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R-matrix calculation of the energy-positions of high-lying 4fnf \( J = 5, 6 \) autoionising levels of barium

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Abstract. — Theoretical energy-positions of 4fnf \( J = 5, 6 \) autoionising levels of barium are obtained by a combination of the eigenchannel \( R \)-matrix and the Multichannel Quantum Defect Theory (MQDT) methods. High-lying 4fnf \( J = 5, 6 \) levels \( (n > 8) \) located below the Ba\(^+\) 4f\(_5/2\) threshold are investigated. The calculation accounts for the mixing of 4fnf series with 4fnp and 7pnf series, as well as for the interaction with thirty continua. Calculated energies agree well with recent measurements obtained in a two-step laser experiment. Strong mixing between 4f\(_5/2\)n\(_7/2\) and 4f\(_7/2\)n\(_5/2\) series is found, while the 4f\(_5/2\)n\(_5/2\) and 4f\(_7/2\)n\(_7/2\) series are almost pure \( jj \)—coupled. Because of strong centrifugal barrier and two-electron correlation effects, the 4fnf series have large quantum defects depending strongly on the series studied.

1. Introduction.

In the last few years, several theoretical investigations devoted to alkaline-earths Ca to Ra (1-7, and references therein) have demonstrated that a very realistic description of these atoms

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can be attained by combining the eigenchannel $R-$matrix approach [8] with the Multichannel Quantum Defect Theory (MQDT) [9]. Various studies deal with bound or autoionising Rydberg levels observed experimentally in one photon absorption from the ground state $m_{D}2$ or populated using multistep laser spectroscopy. Various observables, such as energy positions, autoionisation widths, profiles of the resonances or photoelectron angular distributions, are well reproduced by the calculations. Most of these studies concern low-lying doubly-excited levels $m'l'nl J$ located below the lowest $m_{D}0$ threshold, involving small orbital momenta $l' \leq 2$ and $l \leq 3$, and corresponding to small $J$ values, $(J \leq 3)$.

The applicability of the eigenchannel $R-$matrix method for handling more excited autoionising states, or series involving higher angular momenta remains to be probed. Indeed, at an energy high above the first ionisation limit of the neutral atom, a multitude of interacting series exists. Furthermore, orbitals with increasing $l-$values are concentrated further from the core: this makes them more sensitive to correlation effects. Concerning the extension to the high-energy range, one study should be mentioned: Kim and Greene calculated the photoabsorption spectrum of Ca up to the 6s threshold [2], but no experimental data are available to check the reliability of their predictions.

This paper deals with the $4fnf J = 5,6$ doubly-excited autoionising Rydberg series in barium, converging toward the $4f_{j/2}$ and $4f_{7/2}$ Ba$^+$ ionisation thresholds, located respectively at 90 293.49 cm$^{-1}$ and 90 518.19 cm$^{-1}$ above the ground state $6s^2 1S_0$, that is approximately 50 000 cm$^{-1}$ above the first ionisation limit Ba$^+$ 6s$_{1/2}$, but only 30 000 cm$^{-1}$ below the double-ionisation limit Ba$^{2+}$ 1S$_0$ located at 122 721.29 cm$^{-1}$. The energy range studied extends from 88 500 cm$^{-1}$ up to the $4f_{5/2}$ threshold, i.e. it corresponds to effective quantum numbers $\nu_{4f_{5/2}} \geq 8.03$ and $\nu_{4f_{7/2}} \geq 7.55$ respective to the $4f_{5/2}$ and $4f_{7/2}$ thresholds.

The investigation of the $4fnf$ series of Ba is a theoretical challenge, because both electrons correspond to $l = 3$ orbitals with a particular behaviour. Indeed, in Ba$^+$ the effective potential resulting from the Coulomb and centrifugal potentials exhibits two wells [10]. The deep inner valley induces a large quantum defect ($\delta_{nf} \approx 0.9$) for the highest members of the $nf$ series [11], the corresponding orbitals being mainly concentrated in the outer minimum. On the opposite, the $4f$ orbital collapses in the inner well, which is reflected in its smaller quantum defect $\delta_{4f} \approx 0.31$, and in the rapid increase of $\delta_{nf}$ for low $n-$values [11]. In the $4fnf$ series of Ba, electron correlation effects are expected to be large and to strongly influence the behaviour of both f-orbitals.

The $4fnf$ series have been recently investigated by de Graaff et al. [12] using a two-step pulsed laser-excitation scheme starting from the 5d$^2$ metastable levels and using the 5dnf autoionising resonances as intermediate levels. Only results concerning the energy-positions of resonances are discussed here, a more complete study including the excitation spectra and the $J = 4$ spectrum will be presented in a forthcoming paper [13].


