$

$$= \delta(\alpha'\alpha)\delta(S'S)\delta(L'L)\delta(S_1'S_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1)(-1)^{S_1+L_1+L_1'+J_1'+L+l'}$$

$$\times[(2L_1+1)(2L_1'+1)(2J_1+1)(2J_1'+1)]^{1/2}$$

$$\times\sum_{ka_0}\begin{Bmatrix} L_1' & L_1 & k \\ l' & l' & L \end{Bmatrix}\begin{Bmatrix} J_1' & J_1 & k \\ L_1 & L_1' & S_1 \end{Bmatrix}(l'\|u^k\|l')\, f\begin{pmatrix} J_1' & J_1 & k \\ a_1'\Gamma_1\gamma_1 & a_1\Gamma_1\gamma_1 & a_0\Gamma_0\gamma_0 \end{pmatrix}D[ka_0]_{n'l'}\ . \qquad (13)$$

Equations (8)−(13) can then be transformed to pass from the just considered Hamiltonian $H_f(nl^N,n'l')$ to the photoemission final Hamiltonian $H_f(nl^N,n'\overline{l'})$ owing to the aforementioned remark [cf. Eq. (7)]. The so-transformed equations involve the Slater-Condon-Shortley parameters $F^k(nl,nl)$, $F^k(n'l',n'l')$, $F^k(nl,n'l')$, and $G^k(nl,n'l')$, the spin-orbit parameters ζ_{nl} and $\zeta_{n'l'}$, and the crystal-field parameters $D[ka_0]_{nl}$ and $D[ka_0]_{n'l'}$. Here again all these parameters must be determined from *ab initio* calculations or fitting procedures. The various other ingredients in the transformed equations bear the same significance as in Eqs. (2)−(4).

In exactly the same way as for the initial Hamiltonian $H_i(nl^N)$, the use of an $O_3 \supset G$ symmetry adapted basis makes it possible to label the eigenvectors of $H_f(nl^N,n'\overline{l'})$ (in addition to the associated eigenvalues W_f) with IRC's of G (or G^*), a fact of considerable importance for the calculation of the photoemission intensities. The eigenvalues W_f directly give the position of the photopeaks while the eigenvectors $|nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f\rangle$ serve to construct the photoemission final states. To be more explicit, the eigenvectors $|nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f\rangle$ can be expressed in terms of the symmetry adapted weak-field state vectors $|nl^N(\alpha SL),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_1\gamma_1\rangle$ as

$$|nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f\rangle = \sum_{\substack{\alpha SL \\ S_1L_1J_1a_1}} \langle nl^N(\alpha SL),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_f\gamma_f|nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f\rangle|nl^N(\alpha SL),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_f\gamma_f\rangle\ , \qquad (14)$$

where the coefficients $\langle\ ,\ |\ \rangle$ are obtained from the diagonalization of $H_f(nl^N,n'\overline{l'})$. Then, a given photoemission final state $|f\rangle$ corresponds to the coupling of a given eigenvector $|nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f\rangle$ with a state $|C\rangle$ of the continuum into which the photoemitted electron $n'l'$ is raised, i.e.,

$$|f\rangle \equiv |nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f\rangle \otimes |C\rangle\ . \qquad (15)$$

C. Intensities

After having found the eigenvector $|nl^NW_i\Gamma_i\gamma_i\rangle$ of $H_i(nl^N)$ which describes the photoemission initial state $|i\rangle$, the eigenvalues W_f of $H_f(nl^N,n'l')$ which provide an estimate of the photopeak position, and the eigenvectors $|nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f\rangle$ of $H_f(nl^N,n'\overline{l'})$ which are necessary for constructing the photoemission final states $|f\rangle$, the next step is to deal with the photoemission transitions themselves.

The determination of the photoemission intensities for the core levels depends exactly on the same first principles as for the valence band.[4,5] Hence, we start from the general formula (cf. Part I)

$$I(i\rightarrow f)=\sum_{m_i m_f}|N_i^{1/2}\langle f|T|i\rangle|^2\ , \tag{16}$$

which gives the (relative) intensity $I(i\rightarrow f)$ of the transition $i\rightarrow f$ via the operator T. In Eq. (16), N_i denotes the number of electrons of the initial level concerned with the transition, so that in our case we have $N_i=4l'+2$. The labels m_i and m_f are to be used when the degeneracies of the levels i and f are greater than 1, so that in our case we have $m_i=\gamma_i$ and $m_f=\gamma_f$.

