# Calculation of multiplet structure of core p-vacancy levels

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The multiplet splittings of core p-vacancy levels have recently been observed in various transition-metal complexes and in some rare-earth as well as actinide complexes. This paper presents the calculation of the multiplet structure of core p-vacancy levels in the Hartree-Fock free-ion approximation. The spin-orbit and crystal-field effects have been included. The cases studied are  $Mn^{2+}$  in  $MnF_2$  and the free ion  $Fe^{3+}$ . For 3p vacancies these effects appear to be unimportant from the point of view of photoelectron spectroscopy owing to the limited resolution of the technique. For 2p vacancies the spin-orbit interaction is comparable to the electrostatic interaction between the electrons and both the interactions must be considered simultaneously. The conclusion is that the x-ray photoelectron spectra of inner-core electrons are more suitable for chemical analysis than those of outer electrons which, in addition, contain large correlation and many-body effects.

#### I. INTRODUCTION

X-ray photoelectron spectroscopy has been used extensively and successfully for studying the corevacancy energy levels of atoms in free and compounded states. The measurement of shifts in the energy levels provides information about the average change in the environment of an atom. Recently some investigations<sup>1-8</sup> have been made on the structure of core-vacancy energy levels by using x-ray photoelectron spectroscopy. The interpretation of s-vacancy level splitting is based essentially on the difference of electrostatic exchange interaction of spin-up and spin-down possible states of the vacancy with the unpaired valence-shell electrons. Bagus et al.<sup>9</sup> have incorporated the effect of correlation and showed it to be of great significance in explaining the 3s-vacancy observations in 3d-transition-metal complexes. The simple exchange-interaction mechanism so useful for *s* vacancies is rather inadequate for p vacancies.<sup>1, 10</sup>

The *p* hole can couple with various *parent* terms of the ion giving more than two *final* terms with the same orbital and spin angular momenta as would be obtained by the coupling of the *p* hole with the ground-state term only. It is then necessary to consider all final terms since the eigenstates will be linear combinations of the final terms having the same orbital and spin angular momenta. Further, it is desirable<sup>9</sup> to include those other than ground-state configurations of the ion which form appropriate final terms. Before considering configuration interaction, it appears appropriate to treat the ground-state configuration as completely as possible.

The purpose of this paper is to treat the groundstate configuration  $p^5 d^5$  including spin-orbit and crystal-field effects. The atomic systems considered are MnF<sub>2</sub> and FeF<sub>3</sub>. In these compounds the transition-metal atoms are almost wholly ionic, Mn<sup>2+</sup> and Fe<sup>3+</sup>, both having ground-state configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ . Theoretically their treatment is the same. However, the difference in the atomic numbers of Mn and Fe results in the difference of energy and intensity of multiplet lines between the two ions, thereby showing an expected trend within the framework of the theory. The energy spread of *p*-vacancy multiplet spectra for  $Mn^{2+}$  is smaller than for Fe<sup>3+</sup>. Inclusion of only spin-orbit interaction for the 2p vacancy gives only two energies, whereas inclusion also of two-electron electrostatic interaction gives seven main eigenvalues with consecutive energy separations of more than 1 eV. Calculation of multiplet structure of p holes gives information about the width and intensity of the observed peaks in the photoelectron spectra.

The term structure of the  $p^5 d^5$  configuration, in conformation with the requirement of this work, is considered in Sec. II. The effect of spin-orbit interaction is treated in Sec. III, and the crystalfield effect is taken up in Sec. IV. Section V deals with the intensity of multiplet levels in the observed photoelectron spectra. Section VI gives the results of the calculations for  $Mn^{3+}$  in  $MnF_2$  and for Fe<sup>4+</sup>, and the conclusions of the work.

## **II. ELECTROSTATIC INTERACTION**

The ground-state configuration of  $Mn^{2*}$  and  $Fe^{3*}$ ions is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ . Slater<sup>11</sup> has tabulated the terms possible in this configuration. Out of all the terms possible, <sup>6</sup>S is the term with lowest energy. Removal of a *p* electron leaves the ion in the  $p^5 d^5$  configuration plus the closed shells. The configuration  $p^5 d^5$  is complementary to the  $pd^5$ configuration. Coupling of the <sup>6</sup>S term with a *p* electron can give <sup>7</sup>P and <sup>5</sup>P terms. However, the <sup>5</sup>P term can also be obtained by coupling of the *p*  The perturbed Hamiltonian of the ion after a p electron is removed could be written as

