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Ab initio evaluation of hyperfine-structure electronic parameters in the iron atom

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Résumé. — Dans le cadre de l’application de la technique des opérateurs effectifs à la structure hyperfine atomique des configurations \(l'Nl'\), nous avons calculé par la méthode MCHF les paramètres électroniques hyperfins relatifs aux opérateurs à deux corps provenant du mélange des termes \((3d^7 4F, 4S)^{3,5F}\) de l’atome de fer avec les configurations lointaines. La comparaison avec les 13 valeurs déduites des mesures expérimentales par Dembczyński (J. Physique 41 (1980) 109) est satisfaisante, sauf pour trois d’entre elles. L’un de ces désaccords reste inexpliqué.

Abstract. — In the frame of the effective-operator technique applied to atomic hyperfine structure in the \(l'Nl'\) configurations, we have computed ab initio, by means of the MCHF method, the electronic hfs parameters relevant to the two-body far-configuration-mixing effects on the \((3d^7 4F, 4S)^{3,5F}\) terms of the iron atom. The comparison with the 13 values deduced from experimental measurements by Dembczyński (J. Physique 41 (1980) 109) is satisfactory, except for three of them. One of these discrepancies remains unexplained.

1. Introduction.

The use of effective operators and effective parameters has been for dozens of years an essential tool in phenomenological physics. In atomic spectroscopy, whose fundamental interactions are well known, it has been applied first to the refined interpretations of the level energies [1, 2], then to the hyperfine structures, etc. When it comes to a high degree of sophistication, many experimental accurate values are needed for the determination of numerous parameters. This is generally not a real problem in the field of level energies, but may become one for hyperfine structures, whose accurate measurements are painstaking.

The most sophisticated phenomenological formalism for atomic hyperfine structures (hfs) is by now that of Bauche-Arnoult for the case of \(l'Nl'\) configurations [3]. It is the generalization of the results of the same author for the \(l^N\) configurations [4], which are in the line of the study of the \(p^N\) levels by Judd [5]. The simplest cases for \(l'Nl'\) are clearly those with \(l' = 0\). However, not less than 17 electronic hyperfine parameters are already needed in the \(d^N\) configurations, for example, for describing the one- and two-body far-configuration-mixing corrections to the expectation values of the three parts of the magnetic dipole hfs operator

\[
H_m = \frac{2 \beta \beta_N \mu_N}{I} \left( \sum_{\ell=1}^{N} [I^{(1)}_{\ell}] - \sqrt{10} \{ s^{(1)}_1 C^{(2)}_{1} \}^{(1)} + \frac{8 \pi}{3} \delta(s_{1}) s^{(1)}_{1} I^{(1)} \right)
\]

in classical notations [6]. In Bauche-Arnoult’s formalism, each hfs parameter \(a_{sL}^{k}\) for a given Russell-Saunders term \(aSL\) and one of the three parts of \(H_m\) (where \((kk) = (01)\), (12) and (10) respectively) is written \(a^{k}(1 + A_{sL}^{k})\), where \(a^{k}\) does not depend on the term, and \(A_{sL}^{k} (< 1)\) can be expanded numerically over parameters denoted \(x_i\).

For finding an application of this formalism, the \(d^N\) configurations are the best candidates, because:

(i) compared to the \(p^N\) configurations, they are complex enough for a sufficient number of measurements to be achieved;
(ii) compared to the \(f^N\) configurations, their close-configuration-mixing situation is clear, because the low-lying \((d + s)^N\) group of configurations in the transition metals is generally well isolated from perturbing even configurations.

The \(3d^N4s\) configurations have one extra advantage: their mixing with \(3d^{N-1} 4s^2\) and \(3d^{N+1}\) is small in the neutral atoms and singly-charged ions [2].