The present approach, which combines the eigenchannel $R-$matrix and MQDT methods, is described elsewhere [1-7] and only some key elements are summarized here. Independent $R-$matrix calculations are performed for each given $LS-$symmetry. The $LS-$coupled wavefunctions of the pair of valence electrons outside a frozen core are determined within a finite reaction volume $V$, using the eigenchannel $R-$matrix method. The variational calculation gives the logarithmic derivatives of the escaping electron’s wavefunctions on the surface of the reaction volume. Matching the wavefunctions to Coulomb expansions valid outside $V$, leads to $LS-$coupled short-range reaction matrices $K^{LS}(E)$ depending smoothly on energy and
characterising the interactions between all open and closed channels. In the present problem, calculations deal with the $^3G_e$, $^1S_H$, $^1S_P$ and $^3J_e$ symmetries occurring in the description of the 4fnf series of Ba with $J = 5, 6$. The latter $^3J_e$ symmetry is not involved directly in the analysis of the 4fnf series, but appears indirectly owing to the coupling of the 4fnf series with the ml'el continua with high $l$—values ($l \geq 4$) built on less excited Ba$^+ml'$ cores.

The $LS$—coupled two-electron basis-functions of the form ml'n'l used in the variational calculation are chosen to describe two different groups of channels. The first group contains the open or “weakly closed” channels, in which the outermost electron can escape from $V$. This set includes ml'n'l channels converging to the Ba$^{+}6s$, 5d, 6p, 7s, 6d, 4f and 7p thresholds. For the open channels corresponding to an ionisation threshold energy lower than, or equal to Ba$^{+}6d$, all possible $l$—values are introduced. Concerning the “weakly closed” channels 4fnl and 7pnl, the $l$—values are restricted to $l \leq 3$, in order to avoid to handle too many channels in the MQDT treatment. The 7pnl channels are treated as “weakly closed”, because the interaction between the series 4fnp and 7pnf is very strong. The 4fnf $J = 6$ series are not perturbed by the 4fnp or 7pnf ones. For the 4fnf $J = 5$ series, the 4fnp and 7pnf series contribute only to the $^3G_e$ symmetry. The Ba$^{+}7p_{1/2}$ and $7p_{3/2}$ limits are located at 91 424.95 cm$^{-1}$ and 92 046.15 cm$^{-1}$, i.e. relatively close to the 4f limits. The 4fnl and 7pnl channels being treated as “weakly closed” in the present calculation, a reaction volume of radius $r_0 = 30$ au, large enough to enclose the charge distributions of the Ba$^{+}4f$ and 7p wavefunctions has been chosen. The second group of basis-functions, which is the largest one, corresponds to “strongly closed” channels, where both electrons are confined within $V$; these channels converge to Ba$^{+}$ thresholds more excited than the 7p one and were found to be essential to describe correlation and polarisation effects. This second group contains all possible ml'n'l functions with $l' \leq 7$ and $l \leq 8$ and includes two to eight different $m$—values. Depending on the $LS$—symmetry, 300 to 400 two-electron basis-functions are introduced in the variational calculation.

Spin–orbit effects are completely neglected within the reaction volume, but introduced in the asymptotic region. Fine-structure effects are accounted for using the $(jj - LS)$ frame-transformation. This allows the $LS$—coupled reaction-matrice $K^{LS}(E)$ to be recoupled in larger $jj$—coupled reaction-matrices $K(E)$ referring to the $jj$—coupled dissociation channels $i$. It has been verified that for 4fnf levels, the $jj$—coupling is better adapted than the $jk$—coupling for describing the resonances.

In the study of even-parity states of barium with $J = 5$, (respectively $J = 6$), 36 channels, (respectively 33), are included in the $R$—matrix calculation of the short-range reaction-matrice $K(E)$. The corresponding dissociation channels are displayed in tables I and II. Channels which are open in the energy range studied are denoted by ml'el'l; they describe all the thirty continua available for ionisation from the 4fnf levels. Simultaneously, ml'l'l'njl denotes “weakly closed” channels. Let us recall that “weakly closed” channels corresponding to a high angular-momentum Rydberg electron $l \geq 5$ have not been introduced in the present calculation.

At this point, the method links with standard MQDT procedures [9]. This permits us to calculate observable quantities from the eigenvalues $\mu_{a}$ and the eigenvectors $U_{i\alpha}$ of the short-range reaction matrices. At this stage of the calculation, the introduction of experimental $j$—dependent ionisation threshold energies accounts for fine-structure effects.

The structure of the autoionising spectra results from the coupling of $N_{c}$ closed channels with a larger number $N_{o}$ of open channels. The determination of the energies of the doubly-excited states can be obtained from the complex reaction-matrix

$$\kappa_{cc} = K_{cc} - K_{co}(i\mu_{oo} + K_{oo})^{-1}K_{oc}$$

restriction of the $K$—matrix to the closed-channel space [9]. Standard MQDT techniques adapted to bound spectra, applied using $K_{eff}$ the real part of $\kappa_{cc}$, give the positions of resonant
Table I. — Dissociation channels in $jj$-coupling for even-parity states of barium with $J = 5$.
Dimension: 36. $ml_j$: inner electron orbital: 6s$_{1/2}$, 5d$_{3/2}$, 5d$_{5/2}$, 6p$_{1/2}$, 6p$_{3/2}$, 7s$_{1/2}$, 6d$_{3/2}$, 6d$_{5/2}$, 4f$_{5/2}$, 4f$_{7/2}$ or 7p$_{3/2}$. $\epsilon l_j$ or $nl_j$: outer electron orbital $\epsilon l_j$ belongs to an open channel. $nl_j$ belongs to a "weakly closed" channel.