 $H=H_0+\sum_d \frac{1}{\mathcal{V}_{pd}} ,$ 

where  $H_0$  is the unperturbed Hamiltonian of the ground-state configuration  $d^5$ , and the second term is the electrostatic interaction between the p electron and all the d electrons. In order to find the relative eigenvalues and eigenvectors corresponding to the three  ${}^{5}P$  terms one has to consider all possible matrix elements of  $\sum_{d} (1/r_{bd})$  between the three unperturbed wave functions  ${}^{5}P({}^{6}S(d^{5}),p)$ ,  ${}^{5}P({}^{4}P(d^{5}),p)$ , and  ${}^{5}P({}^{4}D(d^{5}),p)$ . Since the  ${}^{7}P$  term could only be obtained from  $\binom{6}{S(d^5)}$ , p), all nondiagonal matrix elements  $\langle {}^{7}P | \sum_{d} (1/r_{pd}) | {}^{5}P \rangle$  are zero, and  $\langle {}^{7}P | \sum_{d} (1/r_{pd}) | {}^{7}P \rangle$  is the eigenvalue while  ${}^{7}P({}^{6}S(d^{5}),p)$  is the eigenfunction for the single  ${}^{7}P$ term. To find the eigenvalues and eigenvectors corresponding to the three  ${}^{5}P$  terms a  $3 \times 3$  matrix of the type  $\langle {}^{5}P | \sum_{d} (1/r_{pd}) | {}^{5}P' \rangle$  is constructed and diagonalized. Slater<sup>11</sup> has tabulated diagonal and nondiagonal matrix elements for the  $pd^5$  configuration and the results could be obtained easily for Mn<sup>3+</sup> and Fe<sup>4+</sup> in the configuration  $p^5 d^5$ . It should be noted that in going from the  $pd^5$  to  $p^5d^5$  configuration, the only change occurs in the sign of nondiagonal matrix elements

$$\langle {}^{5}P({}^{6}S(d^{5}),p) | \sum_{d} \frac{1}{r_{pd}} | {}^{5}P({}^{4}P(d^{5}),p) \rangle$$

and

$$\langle {}^{5}P({}^{4}P(d^{5}),p) | \sum_{d} \frac{1}{r_{pd}} | {}^{5}P({}^{4}D(d^{5}),p) \rangle ,$$

but this does not lead to any change in either the eigenvalues or the eigenvectors of the three  ${}^5P$  terms.<sup>11</sup>

#### **III. SPIN-ORBIT INTERACTION**

The spin-orbit interaction could be written as<sup>11</sup>

$$\sum \gamma_i (\vec{1}_i \cdot \vec{s}_i)$$

The index *i* runs over all the electrons in the incomplete shells, and  $\gamma_i$  is given by

$$\gamma_i = \frac{1}{2} \alpha^2 \langle Z_{fi}(r)/r^3 \rangle_i$$
.

The quantity  $\alpha$  is the fine-structure constant  $(=\frac{1}{137})$ .  $Z_{fi}(r)$  is the effective charge seen by the electron *i* when it is at a radial distance *r* from the nucleus:

$$Z_{fi}(r) = Z - \int_0^r \sum_{j \neq i} u_{n_j l_j}^{\prime 2}(r') dr'$$

where  $u_{n_j l_j}^{\prime 2}(r)$  is r times the radial part of the wave function of the electron j.

It is convenient to start with the parent configuration  $d^5$ , for which the matrix elements of the spinorbit interaction could easily be calculated using Racah's formulation<sup>11</sup>:

$$\begin{split} \langle \alpha L_2 S_2 J_2 M_2 \Big| \sum_{a} \gamma_d (\vec{1} \cdot \vec{s})_d \Big| \alpha' L_2' S_2' J_2' M_2' \rangle \\ &= (-1)^{S_2 \star L_2' \cdot J_2} \gamma_d (30)^{1/2} \langle \alpha L_2 S_2 \| V^{11} \| \alpha' L_2' S_2' \rangle \\ &\times W(L_2 S_2 L_2' S_2'; J_2 1) \delta_{J_2 J_2'} \delta_{M_2 M_2'} \quad . \end{split}$$

Here  $|_{\alpha}L_{2}S_{2}J_{2}M_{2}\rangle$  is a state of the configuration  $d^{5}$ .  $\langle_{\alpha}L_{2}S_{2}||V^{11}||_{\alpha}'L'_{2}S'_{2}\rangle$  is the reduced matrix element of the double tensor operator  $V^{11}_{1rq} = \sum_{d} s_{r}^{(1)}(d)u_{q}^{(1)}(d)$ , with  $s_{r}^{(1)}$  and  $u_{q}^{(1)}$  as the unit tensor operators following Racah, where  $s_{r}^{(1)}$  operates only on the spin part and  $u_{q}^{(1)}$  operates only on the orbital part of the one-electron wave function. W is the Racah coefficient. The reduced matrix elements are zero unless  $(L_{2}, L'_{2}, 1)$  and  $(S_{2}, S'_{2}, 1)$  form triangles.

