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Discrete-spectrum contributions to the Bauche-Arnoult hyperfine structure parameters for the first row transition metal atoms

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Résumé. — Les auteurs ont calculé par la technique Hartree-Fock les contributions du spectre discret aux paramètres décrits par les effets croisés du second ordre des interactions électrostatiques et hyperfines (paramètres de Bauche-Arnoult) pour les configurations 3dN 4s et 3dN−1 4s2 des éléments du groupe du fer. Ils proposent une méthode d’extrapolation pour estimer les contributions totales des états liés. Ils montrent que, dans le cas de la configuration 3dN 4s, les contributions les plus importantes proviennent des excitations 4s → ns, 3d → nd, ns → 3d et ns → 4s; tandis que, dans le cas de la configuration 3dN−1 4s2, elles proviennent des excitations 3d → nd et ns → 3d. Les contributions de 3d → ng et de 3d → ns sont toujours très petites.

Abstract. — Hartree-Fock values of discrete spectrum contributions to the parameters describing crossed second-order effects of electrostatic and hyperfine interactions (Bauche-Arnould parameters) have been calculated for 3dN 4s and 3dN−1 4s2 configurations of the first row transition metal atoms. An extrapolation procedure is proposed to estimate the total bound state contributions. It is shown that in the case of 3dN 4s configuration the most important are the 4s → ns, 3d → nd, ns → 3d and ns → 4s excitations, while, in the case of 3dN−1 4s2, they are the 3d → nd and ns → 3d ones. The contributions from 3d → ng and 3d → ns excitations are always very small.

1. Introduction.

Recent developments in the laser spectroscopy [1, 2] allow to study with a great accuracy hyperfine structure (hfs) of numerous levels in a given excited electronic configuration. This provides new possibilities of exploiting the effective-operator technique to study configuration interaction (CI) effects on the hfs [3-6]. The formal theory has been developed by Bauche-Arnoult [7, 8] following the general method of Judd [9]. It was shown that 13 parameters in the case of dN s and 7 parameters in the case of dN−1 s2 configuration describe all second-order effects of electrostatic and hyperfine interactions. We shall refer to these parameters as the Bauche-Arnoult (BA) parameters. The least square fits of BA parameters for the ground configurations of some of the first row transition metal atoms have recently been determined by Dembczyński [3, 10]. Very little is however known on their Hartree-Fock (HF) values. The aim of this paper is to estimate the discrete-spectrum HF values of BA parameters for the case of 3dN 4s and 3dN−1 4s2 configurations of the neutral iron group atoms. A comparison of the fitted values of the parameters to the HF ones contributes to an understanding of the absolute values of the individual parameters. On the other hand on the basis of the HF parameter values one may reduce the number of independent parameters in the least squares procedure (e.g. by imposing a requirement for their ratios to be equal to the HF ones).

2. Bauche-Arnoult parameters.

Four types of excitations contribute to the crossed second order hfs Hamiltonian for 3dN 4s configurations: (a) excitation of a closed-shell electron to an empty shell, (b) excitation of an open-shell electron to an empty shell, (c) excitation of a closed-shell electron to an open shell, (d) an open to open shell excitation. Excitation types (a), (b) and (c) give contributions to 3dN−1 4s2 configurations Hamiltonian as well. Though
the closed to empty shell excitations (type (a)) give
contributions independent of the term and of the
number \( N \) of 3d electrons, they are also taken into
account in our present study. For a discussion of the
possibility of an experimental estimation of their values
see reference [3]. Excitation types (a), (b), (c) and (d)
lead, respectively, to 4, 10, 2 and 2 radial hfs parame-
ters.

Detailed expressions defining the hfs parameters
were given by Judd [9] (excitation type (a)) and by
Bauche-Arnoult [8] (excitations (b), (c), (d)). We shall
modify slightly the original notation in order to make
it more uniform and condensed. Let \( n_0 \) \( l_0 \) and \( n_1 \) \( l_1 \)
denote, respectively, the shells from and to which the
excitation takes place. Let us define the following
quantities :

\[
\Phi_{nl}(n_0 l_0, n_1 l_1) = \begin{cases} 
(n_0 l_0 | r^{-3} | n_1 l_1) / (nl | r^{-3} | nl) & \text{if } l_0 + l_1 \neq 0 \\
\psi_{n_0 l_0}(0) \psi_{n_1 l_1}(0) / |\psi_{n_0 l_0}(0)|^2 & \text{if } l_0 + l_1 = 0
\end{cases}
\]