In view of preparing the calculation below, it is convenient as a first step to express the photoemission initial state $|i\rangle$ in a form paralleling the one obtained for the photoemission final state $|f\rangle$. This may be achieved by introducing the completely closed shell $n'l'^{4l'+2}\equiv n'\overline{l'}^{0}$ into $|i\rangle$. Thus, we have

$$|i\rangle\equiv|nl^N n'\overline{l'}^{0}W_i\Gamma_i\gamma_i\rangle\ . \tag{17}$$

Therefore, the initial state vector $|i\rangle$ can be regarded as resulting from the coupling of all the state vectors $|nl^N n'\overline{l'}W_f\Gamma_f\gamma_f\rangle$ of the configuration $nl^N n'\overline{l'}$ with all the state vectors $|n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2\rangle$ of the outgoing electron $n'l'$. More precisely, we have

$$|i\rangle=\sum_{\substack{W_f\Gamma_f\gamma_f\\ J_2a_2\Gamma_2\gamma_2}}\langle nl^N n'\overline{l'}W_f\Gamma_f\gamma_f,n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2|nl^N n'\overline{l'}^{0}W_i\Gamma_i\gamma_i\rangle|nl^N n'\overline{l'}W_f\Gamma_f\gamma_f\rangle\otimes|n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2\rangle\ . \tag{18}$$

Equations (15) and (18) allow us to specialize the starting formula [Eq. (16)] as

$$I(nl^N W_i\Gamma_i\rightarrow nl^N n'\overline{l'}W_f\Gamma_f)$$
$$=\sum_{\gamma_i\gamma_f}\left|\sum_{J_2a_2\Gamma_2\gamma_2}(4l'+2)^{1/2}\langle nl^N n'\overline{l'}W_f\Gamma_f\gamma_f,n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2|nl^N n'\overline{l'}^{0}W_i\Gamma_i\gamma_i\rangle\langle C|T|n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2\rangle\right|^2\ . \tag{19}$$

The coupling coefficient $\langle,\ |\rangle$ in Eq. (19) may be developed with the help of Eqs. (5) and (14). This yields

$$I(nl^N W_i\Gamma_i\rightarrow nl^N n'\overline{l'}W_f\Gamma_f)$$
$$\begin{aligned}=\sum_{\gamma_i\gamma_f}\Bigg|\sum_{\substack{J_2a_2\Gamma_2\gamma_2\\ \alpha SLJa\alpha'S'L'\\ S_1L_1J_1a_1}}&(4l'+2)^{1/2}\langle nl^N n'\overline{l'}W_f\Gamma_f\gamma_f|nl^N(\alpha'S'L'),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_f\gamma_f\rangle\\ &\times\langle nl^N\alpha SLJa\Gamma_i\gamma_i|nl^N W_i\Gamma_i\gamma_i\rangle\\ &\times\langle nl^N(\alpha'S'L'),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_f\gamma_f\ ;\\ &\times n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2|nl^N(\alpha SL),n'\overline{l'}^{0}({}^1S)SLJa\Gamma_i\gamma_i\rangle\langle C|T|n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2\rangle\Bigg|^2\ .\end{aligned} \tag{20}$$

The next step consists, as in the case of the valence band,[5] to transfer to operators the properties first thought of as being characteristics of state vectors by using second quantization techniques. Then, the coupling coefficient $\langle;\ |\rangle$ in Eq. (20) becomes

$$\langle nl^N(\alpha'S'L'),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_f\gamma_f;n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2|nl^N(\alpha SL),n'\overline{l'}^{0}({}^1S)SLJa\Gamma_i\gamma_i\rangle$$
$$=(-1)^{J-J_1-J_2}(4l'+2)^{-1/2}f\begin{pmatrix}J & J_1 & J_2\\ a\Gamma_i\gamma_i & a_1\Gamma_f\gamma_f & a_2\Gamma_2\gamma_2\end{pmatrix}^*$$
$$\times(nl^N(\alpha'S'L'),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1\|a^{(l'/2)J_2}\|nl^N(\alpha SL),n'\overline{l'}^{0}({}^1S)SLJ)\ , \tag{21}$$