In order to calculate the matrix elements of the spin-orbit interaction between the states of the configuration  $pd^5$  one first obtains the states  $|_{\alpha}LSJM\rangle$  by coupling  $|_{\alpha}L_2S_2J_2M_2\rangle$  with the states  $|l_1s_1j_1m_1\rangle$  of the p electrons<sup>12</sup>:

$$\left| \alpha LSJM \right\rangle = \sum_{j_1 j_2} \overline{X}(l_1 s_1 j_1; L_2 S_2 J_2; LSJ) \sum_{m_1} C(j_1 J_2 J; m_1, M - m_1) \left| l_1 s_1 j_1 m_1 \right\rangle \left| \alpha L_2 S_2 J_2 M - m_1 \right\rangle,$$
(2)

where

$$\overline{X}(l_1s_1j_1; L_2S_2J_2; LSJ) = [(2j_1+1)(2J_2+1)(2L+1)(2S+1)]^{1/2}X(l_1s_1j_1; L_2S_2J_2; LSJ) ,$$

with X as the Wigner 12-*j* symbol, and C the Clebsch-Gordan coefficient. The matrix elements of the spinorbit interaction are then

$$\langle \alpha LSJM | [\gamma_{p}(\vec{1}_{p} \cdot \vec{s}_{p}) + \gamma_{d}(\vec{L}_{d} \cdot \vec{s}_{d})] | \alpha' L'S'J'M' \rangle$$
  
-  $\sum_{j_{1}j_{2}} \overline{X}(l_{1}s_{1}j_{1}; L_{2}S_{2}J_{2}; LSJ) \sum_{j_{1}'j_{2}'} \overline{X}(l_{1}'s_{1}'j_{1}'; L_{2}'S_{2}'J_{2}'; L'S'J') \sum_{m_{1}} C(j_{1}J_{2}J; m_{1}, M-m_{1})$ 

$$\times \sum_{m_{1}'} C(j_{1}'J_{2}'J'; m_{1}', M' - m_{1}') [\langle l_{1}s_{1}j_{1}m_{1} | \gamma_{p}(\vec{l}_{p} \cdot \vec{s}_{p}) | l_{1}'s_{1}'j_{1}'m_{1}' \rangle \langle \alpha L_{2}S_{2}J_{2}M - m_{1} | \alpha' L_{2}'S_{2}'J_{2}'M' - m_{1}' \rangle$$
  
+  $\langle l_{1}s_{1}j_{1}m_{1} | l_{1}'s_{1}'j_{1}'m_{1}' \rangle \langle \alpha L_{2}S_{2}J_{2}M - m_{1} | \gamma_{d}(\vec{L}_{d} \cdot \vec{s}_{d}) | \alpha' L_{2}'S_{2}'J_{2}'M' - m_{1}' \rangle ].$  (3)

The matrix elements of the operator  $(\overline{1\cdot s})$  are nonzero only between the states having same j and m, i.e.,  $j_1 = j'_1, J_2 = J'_2, m_1 = m'_1, M - m_1 = M' - m'_1$ , and therefore M = M' and J = J'. Since the matrix elements are independent of m, one could choose M = M' = 0 and obtain

$$\langle \alpha LSJ0 | [\gamma_{p}(\vec{l}_{p} \cdot \vec{s}_{p}) + \gamma_{d}(\vec{L}_{d} \cdot \vec{S}_{d})] | \alpha'L'S'J0 \rangle = \sum_{j_{1}J_{2}} \vec{X} \langle l_{1}s_{1}j_{1}; L_{2}S_{2}J_{2}; LSJ \rangle \vec{X} \langle l_{1}'s_{1}'j_{1}; L_{2}'S_{2}'J_{2}; L'S'J \rangle$$