<table>
<thead>
<tr>
<th>$6s_{1/2}$</th>
<th>5d$_{3/2}$</th>
<th>5d$_{5/2}$</th>
<th>6p$_{1/2}$</th>
<th>6p$_{3/2}$</th>
<th>7s$_{1/2}$</th>
<th>6d$_{3/2}$</th>
<th>6d$_{5/2}$</th>
<th>4f$_{5/2}$</th>
<th>4f$_{7/2}$</th>
<th>7p$_{3/2}$</th>
</tr>
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<tbody>
<tr>
<td>$\epsilon g_{9/2}$</td>
<td>$\epsilon g_{7/2}$</td>
<td>$\epsilon e_{11/2}$</td>
<td>$\epsilon e_{13/2}$</td>
<td>$\epsilon e_{13/2}$</td>
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<td>$\epsilon i_{11/2}$</td>
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<tr>
<td>$\epsilon k_{15/2}$</td>
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<td>$\epsilon k_{15/2}$</td>
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</tbody>
</table>

states and the admixture of $jj$—coupled dissociation channels $i$ into each level. Channel mixing can also be displayed using Lu-Fano plots. The $N_c$ closed channels considered in the MQDT treatment are identical to the "weakly closed" channels appearing in the $R$-matrix calculation. In the present study, the MQDT analysis of the resonance energies of $J = 6$ states reduces to a three-closed channel problem involving 4f$_j$-nf$_j$ series only. For $J = 5$ states, the six-channel calculation includes the four channels 4f$_j$-nf$_j$ and the two channels 4f$_{7/2}$np$_{3/2}$ and 7p$_{3/2}$nf$_{7/2}$.

3. MQDT analysis of the resonances below the Ba$^+$ 4f$_{5/2}$ threshold and discussion.

3.1 Eigenchannel MQDT parameters. — The $\mu_\alpha$ and $U_{i\alpha}$ MQDT parameters relevant to the calculation of the resonance-energies are given by the eigenvalues and eigenvectors of the $K_{\text{eff}}(E)$ matrices. However the main properties of these MQDT parameters can be inferred from the analysis of the $K^{LS}(E)$ matrices whose eigenvalues are denoted $\bar{\mu}_\alpha$. Let us emphasize that these quantum defects $\bar{\mu}_\alpha$ are equal to those of the $K(E)$ matrices.

In the studied energy-range, from 88 500 cm$^{-1}$ up to the Ba$^+$ 4f$_{7/2}$ threshold, the eigenvalues $\bar{\mu}_\alpha$ of the short-range reaction-matrices $K^{LS}(E)$ are nearly energy-independent, except for the eigenquantum defect labelled $\bar{\mu}_{6dni}$ according to the dominant 6dni ($l = 6$) character of the corresponding eigenvector. For the $^3J^e$, $^1I^e$ and $^3F^e$ symmetries, $\mu_{6dni}$ increases from about 0.1
(mod. 1) to 0.95 (mod. 1), when the energy increases from 88 500 cm\(^{-1}\) up to 90 500 cm\(^{-1}\). For the \(^1\)H\(^e\), \(^3\)H\(^e\) and \(^3\)G\(^e\) symmetries, this variation reduces to 0.1 (mod. 1) to 0.3 (mod. 1).

Concerning the \(\mu_{4fnf}\) eigenquantum defects, the differences between the values calculated for the \(1^1\)L\(^e\) and \(3^1\)L\(^e\) terms |\(\Delta \mu_{4fnf}(L)\)| = |\(\mu_{4fnf}(1^1\)L\(^e\)\) - \(\mu_{4fnf}(3^1\)L\(^e\)\)| are large and respectively equal to 0.480 (mod. 1) and 0.390 (mod. 1) for the \(1^3\)L\(^e\) and \(3^3\)L\(^e\) terms. These values are very close to the maximum value |\(\Delta \mu\)| = 0.5 (mod. 1). This point will be commented further in section 3.2.

The eigenvectors of the \(K^{LS}(E)\) matrices show that an important mixing, due to electronic interaction only, exists between the various \(ml'nl\) channels. This mixing reflects the importance of correlation effects. In particular, the 4fnf \(LS\) eigenchannels are strongly coupled with other \(ml'nl\) \(LS\) channels. The importance of channel mixing is not equal for the two 4fnf \(1^1\)L\(^e\) and \(3^1\)L\(^e\) eigenchannels with the same \(L\) value. The channels corresponding to an even value for \((L + S)\) are more strongly mixed. Indeed, the corresponding functions, which, when \(l = l'\), are antisymmetrical in the interchange of the angular \((\theta_1, \phi_1)\) and spin \((m_s)\) coordinates of the two valence electrons are symmetrical in the exchange of \(r_1\) and \(r_2\), the radial distances of the two electrons from the nucleus. Therefore, in the two-electron wavefunction, the electronic probability density is maximum at \(r_1 = r_2\) when \((L + S)\) is even and the corresponding states are more strongly correlated than the states \(l = l'\) and \((L + S)\) odd with a vanishing electronic density at \(r_1 = r_2\) [14]. For example for the \(3^1\)L\(^e\) symmetry, the eigenchannel corresponding to the largest weight of the \(LS\)–coupled channel 4fnf can be expanded as:

\[
\sqrt{0.82} \ 4fnf - \sqrt{0.11} \ 6dn - \sqrt{0.06} \ 6pn - \sqrt{0.01} \ 6ng + ... 
\]

and differs from the corresponding eigenfunction of the \(1^1\)L\(^e\) eigenchannel:

\[
\sqrt{0.47} \ 4fnf - \sqrt{0.32} \ 6dn - \sqrt{0.18} \ 5dng - \sqrt{0.02} \ 6dn - \sqrt{0.01} \ 6pn + ... 
\]