where the reduced matrix element $(\| \ \|)$ of the annihilation operator $a^{(l'/2)J_2}$ can be obtained from the master formula

$$
\begin{aligned}
&(n_1l_1^{N_1}(\alpha_1'S_1'L_1'),n_2l_2^{N_2-1}(\alpha_2'S_2'L_2')S_3'L_3'J_3' \| a^{(l_2/2)J_2} \| n_1l_1^{N_1}(\alpha_1S_1L_1),n_2l_2^{N_2}(\alpha_2S_2L_2)S_3L_3J_3)\\
&\qquad = \delta(\alpha_1'\alpha_1)\delta(S_1'S_1)\delta(L_1'L_1)(-1)^{S_1+L_1+S_2'+L_2'+S_3'+L_3'+N_2}\\
&\qquad\quad \times[N_2(2S_2+1)(2L_2+1)(2S_3+1)(2L_3+1)(2J_3+1)(2S_3'+1)(2L_3'+1)(2J_3'+1)(2J_2+1)]^{1/2}\\
&\qquad\quad \times \langle l_2^{N_2-1}\alpha_2'S_2'L_2' \| \} l_2^{N_2}\alpha_2S_2L_2\rangle \begin{Bmatrix} S_3' & \frac{1}{2} & S_3\\ S_2 & S_1 & S_2' \end{Bmatrix} \begin{Bmatrix} L_3' & l_2 & L_3\\ L_2 & L_1 & L_2' \end{Bmatrix} \begin{Bmatrix} S_3' & S_3 & \frac{1}{2}\\ L_3' & L_3 & l_2\\ J_3' & J_3 & J_2 \end{Bmatrix} . \qquad (22)
\end{aligned}
$$

In the case being studied, Eq. (22) specializes to

$$
\begin{aligned}
&(nl^N(\alpha'S'L'),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1 \| a^{(l'/2)J_2} \| nl^N(\alpha SL),n'\overline{l'}^{0}({}^1S)SLJ)\\
&\qquad = \delta(\alpha'\alpha)\delta(S'S)\delta(L'L)[(2S_1+1)(2L_1+1)(2J_1+1)(2J_2+1)(2J+1)]^{1/2} \begin{Bmatrix} S_1 & S & \frac{1}{2}\\ L_1 & L & l'\\ J_1 & J & J_2 \end{Bmatrix} . \qquad (23)
\end{aligned}
$$

It is then a simple matter to calculate $I(nl^NW_i\Gamma_i \rightarrow nl^Nn'\overline{l'}W_f\Gamma_f)$ by collecting together all the above results. Thus, the combination of Eqs. (20), (21), and (23) leads to the final expression

$$
\begin{aligned}
&I(nl^NW_i\Gamma_i \rightarrow nl^Nn'\overline{l'}W_f\Gamma_f)\\
&\quad = \sum_{\gamma_i\gamma_f} \Bigg| \sum_{\substack{J_2a_2\Gamma_2\gamma_2\\ \alpha SLJa\\ S_1L_1J_1a_1}} \langle nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f | nl^N(\alpha SL),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_f\gamma_f\rangle\\
&\qquad\qquad \times \langle nl^N\alpha SLJa\Gamma_i\gamma_i | nl^NW_i\Gamma_i\gamma_i\rangle(-1)^{J-J_1-J_2}\\
&\qquad\qquad \times[(2S_1+1)(2L_1+1)(2J_1+1)(2J_2+1)(2J+1)]^{1/2}\\
&\qquad\qquad \times \begin{Bmatrix} S_1 & S & \frac{1}{2}\\ L_1 & L & l'\\ J_1 & J & J_2 \end{Bmatrix} f\begin{pmatrix} J & J_1 & J_2\\ a\Gamma_i\gamma_i & a_1\Gamma_f\gamma_f & a_2\Gamma_2\gamma_2 \end{pmatrix}^{*} \langle C|T|n'l'(\tfrac{1}{2}l')J_2a_2\Gamma_2\gamma_2\rangle \Bigg|^2 . \qquad (24)
\end{aligned}
$$