$$\times \sum_{m_{1}} C^{2} \langle j_{1}J_{2}J; m_{1}, -m_{1} \rangle [ \langle l_{1}s_{1}j_{1}m_{1} | \gamma_{p}(\vec{l}_{p} \cdot \vec{s}_{p}) | l_{1}'s_{1}'j_{1}m_{1} \rangle \delta_{\alpha\alpha'} \delta_{L_{2}L_{2}'} \delta_{S_{2}}s_{2}' + (-1)^{S_{2}+L_{2}'-J_{2}} \gamma_{d} \langle 30 \rangle^{1/2}$$

$$\times \langle \alpha L_{2}S_{2} | V^{11} | | \alpha'L_{2}'S_{2}' \rangle W \langle L_{2}S_{2}L_{2}'S_{2}'; J_{2}1 \rangle \delta_{l_{1}l_{1}'} \delta_{s_{1}s_{1}'} ] .$$

$$(4)$$

Here  $\gamma_p(\mathbf{l}_p \circ \mathbf{s}_p)$  is a single-electron operator and  $|l_1s_1j_1m_1\rangle$  are single-electron states. The first term on the right-hand side is zero unless  $l'_1 = l_1$  and  $s'_1 = s_1$ . Since  $\langle l_1s_1j_1m_1 | \gamma_p(\mathbf{l}_p \cdot \mathbf{s}_p) | l_1s_1j_1m_1 \rangle$  is same for all values of  $m_1$ , one can put  $\sum_{m_1} C^2(j_1J_2J, m_1, -m_1) = 1$ . Now

$$\langle l_1 s_1 j_1 m_1 | \gamma_p (\vec{l}_p \cdot \vec{s}_p) | l_1 s_1 j_1 m_1 \rangle$$
  
=  $\frac{1}{2} \gamma_p [ j_1 (j_1 + 1) - l_1 (l_1 + 1) - s_1 (s_1 + 1) ] ,$ 

while the reduced matrix elements  $\langle \alpha L_2 S_2 || V^{11} || \alpha' L'_2 S'_2 \rangle$  for the  $d^5$  configuration are available from the literature.<sup>11,13</sup> The coefficients W and X could be obtained from the tables<sup>14</sup> or calculated. The knowledge of the radial wave functions<sup>15</sup> enables one to compute  $\gamma_p$  and  $\gamma_d$ . Equation (4) then gives all the matrix elements of the spin-orbit interaction for the configuration  $pd^5$ . However, our interest is in the configuration  $p^5 d^5$ , and it can be easily verified<sup>16</sup> that the only change in going from the  $pd^5$  to  $p^5 d^5$  configuration is the change of sign of the first term in the right-hand side of Eq. (4).

# IV. CRYSTAL-FIELD INTERACTION

The crystal-field operator could be written as<sup>17</sup>

$$\sum_{k} \sum_{q=-k}^{k} A_{k}^{q} \sum_{i} r_{i}^{k} Y_{k}^{q}(\theta_{i}, \phi_{i})$$
$$\equiv \sum_{k} \sum_{q=-k}^{k} A_{k}^{q} \left[ T_{q}^{k}(p) + \sum_{d} T_{q}^{k}(d) \right],$$

where  $A_k^q$  are the crystal-field parameters,  $\gamma_k^q(\theta,\phi)$ are the spherical harmonics, and the index *i* runs over the electrons in incomplete shells. The crystal-field tensor operator is independent of spin, and therefore its operation on a state cannot change the spin of the state. The matrix elements of the tensor operator  $A_k^q [T_q^k(p) + \sum_d T_q^k(d)]$  between the *j*-*j* coupled states of Sec. III are<sup>18</sup>

$$\langle \alpha LSJM \left| A_{k}^{q} \left[ T_{q}^{k}(p) + \sum_{d} T_{d}^{k}(d) \right] \right| \alpha' L'SJ'M' \rangle$$

$$= (-1)^{J-M} A_{k}^{q} \langle \alpha LSJ \left| \left| \left[ T^{k}(p) + \sum_{d} T^{k}(d) \right] \right| \left| \alpha' L'SJ' \rangle \right.$$

$$\times V(\frac{JJ'k}{-MM'q}) .$$

$$(5)$$

Here  $\overline{V}$  are related to Wigner 3-*j* symbols by a phase factor.<sup>18</sup> The reduced matrix elements could be written as

$$\langle \alpha LSJ \left\| \left[ T^{k}(p) + \sum_{d} T^{k}(d) \right] \right\| \alpha' L'SJ' \rangle$$

$$= (-1)^{L+S+J'+k} \langle \alpha L \left\| \left[ T^{k}(p) + \sum_{d} T^{k}(d) \right] \right\| \alpha' L' \rangle$$