This large channel mixing between the 4fnf channels and channels \(ml'nl\) with high \(l\) values converging toward lower ionisation thresholds \(ml'\) justifies the introduction of basis-functions \(ml'nl\) with large \(l\) and \(l'\) values in the \(R\)–matrix variational calculation.

The restriction of the \(K_{eff}(E)\) matrices to the space of “weakly closed” channels induces a change in the eigenquantum defects \(\mu_\alpha\) of the eigenchannels, this change being especially large for strongly mixed channels. For example, for the \(1^1\)L\(^e\) symmetry, the eigenquantum defect \(\mu_{4fnf}\) of the \(K_{eff}\) matrix is 20% smaller than the value \(\mu_{4fnf}\) obtained for the \(K^{LS}(E)\) matrix. This restriction increases |\(\Delta \mu_{4fnf}(L)\)|, with respect to |\(\Delta \mu_{4fnf}(L)\)| and leads to |\(\Delta \mu_{4fnf}(L = 0)\)| = 0.485 and |\(\Delta \mu_{4fnf}(L = 5)\)| = 0.475 respectively. The eigenquantum defects \(\mu_\alpha\) used in the MQDT analysis are reported in table III. The eigenchannels \(\alpha\) are identified according to the dominant component in the eigenvectors.

The orthogonal matrix \(U_{i\alpha}\), which connects the dissociation channels \(i\), strictly \(jj\)–coupled, to the \(K_{eff}(E)\) matrix eigenchannels \(\alpha\), reduces for \(J = 6\) to the standard \((jj – LS)\) transformation, but for \(J = 5\) it accounts for the mixing due to the electrostatic interaction of the three \(3^G\)\(^e\) terms belonging to the 4fnp, 4fnf and 7pnf configurations. The 7pnf and 4fnp levels are strongly mixed, the admixture amounting to 30%, but the latter system (7pnf+ 4fnp) is nearly disconnected from the 4fnf levels, the mixing being less than 0.1%. Because the 4fnf configuration involves two electrons with equal orbital momentum, each \(jj\)–coupled level 4fnf\(_{3/2,3/2}\) or 4fnf\(_{1/2,1/2}\) is connected unambiguously to a single \(LS\)–coupled level – (this correspondence is reported in Tab. IV) –, meanwhile the two \(jj\)–coupled levels 4fnf\(_{3/2,3/2}\)\(_{1/2}\) and 4fnf\(_{1/2,1/2}\)\(_{3/2}\) are mainly related to the two levels \(1^1L_{J=1}\) and \(3^3L_{J=1}\), the expansion coefficients on the other \(LS\)–coupled terms being very small. In addition, the 4fnf\(_{3/2,3/2}\)\(_{1/2}\) and 4fnf\(_{1/2,1/2}\)\(_{3/2}\) eigenchannels are equally shared on the \(jj\)–coupled dissociation channels 4fnf\(_{3/2,3/2}\)\(_{1/2}\) and 4fnf\(_{1/2,1/2}\)\(_{3/2}\),
Table III. — Eigenchannel quantum defects $\mu_\alpha$ (mod. 1) for even-parity states of barium with $J = 5$ or 6. The theoretical values are the eigenvalues of the $K_{\text{eff}}(E)$ matrices at the energy $E = 89\,910$ cm$^{-1}$ above the ground state. The eigenchannels $\alpha$ are labelled according to the dominant component in the eigenchannel functions. (\*) : eigenchannel involved in the analysis of $J = 6$ levels. (+) : eigenchannel involved in the analysis of $J = 5$ levels.

<table>
<thead>
<tr>
<th>Eigenchannel $\alpha$</th>
<th>$\mu_\alpha$</th>
<th>$J = 6$</th>
<th>$J = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4$fnf$ $^1$I</td>
<td>0.321</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>4$fnf$ $^3$I</td>
<td>0.805</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>4$fnf$ $^1$H</td>
<td>0.846</td>
<td>*</td>
<td>+</td>
</tr>
<tr>
<td>4$fnf$ $^3$H</td>
<td>0.371</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>4$fn$ $^3$G</td>
<td>0.848</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>4$nf$ $^3$G</td>
<td>0.885</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>7$pnf$ $^3$G</td>
<td>0.023</td>
<td></td>
<td>+</td>
</tr>
</tbody>
</table>

Table IV. — Quantum defects $\delta$ (mod. 1) for the weakly perturbed even-parity levels of barium with $J = 5$ or 6, in the energy-range extending from 88 500 cm$^{-1}$ up to the Ba$^+$ 4$fs_f$/2 ionisation threshold. The exact values of some quantum defects, including the entire parts, are tentatively given in the third column (see Sect. 3.2). The levels are labelled in $jj-$coupling and the corresponding $LS-$labels unambiguously affected to these levels are indicated.