The just derived photoemission intensity formula [Eq. (24)] involves the transformation coefficients

$$\langle nl^N\alpha SLJa\Gamma_i\gamma_i | nl^NW_i\Gamma_i\gamma_i\rangle$$

and

$$\langle nl^N(\alpha SL),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_f\gamma_f | nl^Nn'\overline{l'}W_f\Gamma_f\gamma_f\rangle$$

which arise from the diagonalization of $H_i(nl^N)$ and $H_f(nl^N,n'\overline{l'})$, respectively (cf. Secs. II A and II B). These coefficients give an account of the mixing of the state vectors of the configurations nl^N and $nl^Nn'\overline{l'}$ under the action of $H_i(nl^N)$ and $H_f(nl^N,n'\overline{l'})$, respectively. Equation (24) also involves the monoelectronic transition amplitude $\langle C|T|n'l'(\frac{1}{2}l')J_2a_2\Gamma_2\gamma_2\rangle$ between a state vector of the outgoing electron and a state density of the continuum. Needless to say *ab initio* calculation of such an amplitude is far from easy. Indeed, in actual calculations we may consider, at least in a first approximation, the various transition amplitudes $\langle C|T|n'l'(\frac{1}{2}l')J_2a_2\Gamma_2\gamma_2\rangle$ as independent of $J_2a_2\Gamma_2\gamma_2$. With this approximation disposed of, the transition amplitudes $\langle C|T|n'l'(\frac{1}{2}l')J_2a_2\Gamma_2\gamma_2\rangle$ may be taken to be equal to 1 in the relative intensity formula [Eq. (24)]. Finally, the selection rules of the transitions between the (pure) symmetry adapted weak-field state vectors

$$|nl^N\alpha SLJa\Gamma_i\gamma_i\rangle$$

and

$$|nl^N(\alpha SL),n'\overline{l'}(\tfrac{1}{2}l')S_1L_1J_1a_1\Gamma_f\gamma_f\rangle \otimes |C\rangle$$

via the operator T clearly appear in Eq. (24) from the product of the $9-j$ coefficient $\{\ \}$ with the coefficient $f(\ )^*$: the product $\{\ \}f(\ )^*$ is zero if one of the six triads (S_1,L_1,J_1), $(\frac{1}{2},l',J_2)$, (S,L,J), $(S_1,\frac{1}{2},S)$, (L_1,l',L), and (J_1,J_2,J) does not satisfy the triangular rules or if the IRC Γ is not contained in the internal Kronecker product $\Gamma_1 \otimes \Gamma_2$.

III. CASE OF $3d^N$ IN O

In order to facilitate subsequent applications of the formalism developed in Sec. II to the case of iron-group ions ($l \equiv d$) in octahedral symmetry ($G \equiv O$), we now discuss those aspects which are particular to $3d^N$ in O.

A. Initial state

In accordance with the usual practice, the matrix elements of the Coulomb interaction $H_C(3d^N)$ are written in terms of the Racah parameters A, B, and C.[6,8] In the same vein, the matrix elements of the crystal-field interaction $H_{\text{cf}}(3d^N)$ are usually parametrized in terms of the Schlapp and Penney parameter $10Dq$ when the symmetry is cubic. This parameter is connected to the parameter $D[4]_{3d}$, which corresponds to the general parameter $D[ka_0]_{nl}$ of Sec. II A, by

$$Dq = D[4]_{3d}/(6\sqrt{30}) \ . \tag{25}$$

Appropriate values of the parameters A, B, C, ζ_{3d}, and Dq necessary for diagonalizing the photoemission initial Hamiltonian $H_i(3d^N)$ may be actually determined from experimental data (e.g., absorption spectra data) scattered in the literature. Another possibility may be to assume the Racah parameters A, B, and C to have values resulting from self-consistent-field calculations.[15] In this case, a good agreement between theory and experiment is generally reached when the self-consistent-field values are brought down by a factor β ($\beta \sim 20\%$ for divalent $3d^N$ ions), the so-called nephelauxetic factor.[16]