$$\times [(2J+1)(2J'+1)]^{1/2} \overline{W} ( {}^{JJ'k}_{L'LS} ), \qquad (6)$$

where

$$\overline{W}(_{def}^{abc}) = (-1)^{a+b+d+e} W(abed; cf)$$

The reduced matrix elements  $\langle \alpha L \| [T^{k}(p) + \sum_{d} T^{k}(d)] \| \alpha' L' \rangle$  could be further reduced by realizing that  $| \alpha L \rangle$  are obtained by coupling  $|l_{1}\rangle$  with  $| \alpha L_{2} \rangle$ :

$$\langle \alpha L \left\| \left[ T^{k}(p) + \sum_{d} T^{k}(d) \right] \right\| \alpha' L' \rangle \equiv \langle l_{1}, \alpha L_{2}, L \right\| \left[ T^{k}(p) + \sum_{d} T^{k}(d) \right] \right\| l_{1}', \alpha' L_{2}', L' \rangle$$

$$= (-1)^{l_{1}+l_{2}+L'+k} \langle l_{1} \| T^{k}(p) \| l_{1}' \rangle [(2L+1)(2L'+1)]^{1/2} \overline{W} (\frac{LL'}{l_{1}'l_{1}L_{2}}) \delta_{\alpha\alpha'} \delta_{L_{2}L_{2}'} + (-1)^{l_{1}+l_{2}+L'+k}$$

$$\times \langle \alpha L_{2} \| \sum_{d} T^{k}(d) \| \alpha' L_{2}' \rangle [(2L+1)(2L'+1)]^{1/2} \overline{W} (\frac{LL'}{l_{2}L_{2}l_{1}}) \delta_{l_{1}l_{1}'} .$$

$$(7)$$

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Analysis of this expression shows immediately the following simplifications: The first term is non-zero only for k = 0 and k = 2, since  $l_1 = l'_1 = 1$ . The second term is zero for k > 4. The cases under consideration have L = L' = 1 and  $\overline{W}$  is nonzero only for k < 2. One is therefore left with the calculation of reduced matrix elements  $\langle l_1 || T^k(p) || l_1 \rangle$  and  $\langle \alpha L_2 || \sum_d T^k(d) || \alpha' L'_2 \rangle$  for k < 2.

The reduced matrix elements  $\langle l_1 || T^k || l_1 \rangle$  could be evaluated directly:

$$\langle l_{1} \| T^{k} \| l_{1} \rangle$$

$$- \langle r^{k} \rangle_{p} \langle l_{1} \| Y^{k} \| l_{1} \rangle$$

$$= \langle r^{k} \rangle_{p} (-1)^{k+l} (2l_{1}+1) [(2k+1)/4\pi]^{1/2} \overline{V} (l_{0}^{l_{1}} l_{0}^{k} l_{1}^{l_{1}}).$$
(6)

The reduced matrix elements  $\langle \alpha L_2 \| \sum_d T^k \| \alpha' L_2' \rangle$ could be written in terms of unit tensor operator  $U^k$ :

$$\langle \boldsymbol{\alpha} L_{2} \Big\| \sum_{d} T^{k}(d) \Big\| \boldsymbol{\alpha}' L_{2}' \rangle$$

$$= \langle \boldsymbol{r}^{k} \rangle_{d} \langle l_{2} \| \boldsymbol{Y}^{k} \| l_{2} \rangle \langle \boldsymbol{\alpha} L_{2} \| \boldsymbol{U}^{k} \| \boldsymbol{\alpha}' L_{2}' \rangle$$

$$= \langle \boldsymbol{r}^{k} \rangle_{d} (-1)^{k+l_{2}} (2l_{2}+1) [(2k+1)/4\pi]^{1/2}$$

$$\times \overline{V} ( \begin{smallmatrix} l_{2} & k & l_{2} \\ 0 & 0 & 0 \end{smallmatrix}) \langle \boldsymbol{\alpha} L_{2} \| \boldsymbol{U}^{k} \| \boldsymbol{\alpha}' L_{2}' \rangle ,$$

$$(9)$$

where  $l_2$  is the orbital angular momentum of all equivalent electrons forming states  $|\alpha L_2\rangle$ . The reduced matrix elements  $\langle \alpha L_2 || U^2 || \alpha' L_2' \rangle$  are available from the literature.<sup>11,13</sup> The fact that the configuration to be considered is  $p^5 d^5$  instead of  $pd^5$  results in the change of sign of  $\langle l_1 || T^k || l_1 \rangle$ .