(1)

\[
W^k_{nl}(n_0 l_0, n_1 l_1) = R^k(nl, n_0 l_0, n_1 l_1) \Phi_{nl}(n_0 l_0, n_1 l_1) / |\Delta E(n_0 l_0, n_1 l_1)|
\]

(2)

\[
V^k_{nl}(n_0 l_0, n_1 l_1) = R^k(nl, n_0 l_0, n_1 l_1) \Phi_{nl}(n_0 l_0, n_1 l_1) / |\Delta E(n_0 l_0, n_1 l_1)|
\]

(3)

where \( R^k \) is the Slater integral and \( |\Delta E(n_0 l_0, n_1 l_1)| \) is the absolute value of the difference between average
energies of the two configurations involved. The second-order radial hfs parameters for the 3d\( ^N \) 4s configurations
may then be expressed in the following way :

(a) Closed to empty shell excitations :

\[
x^2_{3d}(l_0 l_1) = \sum_{n_0 = 2}^{\infty} \sum_{n_1 = 4}^{\infty} W^k_{3d}(n_0 l_0, n_1 l_1),
\]

(4)

where \( l_0 = 1; l_1 = 1, 3; k = 1, 3. \)

(b) Open to empty shell excitations :

\[
x^k_{3d}(n_0 l_0, l_1) = A^k(l_0, l_1) \sum_{n_1 = n_0}^{\infty} W^k_{3d}(n_0 l_0, n_1 l_1)
\]

(5)

where \( n_0 l_0 = 3d, 4s; l_1 = l_0, l_0 \pm 2; \)

\[
A^k(l_0, l_1) = \begin{cases} 
4 & \text{if } l_1 = 2 \\
5 & \text{otherwise;}
\end{cases}
\]

\[
nl = \begin{cases} 
3d, 4s & \text{if } l_0 = l_1 = 2 \text{ and } k = 2 \\
3d & \text{otherwise;}
\end{cases}
\]

\[
k = \begin{cases} 
2 & \text{if } l_0 + l_1 \leq 2 \\
2, 4 & \text{otherwise;}
\end{cases}
\]

\[
A^k(l_0, l_1) = \begin{cases} 
1 & \text{if } nl = 4s \\
A(k, l_0, l_1) & \text{otherwise;}
\end{cases}
\]

the values of \( A(k, l_0, l_1) \) coefficients are listed in
Table I. Moreover, in the case of \( 4s \rightarrow nd \) excitations, an
« exchange » parameter appears

\[
x^2_{3d}(n_0 l_0, n_1 l_1) = A(2, l_0, l_1) \sum_{n_1 = 4}^{\infty} V^2_{3d}(n_0 l_0, n_1 l_1)
\]

(6)

where \( n_0 l_0 = 4s, l_1 = d, nl = 3d; \) the prime in the
sums means that both discrete and continuous spectra
contributions should be included.

Table I. — Values of the \( A(k, l_0, l_1) \) coefficients.

<table>
<thead>
<tr>
<th>( A(k, l_0, l_1) )</th>
<th>( k )</th>
<th>( l_0 )</th>
<th>( l_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\sqrt{10}/7)</td>
<td>2</td>
<td>{0 }</td>
<td>{2 }</td>
</tr>
<tr>
<td>\5</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>\10/7</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>\6/5/7</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>(-10\sqrt{10}/7\sqrt{11})</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

(c) Closed to open shell excitations :

\[
x^2_{3d}(l_0, n_1 l_1) = A(2, l_0, l_1) \sum_{n_0 = 1}^{\infty} W^2_{3d}(n_0 l_0, n_1 l_1)
\]

(7)

where \( l_0 = s; n_1 l_1 = 3d, 4s. \)

(d) Open to open shell excitations :

\[
x^2_{3d}(n_0 l_0, n_1 l_1) = \sum_{n_0 = 1}^{\infty} W^2_{3d}(n_0 l_0, n_1 l_1)
\]

(8)

where \( (n_0 l_0, n_1 l_1) \) pair is either \( (3d, 4s) \) or \( (4s, 3d) \).
A complete list of the radial parameters and the correspondence of the present notation to the one of Bauche-Arnoult [8] is given in table II. The parameters corresponding to \(3d^{n-1} \cdot 4s^2\) configurations are defined in the same way except that we have only one open shell in this case. In consequence, no open - open shell excitations are possible. For open - empty shell excitations \(n_0 l_0 = 3d\) and \(l_1 = 0, 2, 4\). In the case of closed - open shell excitations only one possibility exists : \(l_0 = s, n_1 l_1 = 3d\).