To close this section, it is perhaps worthwhile to note that Eqs. (2)–(4) may be worked out only for $N \leqslant 5$ when applied to $3d^N$. In fact, the complementary nature of electrons and holes enables us to pass from the $3d^N$ configuration to the $3d^{10-N}$ ($\equiv 3\bar{d}^N$) configuration owing to the following correspondence rules (a) for the Coulomb interaction $H_C(3d^N)$:

$$\begin{aligned}\langle 3d^N v'S'L'J'a'\Gamma'\gamma' | H_C(3d^N) | 3d^N vSLJa\Gamma\gamma\rangle &\\ = \langle 3d^{10-N} v'S'L'J'a'\Gamma'\gamma' | H_C(3d^{10-N}) | 3d^{10-N} vSLJa\Gamma\gamma\rangle &\\ +\delta(v'v)\delta(S'S)\delta(L'L)\delta(J'J)\delta(a'a)\delta(\Gamma'\Gamma)\delta(\gamma'\gamma)(N-5)(9A-14B+7C) \ , &\end{aligned} \tag{26}$$

(b) for the spin-orbit interaction $H_{\text{so}}(3d^N)$:

$$\langle 3d^N v'S'L'J'a'\Gamma'\gamma' | H_{\text{so}}(3d^N) | 3d^N vSLJa\Gamma\gamma\rangle = -\langle 3d^{10-N} v'S'L'J'a'\Gamma'\gamma' | H_{\text{so}}(3d^{10-N}) | 3d^{10-N} vSLJa\Gamma\gamma\rangle \ , \tag{27}$$

(c) for the crystal-field interaction $H_{\text{cf}}(3d^N)$:

$$\langle 3d^N v'S'L'J'a'\Gamma'\gamma' | H_{\text{cf}}(3d^N) | 3d^N vSLJa\Gamma\gamma\rangle = -\langle 3d^{10-N} v'S'L'J'a'\Gamma'\gamma' | H_{\text{cf}}(3d^{10-N}) | 3d^{10-N} vSLJa\Gamma\gamma\rangle \ . \tag{28}$$

In Eqs. (26)–(28), the well-known seniority number v introduced by Racah for nd^N configurations replaces the general label α of Sec. II.

B. Final states

We now consider the photoemission of a $n'l'$ electron from an inner shell of a $3d^N$ ion in octahedral symmetry. We shall confine ourselves to the cases $n'l' \equiv n's$ and $n'p$ which are among the most relevant ones for $3d^N$ ions photoemission purposes. It is then immediate from Eqs. (12) and (13) that $H_{\text{so}}(n'\bar{s}) = 0$ and $H_{\text{cf}}(n'\bar{s}) = H_{\text{cf}}(n'\bar{p}) = 0$, respectively. Concomitantly with the matrix elements of $H_C(3d^N)$ in terms of the parameters A, B, and C (cf. Sec. III A), the matrix elements of $H_C(3d^N,n's)$ are commonly written in terms of the parameters $F_0(3d,n's)$ and $G_2(3d,n's)$.[17] Similarly, the matrix elements of $H_C(3d^N,n'\bar{p})$ are more conveniently written in terms of the parameters $F_0(3p,n'p)$, $F_2(3p,n'p)$, $F_0(3d,n'p)$, $F_2(3d,n'p)$, $G_1(3d,n'p)$, and $G_3(3d,n'p)$.[8,17–20] The (relative) positions of the photopeaks thus depend on five parameters $[B,C,G_2(3d,n's), \zeta_{3d}, Dq]$ for the photoemission of a $n's$ electron and on eight parameters $[B,C,F_2(3d,n'p), G_1(3d,n'p), G_3(3d,n'p), \zeta_{3d}, \zeta_{n'p}, Dq]$ for the photoemission of a $n'p$ electron. In this regard, self-consistent calculations may provide useful starting values for the various involved interelectronic and spin-orbit parameters.

Finally, to pass from the matrices of $H_f(3d^N,n's)$ and $H_f(3d^N,n'p)$ obtainable from Eqs. (8)–(13), to the desired matrices of $H_f(3d^N,n'\bar{s})$ and

$H_f(3d^N,n'\bar{p})$, respectively, it is sufficient to specialize Eq. (7). This yields (a) for the Coulomb interaction:

$$\begin{aligned}
&\langle 3d^N(v'S'L'),n's(^2S)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_C(3d^N)+H_C(3d^N,n's)|3d^N(vSL),n's(^2S)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\quad=\langle 3d^{10-N}(v'S'L'),n's(^2S)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_C(3d^{10-N}) \\
&\qquad+H_C(3d^{10-N},n's)|3d^{10-N}(vSL),n's(^2S)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\qquad+\delta(v'v)\delta(S'S)\delta(L'L)\delta(S_1'S_1)\delta(L_1'L_1)\delta(J_1'J_1)\delta(a_1'a_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1) \\
&\qquad\times(N-5)[9A-14B+7C+2F_0(3d,n's)-G_2(3d,n's)]\ , \qquad (29)
\end{aligned}$$