## V. INTENSITY

In the photoionization process, one electron belonging to a bound state is transferred to a continuum state. The total ionization cross section is proportional to the sum<sup>19</sup>

$$A = \sum_{f,i} |\langle f| \hat{\mu} |i\rangle|^2$$

where  $|f\rangle$  and  $|i\rangle$  stand for the final (after ionization) and initial (before ionization) states of the

ion-electron system, respectively, and  $\hat{\mu}$  is the operator inducing the change in the state of the ion. If the incident-photon energy is constant, the continuum-electron energy will depend on the state in which it left the ion. At temperatures of interest it is safe to assume that only the lowest-energy term is populated. It is then possible<sup>20</sup> to write the probability that the photoionization event will result in a state  $|f^+\rangle$  of the ion as

$$P_{f+} = \sum_{i_g^+} \left| \left\langle f^+ \right| i_g^+ \right\rangle \right|^2 / \sum_{f^+} \sum_{i_g^+} \left| \left\langle f^+ \right| i_g^+ \right\rangle \right|^2 , \qquad (10)$$

where the summations are over all the unperturbed states  $|i_g^*\rangle = |\alpha_g LSJM\rangle$  obtained by coupling ground states  $|\alpha_g L_2 S_2 J_2 M_2\rangle$  with the electron states before ionization, and over all the final states. The final states of the ion are linear combinations of the states  $|\alpha_L SJM\rangle$ :

$$|f_{j}^{\star}\rangle = \sum_{\alpha J M} C_{\alpha J M}^{j} |\alpha LSJM\rangle.$$

The coefficients  $C_{\alpha JM}^{j}$  are the eigenvectors obtained in the process of the diagonalization of the matrix. Thus the normalized transition probability or intensity could be written as

$$I_{j} = \sum_{J,M} \left| C_{\alpha_{g}JM}^{j} \right|^{2} / \sum_{j} \sum_{JM} \left| C_{\alpha_{g}JM}^{j} \right|^{2} .$$
(11)

## VI. RESULTS AND DISCUSSION

The states of core p photoelectrons will be considered for  $Mn^{2+}$  in  $MnF_2$  and for the Fe<sup>3+</sup> free ion in this paper. The ground-state-configuration Hartree-Fock wave functions of Clementi<sup>15</sup> for  $Mn^{2+}$ and Fe<sup>3+</sup> are used within the framework of Koopman's theorem for photoionized  $Mn^{3+}$  and Fe<sup>4+</sup>. The formulation is equally applicable if the Hartree-Fock wave functions of the appropriate  $Mn^{3+}$  and Fe<sup>4+</sup> configuration are to be used. The crystalfield parameters at an  $Mn^{2+}$  site in  $MnF_2$  are those calculated by Sharma *et al.*<sup>21</sup>

The ground-state configuration of  $Mn^{2+}$  and  $Fe^{3+}$ is  $d^5$ , for which the ground term is <sup>6</sup>S. Following photoionization of a *p* shell, the configuration be-

TABLE I. Relative eigenvalues and normalized transition probabilities of *p*-vacancy multiplets considering only the electrostatic interaction between the *p* and *d* electrons. (Energies are in eV.)

Configuration $3p^5 3d^5$				Configuration $2p^5 3d^5$			
$Mn^{3+}$		$\mathrm{Fe}^{4+}$		Mn <sup>3+</sup>		$\mathrm{Fe}^{4*}$	
Energy	Intensity	Energy	Intensity	Energy	Intensity	Energy	Intensity
8.839	0.278	9.594	0.277	-1.084	0.153	-1.013	0.164
-5.059	0.005	-5.725	0.005	-2.333	0.0002	-2.782	0.00002
-9.991	0.133	-11.314	0.135	-6.128	0.264	-7.197	0.253
-13.608	0.583	-15.514	0.583	-8.669	0.583	-10.228	0.583