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Recently, Dembczynski [7] has chosen very adequately the case of the lowest two Russell-Saunders terms of the 3d\(^7\) 4s configuration of FeI, in which the \(^{57}\)Fe hyperfine structures of seven levels have been measured with high accuracy in Bonn [8] by the Atomic-Beam Magnetic Resonance method following laser illumination (ABMR-LIRF). He has first studied with great care [9] the intermediate coupling inside the 3d\(^7\) 4s configuration and its (small) mixing with 3d\(^6\) 4s\(^2\) and 3d\(^8\) : in the Slater-Condon interpretation, he has gone so far as introducing the two-electron magnetic interactions (spin-spin and spin-other-orbit), and the three-body effective operators for far-configuration mixing. From the eigenvectors, he has deduced the coefficients of all the one-body and two-body hyperfine parameters for the levels of the 3d\(^7\) 4s \(^5\)F and \(^5\)F terms of interest. Through the subsequent least-squares 6-parameter fit of the 7 measurements and the use of other information, he has eventually determined the numerical values of the 4 one-body parameters \(a_{4s}(s), a_{3d}(s), a_{3d}(l), a_{3d}(sC)\) and 11 two-body parameters.

In the present study, we are interested in testing these values through comparison with the results of the Multiconfigurational Hartree-Fock method (MCHF). In § 2, we briefly recall the principles of the calculations, which are very similar to those carried out, for example, by Bauche-Arnoult and Labarthe [10]. The numerical values presented in § 3 confirm, as a whole, the assumption and results of Dembczynski [7]. However, we propose to change three parameter values, and we discuss in § 4 one large and irreducible discrepancy.

2. Computational method.

For interpreting ab initio the hyperfine structures of the 3d\(^7\) 4s levels in FeI, we must evaluate the first-order parameters and the corrections due to the mixing with other configurations. The hyperfine operator \(H_h\) (Eq. (1)) being a monoelectronic operator, the second-order corrections of interest are due to the mixing of 3d\(^7\) 4s with monoexcited configurations only.

Concerning the first-order parameters, the Hartree-Fock (HF) method is adequate. For the corrections linked with the single excitations:

(i) the close-configuration mixing of 3d\(^7\) 4s with 3d\(^6\) 4s\(^2\) and 3d\(^8\) has been treated by Dembczynski [7, 9] in the Slater-Condon parametric scheme;

(ii) the effects of the excitations from the closed subshells to the open subshells can be evaluated from suitable Hartree-Fock (HF) calculations;

(iii) the effects of the excitations from closed or open subshells to empty subshells are conveniently evaluated through the Multiconfigurational Hartree-Fock method (MCHF).

The reason why the mixing of the relevant \(\Psi_o\) state with the infinite set of states resulting from the \(nl \rightarrow n'l'\) excitation (with fixed \(n, l\) and \(l'\), and all possible values of \(n'\), including continuum indices) can be rigorously described as the mixing of \(\Psi_o\) with the state resulting from the excitation of \(nl\) towards one excited \(l'\) orbital (virtual orbital) has been given initially by Löwdin and Shull [11]. It makes the major advantage of the MCHF method for the refined ab initio study of hyperfine structure, through the determination of one virtual orbital for each \((nll')\) case. Labarthe has built computer codes for solving the angular problems [12, 13] and for elaborating approximate virtual orbitals [14] as inputs to the MCHF 77 code of C. Froese Fischer [15].


We list in table I the numerical results of our ab initio computations for 13 second-order parameters listed by Dembczynski and denoted \(x_i\) (i = 1 through 13). All the MCHF calculations, except that for \(x_7\), have