and

$$\begin{aligned}
&\langle 3d^N(v'S'L'),n'p^5(^2P)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_C(3d^N)+H_C(n'p^5)+H_C(3d^N,n'p^5)|3d^N(vSL),n'p^5(^2P)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\quad=\langle 3d^{10-N}(v'S'L'),n'p(^2P)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_C(3d^{10-N})+H_C(3d^{10-N},n'p)|3d^{10-N}(vSL),n'p(^2P)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\quad+\delta(v'v)\delta(S'S)\delta(L'L)\delta(S_1'S_1)\delta(L_1'L_1)\delta(J_1'J_1)\delta(a_1'a_1)\delta(\Gamma_1'\Gamma_1)\delta(\gamma_1'\gamma_1) \\
&\qquad\times(N-5)[9A-14B+7C+6F_0(3d,n'p)-6G_1(3d,n'p)-63G_3(3d,n'p)] \\
&\quad+10F_0(n'p,n'p)-20F_2(n'p,n'p)+20F_0(3d,n'p)-20G_1(3d,n'p)-210G_3(3d,n'p)\ , \qquad (30)
\end{aligned}$$

(b) for the spin-orbit interaction:

$$\begin{aligned}
&\langle 3d^N(v'S'L'),n's(^2S)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{so}}(3d^N)|3d^N(vSL),n's(^2S)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\quad=-\langle 3d^{10-N}(v'S'L'),n's(^2S)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{so}}(3d^{10-N})|3d^{10-N}(vSL),n's(^2S)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle\ , \qquad (31)
\end{aligned}$$

and

$$\begin{aligned}
&\langle 3d^N(v'S'L'),n'p^5(^2P)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{so}}(3d^N)+H_{\text{so}}(n'p^5)|3d^N(vSL),n'p^5(^2P)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\quad=-\langle 3d^{10-N}(vSL),n'p(^2P)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{so}}(3d^{10-N})+H_{\text{so}}(n'p)|3d^{10-N}(vSL),n'p(^2P)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle\ , \qquad (32)
\end{aligned}$$

(c) for the crystal-field interaction:

$$\begin{aligned}
&\langle 3d^N(v'S'L'),n's(^2S)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{cf}}(3d^N)|3d^N(vSL),n's(^2S)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\quad=-\langle 3d^{10-N}(v'S'L'),n's(^2S)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{cf}}(3d^{10-N})|3d^{10-N}(vSL),n's(^2S)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle\ , \qquad (33)
\end{aligned}$$

and

$$\begin{aligned}
&\langle 3d^N(v'S'L'),n'p^5(^2P)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{cf}}(3d^N)|3d^N(vSL),n'p^5(^2P)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle \\
&\quad=-\langle 3d^{10-N}(v'S'L'),n'p(^2P)S_1'L_1'J_1'a_1'\Gamma_1'\gamma_1'|H_{\text{cf}}(3d^{10-N})|3d^{10-N}(vSL),n'p(^2P)S_1L_1J_1a_1\Gamma_1\gamma_1\rangle\ . \qquad (34)
\end{aligned}$$

C. Intensities

We have seen in the general case [cf. Eq. (24)] how the selection rules for the $9-j$ and f symbols control those for the photoemission transitions between the pure symmetry adapted weak-field state vectors. In this respect, the particular case $n'l'\equiv n's$ deserves special attention. Indeed, one of the arguments of the $9-j$ symbol is zero in this case so that the $9-j$ symbol reduces to a $6-j$ symbol up to a multiplicative factor. Hence, for the photoemission of a $n's$ electron Eq. (21) is written

$$\begin{aligned}
&\langle 3d^N(vSL),n's(^2S)S_1L_1J_1a_1\Gamma_f\gamma_f;n's(^2S)J_2a_2\Gamma_2\gamma_2|3d^NvSLJa\Gamma_i\gamma_i\rangle \\
&\quad=\delta(L_1L)\delta(J_2\tfrac{1}{2})\delta(\Gamma_2E')(-1)^{S_1+L+J_1+1}\begin{Bmatrix} J & S & L \\ S_1 & J_1 & \tfrac{1}{2}\end{Bmatrix}[(2S_1+1)(2J_1+1)(2J+1)/2]^{1/2}f\begin{pmatrix} J & J_1 & \tfrac{1}{2} \\ a\Gamma_i\gamma_i & a_1\Gamma_f\gamma_f & E'\gamma_2\end{pmatrix}^*\ ,
\end{aligned}$$