<table>
<thead>
<tr>
<th>Levels labelled in $jj-$coupling</th>
<th>$\delta$ (mod. 1)</th>
<th>$\delta$</th>
<th>Corresponding $LS-$label</th>
</tr>
</thead>
<tbody>
<tr>
<td>4$fs_f$/2$nf/s$/2 $J = 6$</td>
<td>0.36</td>
<td></td>
<td>$^3$H</td>
</tr>
<tr>
<td>4$fs_f$/2$nf/s$/2 $J = 5$</td>
<td>0.81</td>
<td></td>
<td>$^3$I</td>
</tr>
<tr>
<td>4$fs_f$/2$nf/s$/2 $J = 5$</td>
<td>0.85</td>
<td></td>
<td>$^3$G</td>
</tr>
<tr>
<td>4$fs_f$/2$np/s$/2 $J = 5$</td>
<td>0.93</td>
<td>3.93</td>
<td>$^3$G</td>
</tr>
<tr>
<td>7$pnf$/2$nf/s$/2 $J = 5$</td>
<td>0.96</td>
<td>0.96</td>
<td>$^3$G</td>
</tr>
</tbody>
</table>

which converge toward the two different Ba$^+$ ionisation thresholds 4$fs_f$/2 or 4$fs_f$/2. Thus the transformation between the two $jj-$coupled levels 4$fs_f$/2$nf/s$/2$J$ and 4$fs_f$/2$nf/s$/2$J$ and the two $LS-$coupled levels 4$fn$1$L_J=L$ and 4$fn$3$L_J=L$ reduces approximately to a rotation with an angle $\theta$ close to $\pi/4$.

3.2 ENERGY-POSITIONS OF THE RESONANT LEVELS LOCATED BETWEEN 88 500 cm$^{-1}$ AND THE Ba$^+$ 4$fs_f$/2 IONISATION THRESHOLD. — The $\mu_\alpha$ and $U_{i\alpha}$ MQDT parameters associated with the $K_{\text{eff}}$ matrices (Sect. 3.1) are used to determine the energies of the even-parity resonances $J = 5$ and $J = 6$, with an energy greater than 88 500 cm$^{-1}$ These theoretical energies are in good agreement with the experimental values measured for the 4$fn$ resonances by de Graaff et al. [12]. The root-mean-square-deviation between the calculated energies and the experimental values is equal to 0.47 cm$^{-1}$ for the 18 observed resonances $J = 6$, and to 0.22 cm$^{-1}$ for the 21 experimental levels $J = 5$. For all these levels, the theoretical energy lies within the experimental width of the recorded resonance [15]. Let us note that the theoretical procedure using $K_{\text{eff}}$ is adequate to locate the resonance positions with an error comparable to their autoionisation widths.

Figures 1 and 2 display the Lu-Fano plots for the $J = 6$ and $J = 5$ levels in the $-\nu_{4fs_f}$/2
(mod. 1) versus $\nu_{4f_{5/2}}$ plane. The curves depend on the short-range electron-core interactions only, i.e. on $\mu_\alpha$ and $U_{1\alpha}$ only. The location on these curves of the resonances is determined by the energy constraint between the two effective quantum numbers $\nu_{4f_{5/2}}$ and $\nu_{4f_{7/2}}$, which depends on the spin-orbit splitting of the Ba$^+$ 4f threshold. These theoretical energies are represented by dots and the experimental values correspond to squares.

Fig. 1.— Lu-Fano plot $-\nu_{4f_{5/2}}$ (mod. 1) against $n_{4f_{7/2}}$ for the 4fnf $J = 6$ levels of barium below the Ba$^+$ 4f$5/2$ ionisation threshold. (---): 3-channel $R$—matrix calculation. (*) : theoretical energy-positions for the resonances. (□): experimental energy-positions for the resonances. (de Graaff et al.; Ref. 12)

The branches of the Lu-Fano plots include three different kinds of curves, which look like parts of “nearly oblique”, “horizontal” or “vertical” lines. For both even-parity spectra with $J = 6$ and $J = 5$, the “oblique” lines correspond to the “strongly interacting” series 4f$5/2$nf$7/2$ and 4f$7/2$nf$5/2$, as discussed in section 3.3. The “horizontal” line visible in figure 2 is associated with the nearly unperturbed 4f$5/2$nf$5/2$ $J = 5$ series converging to the 4f$5/2$ threshold. The “vertical” lines are associated with almost unperturbed series converging to Ba$^+$ 4f$7/2$ or Ba$^+$ 7p$3/2$, and identified as 4f$7/2$nf$7/2$ for $J = 6$ or 5 and as 4f$7/2$np$3/2$ or 7p$3/2$nf$7/2$ for $J = 5$ only. The quantum defects $\delta$ (mod. 1) for the even-parity weakly perturbed levels with $J = 6$ or 5 are reported in table IV. These quantum defects are nearly energy-independent. Quantum defects for the levels belonging to the two “strongly interacting” series 4f$5/2$nf$7/2$ or 4f$7/2$nf$5/2$ are meaningless, because they are quickly varying functions of energy (see Sect. 3.3). The $J = 6$ experimentally observed resonances are identified as belonging to the “strongly mixed” series 4f$5/2$nf$7/2$ or 4f$7/2$nf$5/2$, except for the two resonances with effective quantum numbers $\nu_{4f_{5/2}}$ equal to 13.63 and 17.70 respectively (see Fig. 1). Among the $J = 5$ resonances, eleven belong to the 4f$5/2$nf$5/2$ series and the other ten to the “strongly mixed” series (see Fig. 2).