Configuration $3p^5 3d^5$				Configuration $2p^5 3d^5$			
Mn <sup>3+</sup>		$\mathrm{Fe}^{4+}$		Mn <sup>3+</sup>		$\mathrm{Fe}^{4+}$	
Energy	Intensity	Energy	Intensity	Energy	Intensity	Energy	Intensity
9.052	0.131	9.867	0.130	2.083	0.147	2.810	0.149
8.743	0.092	9.473	0.092	0.306	0.106	0.633	0.107
8.536	0.055	9.209	0.055	0.208	0.003	0.342	0.003
-4.883	0.002	-5.495	0.002	-1.625	0.036	-1.945	0.034
-4.999	0.002	-5.646	0.002	-1.841	0.014	-2.153	0.014
-5.170	0.002	-5.869	0.002	-3.685	0.031	-4.360	0.032
-9.791	0.063	-11.056	0.064	-4.188	0.017	-4.854	0.019
-10.047	0.045	-11.380	0.046	-4.534	0.018	-5.351	0.018
-10.250	0.027	-11.642	0.027	-8.947	0.063	-10.521	0.061
-13.132	0.138	-14.923	0.138	-9.613	0.127	-11.298	0.126
-13.525	0.194	-15.417	0.193	-10.756	0.188	-12.693	0.188
-13.993	0.250	-15.997	0.250	-12.050	0.250	-14.269	0.250

TABLE II. Relative eigenvalues and normalized transition probabilities of p-vacancy multiplets considering electrostatic interaction and spin-orbit interaction. (Energies are in eV.)

TABLE III. Relative eigenvalues and normalized transition probabilities of p-vacancy multiplets of  $Mn^{3+}$  considering electrostatic interaction, the spin-orbit interaction, and the crystal-field (parameters from Ref. 21) interaction. (Energies are in eV.)

	Mn <sup>3+</sup> configur	ration $3p^5 3d^5$	i	Ν	∕In <sup>3+</sup> configur	ation $2p^5 3d^5$	
Energy	Intensity	Energy	Intensity	Energy	Intensity	Energy	Intensity
9.061	0.0187	-9.791	0.0090	2,085	0.0210	-4.186	0.0057
9.056	0.0187	-9.792	0.0090	2.085	0.0210	-4.186	0.0057
9.053	0.0187	-9.794	0.0090	2.085	0.0210	-4.527	0.0025
9.052	0.0187	-9.797	0.0090	2.083	0.0210	-4.530	0.0026
9.046	0.0187	-10.042	0.0090	2.083	0.0210	-4.530	0.0025
9.045	0.0187	-10.046	0.0090	2.082	0.0210	-4.534	0.0026
9.044	0.0186	-10.050	0.0090	2.080	0.0210	-4.535	0.0026
8.752	0.0185	-10.051	0.0090	0.311	0.0211	-4.539	0.0026
8.751	0.0185	-10.051	0.0090	0.308	0.0212	-4.542	0.0026
8.749	0.0185	-10.249	0.0089	0.303	0.0212	-8.947	0.0211
8.741	0.0185	-10.249	0.0089	0.302	0.0213	-8.947	0.0211
8.735	0.0184	-10.250	0.0089	0.302	0.0213	-8.947	0.0211
8,536	0.0183	-13,122	0.0276	0.209	0.0009	-9.612	0.0254
8.535	0.0183	-13,128	0,0276	0.209	0.0009	-9.613	0.0254
8.534	0.0183	-13.137	0.0276	0.208	0.0009	-9.614	0.0254
-4.881	0.0005	-13,139	0,0276	-1.615	0.0051	-9.614	0.0254
-4.883	0.0005	-13.139	0,0276	-1.621	0.0051	-9.614	0.0254
-4.884	0.0005	-13.494	0.0276	-1.624	0.0051	-10.754	0.0269
-4.987	0.0004	-13.498	0.0276	-1.625	0.0051	-10.755	0.0269
<b>-</b> 4.988	0.0004	-13.500	0.0276	-1.633	0.0051	-10.755	0.0269
-4.990	0.0004	-13.525	0.0276	-1.634	0.0051	-10.756	0.0269
-5.002	0.0004	-13.527	0.0276	-1.635	0.0052	-10.756	0.0269
-5.011	0.0004	-13.537	0.0276	-1.828	0.0026	-10.757	0.0269
-5.158	0.0002	-13.556	0.0276	-1.829	0.0026	-10.758	0.0269
-5.166	0.0002	-13.968	0.0278	-1.832	0.0026	-12.048	0.0278
-5.169	0.0002	-13.983	0.0278	-1.844	0.0027	-12.049	0.0278
-5.170	0.0002	-13.986	0.0278	-1.854	0.0028	-12.049	0.0278
-5.180	0.0002	-13,986	0.0278	-3.678	0.0062	-12.049	0.0278
-5.181	0.0003	-13.998	0.0278	-3.683	0.0062	-12,050	0.0278
-5.182	0.0002	-14.000	0.0278	-3.689	0.0063	-12.050	0.0278
-9.786	0.0090	-14.014	0.0278	-3.691	0.0063	-12.052	0.0278
-9.787	0.0090	-14.015	0.0278	-3.691	0.0063	-12.052	0.0278
-9.787	0.0090	-14.018	0.0278	-4.186	0.0057	-12.052	0.0278