3. Results of calculations.

3.1 Hartree-Fock values. — Closed- and open-shell orbitals for the \(3d^k 4s\) and \(3d^{k-1} 4s^2\) configurations of Ti, V, Cr, Mn and Fe have been obtained solving the corresponding HF equations for the average energy of the appropriate configuration. The calculations have been performed using the numerical HF program developed by Froese-Fischer [11]. The empty shell orbitals are represented by a set of orthonormal virtual orbitals, solutions of the HF equations in which the Fock operator is built from the previously obtained, and then frozen, occupied orbitals. The original Froese-Fischer program has been modified to calculate \(W^k\) and \(V^k\) contributions to the radial hfs parameters. The HF values of the BA parameters given by closed-form expressions (Eqs. (7) and (8)) have been calculated exactly. The values of the other parameters (Eqs. (4), (5) and (6)) have been estimated taking only a few terms of the appropriate expansions. All these values are collected in table II, where the highest \(n_1\) value taken into account is also specified in each case.

The convergence rate of the expansions (4), (5) and (6) may be estimated from the data displayed in table III, where the separate terms of the infinite sums are listed. One can see that the convergence is rather satisfactory. The \(n_1 = 9\) term, in all the cases, constitutes 2-3 % of the parameter value. It is interesting to note that the consecutive terms of the sum, for a given excitation, are equal to the same fraction of the total parameter value. E.g., for the \(3d \rightarrow n_1 d\) excitation, \(n_1 = 4, 5, 6, 7, 8, 9\) terms constitute respectively, 51 %, 20 %, 10 %, 5 %, 3 %, 2 % of the four \(\chi_{3d}^k\) parameters. Therefore it is reasonable to expect that the ratio of the hfs parameters, for each excitation type, is the same as that of the partial sums or even of \(W^k_{3d}\).

3.2 Asymptotic extrapolation values. — Though the convergence of the infinite series corresponding to the excitations to the empty shells is fairly good, it is desirable to estimate the contribution from the neglected terms. One of the methods, rather commonly used, is based on the assumption that in equations (2) and (3) we may set

\[
\Delta E(n_0 l_0, n_1 l_1) \approx \Delta \bar{E}
\]

where \(\Delta \bar{E}\) is \(n_1\)-independent. Then, using the expansion of the identity operator, we may replace equations (4), (5) and (6) by approximate closed-form expressions. In the case under consideration this method suffers from an inconvenience — it leads to completely new types of integrals and, hence, its application is connected with an additional computational effort. On the other hand, due to an uncertainty in \(\Delta \bar{E}\), its accuracy cannot exceed 10 %, Therefore we have chosen another, very simple method of estimation of the infinite sum contributions.

For hydrogenlike orbitals, using results of [12], [13] and [14], after some rather tedious algebra, we may derive asymptotic expressions for \(W_{3d}^k\) and \(V_{3d}^k\) in the limit of \(n_1 \rightarrow \infty, n_1 \gg l_1\)

\[
W_{3d}^k(n_0 l_0, n_1 l_1) \sim D(n_1 - B)^{-C} \quad (10)
\]

where \(B, C\) and \(D\) are constants. Since virtual HF orbitals are rather well approximated by the properly scaled hydrogenic ones, we may use (10) as an extrapolation formula for \(W_{3d}^k\) with \(B, C\) and \(D\) being adjustable parameters. The values of \(B, C\) and \(D\) have been determined by the least square method in which the expression (10) is adjusted to the HF values of \(W_{3d}^k(\chi_{3d}^k)\). Since

\[
\zeta(C, B) = \sum_{n=0}^{\infty} (n + B)^{-C} \quad (11)
\]

is the two-parameters Riemann zeta function [15], we have, according to (5),

\[
\chi_{3d}^k(n_0 l_0, l_1) = A(k, l_0, l_1) D \times \left[\zeta(C, -B) - \sum_{n=0}^{n_1-1} (n - B)^{-C}\right]. \quad (12)
\]

Parameters \(\chi_{3d}^k(n_0 l_0, l_1)\) and \(\chi_{3d}^k(n_0 l_0, l_1)\) may be expressed in a similar way using equations (4) and (5). One should remember that the procedure is applicable to the discrete spectrum contributions only.