Only two members of the 7p$3/2$nf$7/2$ $J = 5$ series appear in the energy range studied. They are located at 89 052 cm$^{-1}$ and 89 819 cm$^{-1}$ and correspond to effective quantum numbers
Fig. 2. — Lu-Fano plot $-\nu_{4f J/2}$ (mod. 1) against $\nu_{4f J/2}$ for the 4fnf $J = 5$ levels of barium below the Ba$^+$4f$\ell_{2}$ ionisation threshold. (—): 6-channel $R$-matrix calculation. (●): theoretical energy-positions for the resonances. (○): experimental energy-positions for the resonances. (de Graaff et al.; Ref. [12])

$\nu_{p_{3/2}}$ equal to 6.05 and 7.02 respectively. These resonances are ascribed to the $7p_{3/2}7f_{7/2}$ $J = 5$ and $7p_{3/2}8f_{7/2}$ $J = 5$ levels characterised by quantum defects 0.95 and 0.98 respectively. These values are of the same order of magnitude as those obtained recently for 6dnf $J = 5$ levels [16], whose quantum defect values range from 0.98 to 1.12. Let us note that the quantum defects for ml$'nl$ series with $l'$ and $l \leq 2$ are found theoretically to increase linearly with $m^{*}$, the effective quantum number of the inner electron, with a slope of about 0.30 – 0.35 [17]. The $6p_{3/2}nf_{7/2}$ $J = 5$ series has a quantum defect around 0.30 [18]. The previous extrapolation formula would predict 0.55 – 0.59 for the 6dnf levels and 0.60 – 0.65 for the $7p_{3/2}nf_{7/2}$ $J = 5$ series. Both values are smaller than the observed or calculated ones. This probably means that the previous law is no longer valid for ml$'nl$ levels with $l = 3$ for the outer electron.

The quantum defects of the 6pnp $J = 0, 1, 2$ autoionising series of barium are equal to about 3.80 [19, 20]. Taking into account the change in the excitation energy between the Ba$^+$ 6p and 4f orbitals, the extrapolation formula [17] predicts a value of about 4.1 for the quantum defect of the 4fnp series. The present calculation leads to 0.93 (mod. 1) for the 4f$\ell_{2}np_{3/2}$ $J = 5$ series. This permits us to tentatively attribute the value 3 to the entire part of the quantum defect, giving the value 3.93.

A large variation, 0.36 to 0.85, exists between the values modulo one of the quantum defects of the 4f$\ell_{j}nf_{j}J$ Rydberg series (see Tab. IV). This may reflect a change in the correlation of the corresponding states. But, inasmuch as the high lying levels of the nf–series of Ba$^+$ have large quantum defects of about 0.9 [11], the large values of the quantum defect of 4fnf states could also arise from the important centrifugal barrier effects for $l = 3$ orbitals. But let us emphasize that correlation effects are very important in the “double-valley” problem [10]. To eliminate the modulo one ambiguity in the 4fnf quantum defects, it is necessary to relate the energies of the highly excited resonances in the series to their lowest member, i.e. to levels belonging either to 4f$^2$ or to 4f5f configurations. Such investigation is in progress [13].
3.3 “STRONGLY MIXED” SERIES 4f⁷/₂nf₇/₂ AND 4f₇/₂nf⁵/₂ — The 4f⁷/₂nf₇/₂J and 4f₇/₂nf⁵/₂ J series, or $^1L_J=L$ and $^3L_J=L$ in LS-coupling scheme, are nearly uncoupled from the other series. Therefore it is possible to consider them, for each $J$-value, in a two-channel model with no energy-dependence of the MQDT parameters.