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Excitation</th>
<th>Type of calculation</th>
<th>(Ab\ initio) value</th>
<th>Experimental value [7]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_1)</td>
<td>3d (\rightarrow) 4s</td>
<td>MCHF</td>
<td>(-63 \times 10^{-6})</td>
<td>(\sim 0)</td>
</tr>
<tr>
<td>(x_2)</td>
<td>3d (\rightarrow) 4d</td>
<td>MCHF</td>
<td>0.134</td>
<td>0.08</td>
</tr>
<tr>
<td>(x_3)</td>
<td>-</td>
<td>-</td>
<td>0.088</td>
<td>0.08</td>
</tr>
<tr>
<td>(x_4)</td>
<td>-</td>
<td>-</td>
<td>-0.031</td>
<td>-0.062</td>
</tr>
<tr>
<td>(x_5)</td>
<td>3d (\rightarrow) 4g</td>
<td>MCHF</td>
<td>0.030</td>
<td>(\sim 0)</td>
</tr>
<tr>
<td>(x_6)</td>
<td>-</td>
<td>-</td>
<td>-0.013</td>
<td>(\sim 0)</td>
</tr>
<tr>
<td>(x_7)</td>
<td>4s (\rightarrow) 4s</td>
<td>MCHF</td>
<td>0.209</td>
<td>0.068</td>
</tr>
<tr>
<td>(x_8)</td>
<td>4s (\rightarrow) 4d</td>
<td>MCHF</td>
<td>(63 \times 10^{-5})</td>
<td>(\sim 0)</td>
</tr>
<tr>
<td>(x_9)</td>
<td>-</td>
<td>-</td>
<td>(17 \times 10^{-4})</td>
<td>(\sim 0)</td>
</tr>
<tr>
<td>(x_{10})</td>
<td>(\text{n's} \rightarrow) 3d</td>
<td>HF</td>
<td>(-0.025)</td>
<td>?</td>
</tr>
<tr>
<td>(x_{11})</td>
<td>(\text{n's} \rightarrow) 4s</td>
<td>HF</td>
<td>(-55 \times 10^{-4})</td>
<td>-0.113</td>
</tr>
<tr>
<td>(x_{12})</td>
<td>3d (\rightarrow) 4s</td>
<td>HF</td>
<td>(\sim 0)</td>
<td>(\sim 0)</td>
</tr>
<tr>
<td>(x_{13})</td>
<td>4s (\rightarrow) 3d</td>
<td>HF</td>
<td>(\sim 0)</td>
<td>(\sim 0)</td>
</tr>
</tbody>
</table>
been made with a fixed core 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 4s and the optimization of the 3d radial function and of the relevant virtual orbital; the « perturbed » state \(\Psi_0\) belonged to the term \(T = (3d^6 4F, 4s)^3F\), and the appropriate off-diagonal energy element was determined by means of Labarthe's angular code. The case of \(x_1\) is described in \$ 4.

The HF calculations for \(x_{10}\) and \(x_{11}\) simply consisted in getting by means of the HF code the values of the off-diagonal energy elements and excited-configuration contributions, easy to obtain from the occupied radial orbitals of the term \(T\). For the cases of \(x_{12}\) and \(x_{13}\), it was only checked that the off-diagonal \(\langle r^{-3}\rangle\) integral

\[
I_{3d4s} = \int_0^\infty R_{3d}(r) \frac{1}{r^3} \int_0^\infty R_{4s}(r) dr \text{ is very small (61 x 10}^{-6}\) when computed, for example, from the HF 3d and 4s orbitals of the term \(T\). This follows Dembczyński's argument [7].

In table I \(n'(\text{resp. } n'')\) is the principal quantum number of the relevant empty (resp. closed) subshell.

4. Discussion.

There appears in table I a qualitative agreement between the values derived by Dembczyński [7] from the seven experimental measurements, and the \textit{ab initio} evaluations. Only three significant discrepancies occur.

First, Dembczyński has assumed that the \(x_2\) and \(x_3\) parameters are equal. Indeed, he could not determine them separately, although they are among the largest in table I. But, actually, their formal expressions only differ in that the radial integral \(R^2(3d 3d, n'd 3d)\) in \(x_3\) is replaced in \(x_2\) by \(R^2(3d 3d, n'd 3d)\) (see Eqs. (3) and (4) in ref. [7]). Now, it has been observed in a number of cases (see [16]) that the ratio \(R^4/R^2\) of that type is remarkably constant, and close to 0.7. This is again true for the \(x_{3}/x_2\) ratio in table I.