The accuracy of the extrapolation procedure has been tested in a calculations of \(\chi_{3d}^k(3d, d)\) parameter for the \(3d^7 4s^1\) configuration of Fe. First, the HF values of \(W_{3d}^k(3d, nd)\) were calculated for \(n = 4, 5, 6, 7, 8, 9\). Then a number of the least square calculations of \(B, C\) and \(D\) were performed, taking into account only a part of the available \(W_{3d}^k\) parameters. The HF values of the remaining ones were compared with the extrapolated values calculated using equation (10). The extrapolation errors

\[
\delta(p) = \frac{|(W_{HF} - W_{EP})|}{W_{HF}} \cdot 100 \%
\]

where EP means that the quantity was extrapolated and \(p\) is equal to the number of HF values used in the least square fit of \(B, C\) and \(D\), is a measure of the accuracy of the method. The HF values of \(W_{3d}^k\), the extrapolation formula constants, the corresponding \(\chi_{3d}^2\) values and the extrapolation errors are listed in table IV. As it is seen, the extrapolation procedure is surprisingly accurate. The extrapolation error does not exceed 4 % of a single \(W_{3d}^k\) value and the final values of the BA parameters are practically independent of the
Table II. — HF values of the second-order radial hfs parameters for the $3d^N 4s$ and $3d^{N-1} 4s^2$ configurations of Ti, V, Cr, Mn and Fe. For parameters expressed by infinite sums, extrapolated values (EP) are also given.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Designation</th>
<th>$n_{4s}^{1/2}$</th>
<th>BA present</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>$e^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3d^N 4s$</td>
<td>$n_0 p \rightarrow n_1 p$</td>
<td>$x_{3d}^1(p, p)$</td>
<td>9p</td>
<td>- 79.2</td>
<td>- 44.6</td>
<td>- 26.4</td>
<td>- 15.8</td>
<td>- 9.38</td>
<td>- 3</td>
</tr>
<tr>
<td>$n_0 p \rightarrow n_1 f$</td>
<td>$x_{3d}^1(p, f)$</td>
<td>9f</td>
<td>2.82</td>
<td>11.2</td>
<td>14.3</td>
<td>15.1</td>
<td>14.9</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>EP</td>
<td>2.85</td>
<td>11.5</td>
<td>14.7</td>
<td>15.5</td>
<td>15.1</td>
<td>- 3</td>
</tr>
<tr>
<td>$3d \rightarrow n_1 s$</td>
<td>$x_{3d}^1(3d, s)$</td>
<td>9s</td>
<td>304.</td>
<td>137.</td>
<td>56.7</td>
<td>18.9</td>
<td>1.48</td>
<td>- 6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$x_{3d}^2(3d, d)$</td>
<td>9d</td>
<td>344.</td>
<td>317.</td>
<td>241.</td>
<td>186.</td>
<td>154.</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td>$3d \rightarrow n_1 d$</td>
<td>$x_{3d}^2(3d, d)$</td>
<td>9d</td>
<td>47.8</td>
<td>34.5</td>
<td>26.4</td>
<td>20.4</td>
<td>16.9</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$x_{3d}^2(3d, d)$</td>
<td>9d</td>
<td>31.7</td>
<td>37.1</td>
<td>28.5</td>
<td>22.6</td>
<td>18.3</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td>$3d \rightarrow n_1 g$</td>
<td>$x_{3d}^2(3d, d)$</td>
<td>9d</td>
<td>- 25.6</td>
<td>- 18.5</td>
<td>- 13.9</td>
<td>- 10.5</td>
<td>- 8.53</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td>$4s \rightarrow n_1 s$</td>
<td>$x_{3d}^2(4s, s)$</td>
<td>9s</td>