The coupling between the two series 4f⁷/₂nf₇/₂ and 4f₇/₂nf⁵/₂ is so strong that in the low-energy range, $\nu_{4f_{7/2}} \leq 12$, it is not possible to ascribe the resonances located on the oblique curves of the Lu-Fano plots either to one series or to the other one. Furthermore two resonances appear in an energy-range corresponding to the increase by one unit of $\nu_{4f_{7/2}}$ (see Figs. 1 and 2), and an important change is observed in the wavefunctions of two successive resonances. For example, the wavefunctions for the first two $J=6$ resonances located at $\nu_{4f_{7/2}} = 8.35$ and 8.77 can be expanded respectively as:

$$\sqrt{0.514} \, 4f_{5/2}2f_{7/2} - \sqrt{0.486} \, 4f_{7/2}n_{5/2} = \sqrt{0.857} \, 1^1 I + \sqrt{0.0002} \, 3^1 I - \sqrt{0.142} \, 3^3 H$$

$$\sqrt{0.592} \, 4f_{5/2}2f_{7/2} + \sqrt{0.408} \, 4f_{7/2}n_{5/2} = \sqrt{0.007} \, 1^1 I + \sqrt{0.992} \, 2^1 I - \sqrt{0.001} \, 3^3 H$$

the contribution of the 4f₇/₂nf₇/₂ dissociation channel being completely negligible. As a result, all the lowest resonances are better described in the LS-coupling scheme.

With increasing energy, all the resonances become well described by $jj$-coupled 4f₅/₂3n₇/₂ wavefunctions. For example, for $\nu_{4f_{7/2}} \approx 18$, the weight of the 4f₅/₂3n₇/₂ channel in the wavefunctions of the “strongly mixed” levels is greater than 0.85 and the value 0.95 is reached near $\nu_{4f_{7/2}} \approx 20$. The resonances 4f₇/₂nf₅/₂ are completely diluted in the 4f₅/₂3n₇/₂ ones, these results in a regular increase for the quantum defect of the resonances with increasing $n$; for example, in the energy range $\nu_{4f_{7/2}} \approx 18$, the effective quantum number $\nu_{4f_{7/2}}$ increases by 0.82 only between two consecutive resonances. An identical behaviour is observed in the “strongly mixed” $J=5$ and also $J=4$ series [13], which results respectively from the mixing of the $1^3$He and $1^3$Ge eigenchannels.

The slopes of the oblique lines are nearly equal in the $J=6$ and $J=5$ Lu-Fano plots (compare Figs. 1 and 2). As quoted above (Sect. 3.2), these curves are determined by the MQDT parameters $\mu_\alpha$ and $U_{i\alpha}$ only, i.e. by the short-range Rydberg-electron Ba⁺-core electrostatic interaction, but not by the spin-orbit interaction of the inner electron 4f. The rotation angle that identifies the $U_{i\alpha}$ orthogonal matrix in the two-channel model is approximately equal to $\theta_{12} \approx \pi/4$ (see Sect. 3.1). Consequently the oblique lines depend only on the difference $|\Delta \mu_\alpha|$ in the eigenquantum defects of the $^1L_j=L$ and $^3L_j=L$ eigenchannels. This difference is close to 0.5, for $J=6$ and $J=5$, which explains the similar behaviour of both Lu-Fano plots. For $J=4$, the difference amounts to 0.44 [13], a value not too far from those obtained for the $J=5$ and $J=6$ channels.

The shifted MQDT parameters introduced by Giusti-Suzor and Fano are better suited to keep the symmetry of two-channel coupling [21]. They can be numerically calculated from the eigenchannel MQDT parameters obtained from the restricted $K_{\text{eff}}(E)$ matrices. They consist in two shifted quantum defects $\tilde{\mu}_1$ and $\tilde{\mu}_2$ and in $\xi$ a parameter which appears as an index for the strength of channel coupling. Indeed, the relative weight of the two dissociation channels in the wavefunction oscillates between the two extremum values $|\xi|^2$ and $1/|\xi|^2$. When the rotation angle is equal to $\pi/4$, the shifted MQDT parameters are equal to:

$$\tilde{\mu}_1 = \tilde{\mu}_2 = (\mu_1 + \mu_2)/2 \quad \text{and} \quad |\xi| = |\sin \pi \Delta \mu_\alpha| \times (1 + |\cos \pi \Delta \mu_\alpha|)^{-1}$$

When $|\Delta \mu_\alpha| = 0.5$ then $|\xi| = 1$, which represents two coupled channels with constant equal admixture of the dissociation channel, independently of the energy.

The shifted MQDT parameters calculated at $E = 89 \, 910 \, \text{cm}^{-1}$ are the following:
for $J = 6: \tilde{\mu}_1 = \tilde{\mu}_2 = 0.563$ (mod. 1) and $|\xi| = 0.953$
for $J = 5: \tilde{\mu}_1 = \tilde{\mu}_2 = 0.609$ (mod. 1) and $|\xi| = 0.924$.

In both cases, $|\xi|$ is very close to the equal-admixture value. Such an example of "strongly mixed" channels has been previously observed in $J = 0$ even-parity states of calcium below the Ca$^+$ 3$^3d_{9/2}$ threshold [22] — see figure 3 and table V in this latter paper [22]. There, the strongly mixed eigenchannels correspond to different $LS$-terms and are identified as 3$^3d$ 1$^1S_0$ and 3$^3d$ 3$^3P_0$; their interaction cannot arise from the exchange electrostatic interaction, but from correlation effects. More precisely, the levels 4$p^2$ 1$^1S_0$ and 4$p^5$ 3$^3P_0$ strongly perturb the 3$^3d$ $J = 0$ series, and this dd-pp coupling induces a large mixing $\delta_{12} = \pi/4$ between the $(m_0 - 1)$ d$^2$ series, which correspond to eigenquantum defect difference $|\Delta \mu_{4fnf}| = 0.21$.