Second, the \(x_2\) and \(x_{11}\) parameters are both quite different in the last two columns of table I. However, it must be observed:

(i) that their sum \(x_7 + x_{11}\) is equal to 0.204 and 0.045 in the \textit{ab initio} and experimental evaluations respectively, showing also a large discrepancy;

(ii) that it is that sum alone, and not both parameters themselves, which can be derived directly from the experimental measurements, more precisely, from the difference between the \(\Delta^{10}\) factors for the \(4F\) and \(3F\) terms, the only ones measured (see Eqs. (21) and (22) in ref. [7]);

(iii) that, due to the correspondence between holes and particles, the numerical difference between the coefficients of \(x_7\) (excitations from 4s to empty shells) and \(x_{11}\) (excitation from closed shells to 4s) in the \(\Delta^{10}\) factor of any RS term of 3d\(^8\) 4s (for a given value of \(N\)) is the same; this property is already apparent in table VI of reference [3], and shows that these parameters definitely cannot be derived separately from measurements inside 3d\(^7\) 4s.

For determining \(x_7\), Dembczyński used a formal relation between the spin polarizations by the 3d\(^6\) and 3d\(^7\) subshells, which is valid to the second order of perturbation in the central-field scheme (Eq. (43) in ref. [7]). Now, first, it is quite unlikely that the central fields adequate for 3d\(^6\) 4s\(^2\) and 3d\(^7\) 4s resemble enough, and, second, the spin-core polarization in 3d\(^7\) 4s\(^2\) results from a near cancellation between the four \(s^2\)-subshell contributions [17]. We used the following alternative way for evaluating \(x_7\). A two-configuration MCHF calculation was run, with the \((3d^7 4F, 4s)^3F\) and \((3d^6 4F, 5s)^3F\) terms, and frozen radial orbitals 1s, 2s, 2p, 3s, 3p, 3d, 4s, as obtained previously in a HF calculation for the center of gravity of the \((3d^7 4F, 4s)\) sub-configuration. Only the 5s virtual orbital was optimized. Of course, due to Brillouin's theorem [18], it would not have converged to anything if the 4s orbital had also been free. Then formula (8) of reference [7] was applied, with \(n''\)'s \(\equiv 5s\), giving the value 0.209 in table I.

Another quicker way for computing \(x_7\) can be proposed. Freezing the orbitals in the same way as above, one can compute two monoconfigurational HF states, with the \((3d^7 4F, 4s)^3F\) and \((3d^6 4F, 5s)^3F\) formal energies respectively. The obtained \(\langle \Psi_{4s}(0) \rangle^2\) values are such that \(x_7 = 0.295\). But it is felt that this value contains larger higher-order contributions than the previous one.

Concerning the \(x_{14}\) value, it is simply the sum of three quantities (see Eq. (12) in ref. [7]), depending only on occupied subshells. Among these quantities, that for 2s largely predominates, which means that the small value obtained for \(x_{14}\) is certain, because it does not result from a near-cancellation.

The puzzling discrepancy actually concerns the sum \(x_7 + x_{11}\), which is directly derived from experiment. We have searched in vain in several directions for solving that difficulty: possibility that the (large) spin-core polarization effect by the 3d electrons be appreciably different for the \(5F\) and \(3F\) terms of interest, far-configuration-mixing effects on the off-diagonal hfs parameters between \(5F\) and \(3F\), or between configurations [19].

5. Conclusion.

The \textit{ab initio} MCHF evaluations essentially agree with the parameter values derived from experiment by Dembczyński [7]. Among the two discrepancies which are noteworthy, one concerns the \(x_{14}\) parameter and is linked with the fact that it is not possible to derive the parameters \(x_7\) and \(x_{11}\) from measurements in the 3d\(^7\) 4s configuration only.

The other discrepancy, which deals with the value of \(x_7 + x_{11}\), is also apparent in the fact that the value of the ratio \(\beta_{3d^7 4s}^4s(4s) = a_{5F}^2(4s)/a_{5F}^2(4s)\) is equal to 0.944 in the abstract of reference [7] and to about 1 + 8 \(\times (x_7 + x_{11})/5 \approx 1.3\) in the \textit{ab initio} evaluation, using equations (21) and (22) of reference [7] and the values in our table I. Actually, in \(p^8\)'s configurations, the large
decrease of $|\Psi(0)|^2$ from the $S' = S + 1/2$ to the $S' = S - 1/2$ term built on the same $(S, L)$ Hund term of $1^N$ is a well-known phenomenon (e.g., see [20]). We have found no explanation for the present discrepancy.

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References