<td>30.6</td>
<td>16.4</td>
<td>6.54</td>
<td>2.95</td>
<td>1.36</td>
<td>- 9</td>
<td></td>
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<tr>
<td>$4s \rightarrow n_1 d$</td>
<td>$x_{3d}^2(4s, d)$</td>
<td>9d</td>
<td>- 29.3</td>
<td>- 38.7</td>
<td>- 36.7</td>
<td>- 34.5</td>
<td>- 31.9</td>
<td>- 6</td>
<td></td>
</tr>
<tr>
<td>$n_0 s \rightarrow 3d$</td>
<td>$x_{3d}^2(3s, 3d)$</td>
<td>9d</td>
<td>- 203.</td>
<td>- 190.</td>
<td>- 160.</td>
<td>- 141.</td>
<td>- 126.</td>
<td>- 6</td>
<td></td>
</tr>
<tr>
<td>$n_0 s \rightarrow 4s$</td>
<td>$x_{3d}^2(3s, 4s)$</td>
<td>9d</td>
<td>- 32.3</td>
<td>- 30.2</td>
<td>- 28.1</td>
<td>- 26.2</td>
<td>- 24.7</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td>$3d \rightarrow 4s$</td>
<td>$x_{3d}^2(3d, 4s)$</td>
<td>9d</td>
<td>- 28.7</td>
<td>- 21.0</td>
<td>- 14.7</td>
<td>- 10.0</td>
<td>- 6.39</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td>$4s \rightarrow 3d$</td>
<td>$x_{3d}^2(4s, 3d)$</td>
<td>9d</td>
<td>- 38.7</td>
<td>- 44.9</td>
<td>87.8</td>
<td>40.5</td>
<td>150.</td>
<td>55.0</td>
<td>- 6</td>
</tr>
<tr>
<td>$3d^{N-1} 4s^2$</td>
<td>$n_0 p \rightarrow n_1 p$</td>
<td>$x_{3d}^1(p, p)$</td>
<td>9p</td>
<td>- 32.5</td>
<td>- 15.3</td>
<td>- 6.03</td>
<td>- 0.81</td>
<td>2.20</td>
<td>- 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>EP</td>
<td>- 33.0</td>
<td>- 15.6</td>
<td>- 6.06</td>
<td>- 0.72</td>
<td>2.30</td>
<td>- 3</td>
</tr>
<tr>
<td>$n_0 p \rightarrow n_1 f$</td>
<td>$x_{3d}^1(p, f)$</td>
<td>9f</td>
<td>22.2</td>
<td>24.3</td>
<td>24.2</td>
<td>23.0</td>
<td>21.5</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>EP</td>
<td>22.7</td>
<td>24.8</td>
<td>24.8</td>
<td>23.4</td>
<td>22.0</td>
<td>- 3</td>
</tr>
<tr>
<td>$3d \rightarrow n_1 s$</td>
<td>$x_{3d}^1(3d, s)$</td>
<td>9s</td>
<td>32.0</td>
<td>51.5</td>
<td>18.2</td>
<td>4.17</td>
<td>- 1.12</td>
<td>- 6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$x_{3d}^0(3d, d)$</td>
<td>9d</td>
<td>171.</td>
<td>134.</td>
<td>108.</td>
<td>86.9</td>
<td>74.1</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td>$3d \rightarrow n_1 d$</td>
<td>$x_{3d}^0(3d, d)$</td>
<td>9d</td>
<td>30.0</td>
<td>23.6</td>
<td>19.0</td>
<td>15.3</td>
<td>13.0</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$x_{3d}^0(3d, d)$</td>
<td>9d</td>
<td>32.3</td>
<td>25.4</td>
<td>20.5</td>
<td>16.8</td>
<td>14.0</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td>$3d \rightarrow n_1 g$</td>
<td>$x_{3d}^2(3d, d)$</td>
<td>9d</td>
<td>- 12.2</td>
<td>- 9.29</td>
<td>- 7.27</td>
<td>- 5.66</td>
<td>- 4.70</td>
<td>- 3</td>
<td></td>
</tr>
<tr>
<td>$n_0 s \rightarrow 3d$</td>
<td>$x_{3d}^2(3s, 3d)$</td>
<td>9d</td>
<td>9.22</td>
<td>3.70</td>
<td>1.91</td>
<td>0.84</td>
<td>0.44</td>
<td>- 9</td>
<td></td>
</tr>
<tr>
<td>$n_0 s \rightarrow 4s$</td>
<td>$x_{3d}^2(3s, 4s)$</td>
<td>9d</td>
<td>- 27.7</td>
<td>- 10.9</td>
<td>- 4.9</td>
<td>- 0.24</td>
<td>- 0.13</td>
<td>- 9</td>
<td></td>
</tr>
</tbody>
</table>

*a* The highest excitation taken into account in the infinite expansion.