(35)

where the $6-j$ symbol may be calculated from the following formulas:

$$\begin{aligned}
\begin{Bmatrix} J & S & L \\ S-\frac{1}{2} & J-\frac{1}{2} & \frac{1}{2} \end{Bmatrix} &= (-1)^{S+L+J}\left[\frac{(L+S+J+1)(J+S-L)}{2S(2S+1)2J(2J+1)}\right]^{1/2} , \\
\begin{Bmatrix} J & S & L \\ S-\frac{1}{2} & J+\frac{1}{2} & \frac{1}{2} \end{Bmatrix} &= (-1)^{S+L+J}\left[\frac{(L+S-J)(L+J-S+1)}{2S(2S+1)(2J+1)(2J+2)}\right]^{1/2} , \\
\begin{Bmatrix} J & S & L \\ S+\frac{1}{2} & J-\frac{1}{2} & \frac{1}{2} \end{Bmatrix} &= (-1)^{S+L+J}\left[\frac{(L+J-S)(L+S-J+1)}{(2S+1)(2S+2)2J(2J+1)}\right]^{1/2} , \\
\begin{Bmatrix} J & S & L \\ S+\frac{1}{2} & J+\frac{1}{2} & \frac{1}{2} \end{Bmatrix} &= (-1)^{S+L+J+1}\left[\frac{(L+S+J+2)(J+S-L+1)}{(2S+1)(2S+2)(2J+1)(2J+2)}\right]^{1/2} .
\end{aligned} \tag{36}$$

For the photoemission of a $n'p$ electron no simplification arises and the general expression given by Eq. (24) has to be considered.

D. Concluding remarks

At this point, it is necessary to establish a connection between the formalism developed here for the core levels and the formalism developed in the first part[5] of this series for the valence band. One may ask why the strong-field formalism[21–23] was adopted in Part I in contradistinction with the weak-field formalism employed in the present work. Indeed, the reason for using the strong-field formalism in the description of the valence-band photoemission spectra of first-row transition-metal ions in cubic symmetry is twofold. First, the strong-field formalism mostly parallels the physical situation $H_{\mathrm{cf}}(3d^N) > H_C(3d^N) >> H_{\mathrm{so}}(3d^N)$. Thus, it is clear that the physical adequacy of the strong-field formalism may provide a useful starting point for an approximation procedure as, for example, a truncation of the Hamiltonian [cf. $H_{\mathrm{so}}(3d^N)=0$ in Part I] or of the basis in the framework of a perturbation approach. Second, from a physical viewpoint it is realistic to assume that the threefold degenerate subshell t_2 and the twofold degenerate subshell e, between which the N electrons of the configuration $3d^N$ are shared, are not spanned merely by pure d-metal orbitals but rather by linear combinations of metal and ligand orbitals. Such an assumption makes it possible to take into account covalency effects in a simple way by using the Koide-Pryce model,[5] a model based upon the strong-field formalism. Therefore, the description of the valence band of $3d^N$ complexes naturally calls upon the strong-field formalism.

We may now briefly examine the complications that would arise when using the strong-field formalism in the description of the core levels. For the photoemission initial configuration $3d^N$, a typical state vector in the strong-field basis would be

$$|t_2^{N_1}(S_1\Gamma_1)e^{N-N_1}(S_2\Gamma_2)S_3\Gamma_3\beta\Gamma\gamma\rangle ,$$