comes  $p^5 d^5$ . The <sup>6</sup>S term of the parent configuration coupled with  $p^5$  shell then gives <sup>7</sup>P and <sup>5</sup>P terms. The  ${}^{5}P$  term can also be obtained by coupling the  $p^5$  shell with  ${}^4P$  and  ${}^4D$  terms of the parent configuration. The effect of spin-orbit coupling is to remove the degeneracy of the terms with respect to their total angular momentum J. Finally the crystal-field effect is to remove the degeneracy of the J multiplets with respect to  $M_J$ . One has to calculate all the diagonal and nondiagonal matrix elements between the 66 states  $|\alpha LSJM_{J}\rangle$  thus resulted. The diagonalization of the  $66 \times 66$  matrix, calculated using Secs. II-IV, gives the eigenenergies of the ion after photoionization within the free-ion single-configuration Hartree-Fock approximation, and hence the energy spectrum of the photoelectrons.

The intensity distribution of the photoelectron spectrum is obtained, using Eq. (11), from the eigenvectors computed for each eigenvalue in the process of matrix diagonalization.

First the electrostatic interaction only is considered and the  $4 \times 4$  matrix diagonalized to calculate the eigenvalues and the transition probabilities. For 3p photoionization of  $Mn^{2+}$  these have been calculated by Fadley *et al.*,<sup>1</sup> and the results obtained here agree with their calculations. Second, the spin-orbit interaction is introduced and the resulting  $12 \times 12$  matrix diagonalized. Finally, the crystal-field interaction is included for  $Mn^{3+}$ in  $MnF_2$ , and the  $66 \times 66$  matrix diagonalized. This has been done to investigate the effect of various interactions on the calculated energy spectra.

Computations presented in this paper took a total of less than 2-min CPU time on the IBM 360/65 system at the University of Manitoba.

For 3p photoionization, the electrostatic interaction is most important, but for 2p photoionization both spin-orbit and electrostatic interactions are important (Tables I and II). The effect of the crystal field is unimportant, as is evident from the case of Mn<sup>3+</sup> (Table III), and therefore no attempt is made to include the crystal field for Fe<sup>4+</sup>.

Fadley *et al.*<sup>1</sup> have observed the photoelectron spectra of various transition-metal ions in their complexes. Our calculations for 2p-hole multiplets are in good agreement with their observations. It is seen from Fig. 1 and Table II that in addition to two main peaks—one composed of four multiplets and the other composed of two multiplets there are an additional two weak peaks with composite intensity about 10% of the total intensity of 2p photoemission. One of the weak peaks appears to be present in the observed spectra of Ref. 1, and the other is probably mixed up with the  $2p_{1/2}$ peak.

Frost *et al.*<sup>3</sup> have observed 2p-electron photoemission spectra for many cobalt complexes. They have shown how measurement of the separation between  $2p_{1/2}$  and  $2p_{3/2}$  peaks could be used to understand the chemical composition of transitionmetal complexes. In fact, the 2p photoemission spectra present considerably greater information than is discernible from the separation between  $2p_{1/2}$  and  $2p_{3/2}$  peaks.

The calculation for 3p photoelectrons has been done to investigate the effect of spin-orbit and crystal-field interactions on the simple spectroscopic-term multiplets. Except for broadening of the terms no new feature is seen. The correlation contribution is expected to be important for 3pvacancy states, and multiconfiguration calculations appear to be the solution.<sup>9</sup>

The 2p-vacancy states appear to be properly described within a single configuration. Therefore, single-configuration molecular-orbital calculations for the whole complex, formed by the metal ion and the neighboring ligands, should be satisfactory. Such calculations are now possible in the framework of Hartree-Fock theory.

One is led to conclude that while inner-core vacancy states depend more on the chemical environment than on solid state and other many-body effects, the outer-core vacancy states are sensitive to the both effects. For chemical analysis it might be more useful to study inner-core vacancy states rather than the outer-core vacancy states.

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FIG. 1. Multiplets of 2p vacancies of  $Mn^{3*}$ . The zero energy is arbitrary, and the total intensity is normalized to 1.

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