*b* All the quantities have to be multiplied by the power of 10 given in the corresponding entry.

*c* The second-order perturbation theory is nonapplicable in this case. See text for a discussion.
Table III. — Hartree-Fock values of $A(k, l_0, l_i) W_{nl}(n_0, l_0, n_1, l_i)$ and $A(k, l_0, l_i) V_{nl}(n_0, l_0, n_1, l_i)$, $n_1 \leq 9$, for Fe(3d$^7$ 4s$^1$). In parentheses the percentage of the total parameter value is given.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>$3d \rightarrow n_1 , s$</th>
<th>$4s \rightarrow n_1 , s$</th>
<th>$4s \rightarrow n_1 , d$</th>
<th>$3d \rightarrow n_1 , d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_1$</td>
<td>$A W^2_{3d}$</td>
<td>$A W^2_{3d}$</td>
<td>$A W^2_{3d}$</td>
<td>$A W^2_{3d}$</td>
</tr>
<tr>
<td>$e^*$</td>
<td>$-8$</td>
<td>$-4$</td>
<td>$-7$</td>
<td>$-6$</td>
</tr>
<tr>
<td>4</td>
<td>131 (88)</td>
<td>380 (62)</td>
<td>147 (41)</td>
<td>60 (43)</td>
</tr>
<tr>
<td>5</td>
<td>12 (8)</td>
<td>106 (17)</td>
<td>38 (11)</td>
<td>14 (10)</td>
</tr>
<tr>
<td>6</td>
<td>3 (2)</td>
<td>45 (7)</td>
<td>22 (6)</td>
<td>8 (6)</td>
</tr>
<tr>
<td>7</td>
<td>1.3 (0.9)</td>
<td>24 (4)</td>
<td>14 (4)</td>
<td>4 (3)</td>
</tr>
<tr>
<td>8</td>
<td>0.7 (0.5)</td>
<td>14 (2)</td>
<td>10 (3)</td>
<td>3 (2)</td>
</tr>
<tr>
<td>9</td>
<td>148 (99)</td>
<td>569 (93)</td>
<td>302 (85)</td>
<td>116 (83)</td>
</tr>
<tr>
<td>$\sum_{\alpha}^a$</td>
<td>149</td>
<td>610</td>
<td>355</td>
<td>140</td>
</tr>
<tr>
<td>$\sum_{\beta}^b$</td>
<td>149</td>
<td>610</td>
<td>355</td>
<td>140</td>
</tr>
</tbody>
</table>

*a* All the quantities in the same column have to be multiplied by the power of 10 given in the corresponding entry.

*b* Extrapolated values (Eq. (12)).

Table IV. — Hartree-Fock values of $W_{3d}^2(3d, n_1 \, d) \times 10^{-6}$ for Fe(3d$^7$ 4s$^1$), extrapolation formula parameters, values of $x_{3d}^2(3d, d) \times 10^{-4}$ and the extrapolation formula errors.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$n_1$</th>
<th>Hartree-Fock values</th>
<th>Extrapolation error (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\delta(3)$</td>
</tr>
<tr>
<td>$W_{3d}^2(3d, n_1 , d)$</td>
<td>4</td>
<td>100.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>40.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>10.9</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>6.8</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>4.5</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.1</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>2.3</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.7</td>
<td>0.9</td>
</tr>
<tr>
<td>$B$</td>
<td></td>
<td>1.20</td>
<td>1.12</td>
</tr>
<tr>
<td>$C$</td>
<td></td>
<td>3.04</td>
<td>3.11</td>
</tr>
<tr>
<td>$D$</td>
<td></td>
<td>1.01</td>
<td>1.19</td>
</tr>
<tr>
<td>$x_{3d}^2(3d, d)$</td>
<td>270.7</td>
<td>282$^b$</td>
<td>281$^b$</td>
</tr>
</tbody>
</table>

*a* Eq. (5) partial sum with $n_1 = 4, 5, \ldots, 12$.

*b* Eq. (12).
number of $W_2^{3d}$ parameters used in the least square procedure.

The optimized values of $B$, $C$ and $D$ for the parameters connected with $n_0 p \rightarrow n_1 f$ excitations are collected in table V. The extrapolated (according to Eq. (12)) hfs parameters are given in table II together with the corresponding HF partial sums.