where $S_1\Gamma_1(S_2\Gamma_2)$ specifies the spin and orbital parts of a state of the configuration $t_2^{N_1}(e^{N-N_1})$, $S_3\Gamma_3$ specifies the total spin and orbital parts of a state of the configuration $t_2^{N_1}e^{N-N_1}$, and Γ is obtained from the coupling of S_3 and Γ_3. The construction of the matrix of $H_i(3d^N)$ within the strong-field basis is less easy to achieve than within a symmetry adapted weak-field basis since, on the one hand, the quantum numbers L and J do not appear in the strong-field states, and on the other hand, the coefficients of fractional parentage, the V (or $3-\Gamma\gamma$), W (or $6-\Gamma$), and X (or $9-\Gamma$) symbols for the (not simply reducible) group O^* are not so well standardized than the corresponding quantities for the (simply reducible) group SU_2.[24–27] Nevertheless, the strong-field matrix elements of $H_i(3d^N)$ are now available for any d^N configuration although within various notations and phase conventions.[21–23,28–33] To treat the photoemission final configuration $3d^Nn'\overline{l'}$ on the same footing as the initial one, we should consider in the strong-field formalism the coupling of three configurations, namely, the previously discussed configurations $t_2^{N_1}$ and e^{N-N_1}, and the configuration $\bar{a}_1$ or $\bar{t}_1$ according to whether as $n'l'\equiv n's$ or $n'l'\equiv n'p$. For the photoemission final configuration $3d^Nn'\overline{l'}$, a typical state vector in the strong-field basis would be then

$$|t_2^{N_1}(S_1\Gamma_1)e^{N-N_1}(S_2\Gamma_2)S_3\Gamma_3,\bar{a}_1(^2A_1)S_4\Gamma_3\beta\Gamma\gamma\rangle$$

if $n'l' \equiv n's$ or

$$|t_2^{N_1}(S_1\Gamma_1)e^{N-N_1}(S_2\Gamma_2)S_3\Gamma_3,\bar{t}_1(^2T_1)S_4\Gamma_4\beta\Gamma\gamma\rangle$$

if $n'l' \equiv n'p$. Of course, the construction of the matrices of $H_f(3d^N,n'\bar{s})$ and $H_f(3d^N,n'\bar{p})$ within the strong-field basis would be a rather formidable task (cf. Refs. 23 and 34). This clearly justifies our choice to use a (symmetry adapted) weak-field basis in our treatment of the core levels. In addition, in spite of the fact that the explicit introduction of covalency effects is hardly possible with such a basis, the spin-orbit interactions $H_{so}(3d^N)$ and $H_{so}(n'\bar{p})$, which turn out to be more relevant than the covalency effects in the case of the core levels, may be restored [cf. Eqs. (3), (9), and (12)] without any difficulty in a symmetry adapted weak-field basis.

To end up with the connection between the core levels and the valence band it is to be emphasized that the photoemission initial state is the same in the ejection of a valence-band electron or of an inner-shell electron. As a consequence, it is necessary at some level of the numerical applications to transform the photoemission initial-state vector from the strong-field coupling scheme to the weak-field coupling scheme or conversely. Along this line, the equivalence between the generalized strong-field model and the generalized symmetry adapted weak-field model recently investigated by two of us[35] may provide some useful information.

To close this paper, some comments about previous works dealing with similar subjects are in order. As already mentioned in the Introduction, the present study as well as Part I take their origin in the work by Cox[2] on the intensities of photoemission transitions of type $nl^N \rightarrow nl^{N-1}$ for $l=d$ and f. In Ref. 2, the intensities are calculated in the strong-field coupling scheme (including mainly H_C and H_{cf}) for $l=d$ and in the Russell-Saunders coupling scheme (including mainly H_C and H_{so}) for $l=d$ and f. Furthermore, it is assumed in both coupling schemes that the photoemission initial state and the photoemission final states only consist of pure (strong-field or Russell-Saunders) state vectors. In this respect, our contribution here and in Part I essentially concerns a more realistic description of the involved Hamiltonians and the consideration of the mixing, under the action of the various interactions considered, between the relevant (strong-field or weak-field) state vectors. Finally, we have also to mention the work by Gupta and Sen[36] that is devoted to the calculation of the position and the intensity of the photopeaks corresponding to the transitions $3d^5(^6S) \rightarrow 3d^5 3\bar{p}(^5P \text{ or } ^7P)$. The peculiarity of the configuration $3d^5$ and the severe truncation of the final Hamiltonian $H_f(3d^5,3p)$ allow them to take a pure (Russell-Saunders) initial state and to consider a limited set of final states. Another important difference between their specific treatment and the general formalism presented here is the absence of a geometrical factor of the form $\{\ \}f(\ )^*$ [cf. Eq. (24)] in their intensity calculation.

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