Since the differences between the partial sums and the extrapolated values do not exceed 20\% of the parameter values and these differences are determined with an accuracy of about 4\%, we estimate, that the discrete spectrum contributions to the hfs parameters have been determined with at least 1\% accuracy. The extrapolation has not been performed for $x_{3d}^d(3d, g)$ and $x_{3d(3d,}^d(p, f)$. Their discrete spectrum HF values are by 5-7 orders of magnitude smaller than the ones of $x_{4s}^d(3d, s)$ or $x_{3d}^*(3d, d)$.

### 4. Discussion

The second-order hfs parameters enter the energy expressions as contributions to the scaling factors of the standard (first-order) hfs parameters [16]. We have

$$a_{SL} = a(1 + \Delta_{SL})$$

where $a$ is the first-order hfs parameter, identical for all levels in one configuration, $\Delta_{SL}$ is a CI generated correction and $a_{SL}$ is the SL-dependent parameter which includes the electron correlation effects. The CI correction $\Delta_{SL}$, within the second order perturbation theory, is expressed as a linear combination of the BA second-order hfs parameters with coefficients ranging from 3 to 1/300 [3, 7, 8]. Hence, only the parameters which are not very small compared to 1 have to be taken into account in a parametric hfs theory. As it was already mentioned, the discrete spectrum contributions to the second-order parameters connected with $n_0 p \rightarrow n_1 f$ and $3d \rightarrow ng$ excitations are always negligible ($|x_{3d}(p, f)| < 3 \times 10^{-6}$ and $|x_{3d}^*(3d, g)| < 5 \times 10^{-8}$). However an inspection of table II shows that also $3d \rightarrow ns$, $4d \rightarrow nd$ and open \rightarrow open shell (3d \rightarrow 4s) excitations generate contributions to the pertinent parameters by 2-4 orders of magnitude smaller than the ones connected with $n_0 p \rightarrow n_1 f$ and with closed \rightarrow open shell excitations. In particular, $|x_{4s}^d(3d, s)| < 3 \times 10^{-4}$, $|x_{3d}^d(4s, d)| < 4 \times 10^{-5}$, $|y_{4s}^d(4s, d)| < 2 \times 10^{-4}$, and $|x_{3d}^d(3d, 4s)| < |x_{3d}^d(3d, 4s)| < 10^{-3}$.

Then, the only second-order parameters containing appreciable discrete-spectrum contributions are those connected with $3d \rightarrow nd$, $4s \rightarrow ns$, $n_0 p \rightarrow n_1 p$ and closed \rightarrow open shell excitations.

The continuous spectrum states may rather substantially influence the values of the hfs parameters describing excitations to the empty shells [17, 18]. As it was shown by Wolter [17], the continuum contributes much stronger than the bound states to the Stemheimer correction factor $R$ [19], being closely related to the second-order hfs parameters. Also Bauche-Arnould and Labarthe [18] in their calculation of the second-order effects on the hfs parameters in Sc and Ti, where continuum contributions were implicitly taken into account, have shown that $p \rightarrow f$ and $3d \rightarrow g$ contributions are far from being negligible. Hence, a smallness of the discrete spectrum contributions does not imply that the corresponding parameters may be omitted in a parametric hfs calculation. On the other hand the continuum contributions do not change values of the parameters connected with closed \rightarrow open and closed \rightarrow closed shell excitations. Hence, the present calculation gives a rather exact estimation of the values of these parameters.

As it was already stated, the ratios of the parameter values corresponding to the same excitation type are almost independent of the number of terms taken into account in the second-order perturbation series expansion. An inspection of table II shows that the ratios are also almost independent of $N$. The parameters associated with the $3d \rightarrow n_1 d$ excitations are

### Table V. — Extrapolation formula constants for hfs parameters describing $3d \rightarrow nd$ and $4s \rightarrow ns$ excitations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th></th>
<th>$B$</th>
<th></th>
<th>$C$</th>
<th></th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3d^n 4s^1$</td>
<td></td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>$x_{3d}^d(3d, d)$</td>
<td>1.97</td>
<td>1.80</td>
<td>1.61</td>
<td>1.41</td>
<td>1.19</td>
<td>2.71</td>
</tr>
<tr>
<td>$x_{3d}^d(3d, d)$</td>
<td>1.96</td>
<td>1.78</td>
<td>1.61</td>
<td>1.37</td>
<td>1.16</td>
<td>2.71</td>
</tr>
<tr>
<td>$x_{3d}^d(3d, d)$</td>
<td>1.97</td>
<td>1.75</td>
<td>1.56</td>
<td>1.37</td>
<td>1.14</td>
<td>2.69</td>
</tr>
<tr>
<td>$x_{3d}^d(3d, d)$</td>
<td>1.70</td>
<td>1.61</td>
<td>1.45</td>
<td>1.31</td>
<td>1.11</td>
<td>2.79</td>
</tr>
<tr>
<td>$x_{3d}^d(4s, s)$</td>
<td>3.45</td>
<td>3.42</td>
<td>3.42</td>
<td>3.43</td>
<td>3.41</td>
<td>2.56</td>
</tr>
<tr>
<td>$3d^{n-1} 4s^2$</td>
<td></td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>$x_{3d}^d(3d, d)$</td>
<td>1.73</td>
<td>1.55</td>
<td>1.31</td>
<td>1.04</td>
<td>0.858</td>
<td>2.80</td>
</tr>
<tr>
<td>$x_{3d}^d(3d, d)$</td>
<td>1.70</td>
<td>1.57</td>
<td>1.35</td>
<td>1.02</td>
<td>0.826</td>
<td>2.81</td>
</tr>
<tr>
<td>$x_{3d}^d(3d, d)$</td>
<td>1.73</td>
<td>1.50</td>
<td>1.33</td>
<td>1.16</td>
<td>0.869</td>
<td>2.80</td>
</tr>
<tr>
<td>$x_{3d}^d(3d, d)$</td>
<td>1.66</td>
<td>1.52</td>
<td>1.32</td>
<td>1.09</td>
<td>0.868</td>
<td>2.82</td>
</tr>
</tbody>
</table>
given in Table VI. A weak linear $N$-dependence appears in the case of $x_{4s}^4(3d, d)/x_{3d}^2(3d, d)$ ratio only. It is interesting to note that the parameter ratios for both the considered configurations are quite similar, while their absolute values are rather different. The $N$-dependence of the BA parameters is regular and may be approximated by quadratic functions of $N$. The corresponding expressions are collected in Table VI. One can expect that these observations may be extended to the exact (including continuum contributions) parameter values. Consequently, the expressions given in Table VI may be applied to reduce the number of independent parameters in semiempirical parametric hf calculations.

The experimental least square fits of the BA parameters for the $3d^N 4s$ configuration atoms have recently been determined by Dembczyński [3, 10] and by Johann [20]. The set of fitted values of the parameters is still rather incomplete and not very accurate. For example, in the case of the $3d^N 4s$ configuration of iron, the fitted values of $x_{2d}(3d, d)$ and $x_{2d}(4s, s)$ vary, respectively, from 0.08 [3] to 0.12 and from 0.07 [3] to 0.19 [20]. Therefore it is premature to perform a detailed comparison of the fitted and calculated parameter values. In general, the fitted parameters are greater (in absolute values) by a factor of 2-3 than the calculated ones. The general form of the $N$-dependence and the relative magnitude of the fitted parameters are however rather well reflected by the ones calculated using the discrete spectrum states only. This result confirms our expectation concerning a practical usefulness of the expressions collected in Table VI.

The most important factor responsible for the differences between the fitted and the calculated parameter values is certainly the neglect of the continuous spectrum contributions. Another reason of the discrepancy is a limited applicability of the perturbation theory. The CI effects may be treated by the second order perturbation theory under condition that the interacting configurations are separated well enough. This condition is usually fulfilled, except for the open $\rightarrow$ open shell excitations. The separation of the HF average energies of $3d^N 4s$ and $3d^{N-1} 4s^2$ configurations is rather small but noticeable. However for Ti and for V they are practically degenerated. Therefore, for this kind of excitations, the perturbation theory results in the case of Fe, Mn and Cr are rather inaccurate. In the case of Ti and V the perturbation theory is not applicable and consequently, the corresponding parameter values have not been included in Table II. From this point of view, a uniform treatment of the $(3d + 4s)^{N+1}$ configuration would be much more adequate. An importance of this kind of effects has already been pointed out by Bauche and Bauche-Arnoult [21].

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References