In the 4$fnf$ series of barium, centrifugal barrier effects, electrostatic exchange interaction and configuration mixing - or equivalently correlation effects - can be called upon to explain the large values of the quantum defects, but the latter two only are responsible for the large dependence of the quantum defects on the series studied. To unravel the respective contributions of exchange and correlation interactions, we have tried to fit the energies of the $LS$-terms in the fictitious unperturbed configuration 4$fnf$ in a Slater and Condon analysis. The theoretical values for the energies of the terms are directly related to the eigenquantum defects $\mu_{4fnf}(S, L)$, providing that the entire part is unambiguously determined, and they may be expressed also as a linear combination of radial Slater integrals $F^k$ and $G^k$, with $k$ even and $0 \leq k \leq 6$ [23]. If one assumes that the $G^0$ integral prevails in the exchange interaction, the singlet-triplet $1^3L$ degeneracies would be removed by the same energy-splitting, but with the singlet higher than the triplet term for even $L$ — values (especially for $1^3G$ and $1^3I$ terms) and the opposite for odd $L$ — values (such as $1^3H$ terms). Then, this condition would lead to $|\Delta \mu_{4fnf}(L)|$ values nearly $L$-independent, but with a sign of $\Delta \mu_{4fnf}(L)$ depending on the $L$-parity. This hypothesis seems to be useful to explain the $L$-independence of $|\Delta \mu_{4fnf}(L)|$ in the 4$fnf$ configuration of barium, but then it would impose that all entire parts are equal in the eigenquantum defects $\mu_{4fnf}(1^3L)$ independently of the $L$ and $S$ values. Unfortunately, with this assumption, it is not possible to obtain a satisfactory analysis of the direct electrostatic interaction, with direct $F^k$ integrals complying the constraints $F^0 > F^2 > F^4 > F^6 > 0$ [24]. At the present time it is not possible to conclude definitely, if this failure results from an incorrect determination of the entire part of all quantum defects for the $1^3F$, $1^3H$ and $1^3Ge$ eigenchannels or from the fact that the 4$fnf$ configuration cannot be treated as isolated. As a matter of fact, a significant change occurs in the $\Delta \mu_{4fnf}(L)$ values, 25% for $L = 6$, when the $K(E)$ matrices are reduced to the "weakly cycled" channels (Sect. 3.1), which could indicate important correlation effects. Further investigations are in progress.

4. Conclusion.

Extensive studies in recent years [1-7] have shown that eigenchannel $R$-matrix method combined with quantum defect method gives an accurate description of low-lying autoionising levels of alkaline-earths, more specially for barium below the Ba$^+$ 6$^2p$ threshold. The present analysis demonstrates, for the first time, that the same techniques can be applied with similar confidence to calculate the energy positions of high members of the 4$fnf$ $J = 5, 6$ autoionising series of barium.

The analysis of the 4$fnf$ $J = 5, 6$ spectra shows that quantum defects are large and depend strongly on the series studied. The 4$^{5/2}f^6/2$ $J = 5, 4f^7/2n^7f^7/2$ $J = 5$ and $J = 6$ series are characterised by quantum defects $\delta$ almost energy-independent and close to the eigenchannel quantum defects $\mu_{4fnf}(3^1I), \mu_{4fnf}(3^1G)$ and $\mu_{4fnf}(3^1H)$ respectively. These series are almost pure
$jj$--coupled and not too far from almost pure $LS$--coupled. At the opposite for both $J$--values, the $4f_5/2nf_7/2$ and $4f_7/2nf_5/2$ series are "strongly mixed". Consequently, along these two series, the quantum defects have a strong, but very regular energy-dependence and the coupling of the levels evolves from $LS$ to $jj$ as $n$ increases. For the lowest $n$--values, the important change in the wavefunctions of two neighbouring resonances belonging to the "strongly mixed" series, should induce strong modifications in their properties, such as excitation probability, autoionisation width or photoelectron angular distributions. Furthermore, between the $Ba^+$ $4f_{5/2}$ and $4f_{7/2}$ thresholds, the $4f_{7/2}nf_{5/2}$ resonances should be broad owing to their coupling with the $4f_{5/2}2f_{7/2}$ open channel. This strong mixing between the $4f_{5/2}nf_{7/2}$ and $4f_{7/2}nf_{5/2}$ series results from both fine-structure effects and short-range bielectronic interaction: the mixing angle around $\pi/4$ is directly related to matrix element of $(jj - LS)$ transformation in a configuration $ml'nl$ with $l' = l$; the strong bielectronic interaction leads to the large values $|\Delta \mu(L)| = |\mu_{4nf}^{(1)L} - \mu_{4nf}^{(3)L}| \approx 0.5$ (mod. 1) of the eigenquantum defect differences for $L = 5$ and $L = 6$, that is for the $J = 5$ and $J = 6$ spectra respectively. The physical interpretation of the similarity between $|\Delta \mu(L = 5)|$ and $|\Delta \mu(L = 6)|$ and of these large values, close to the maximum value, is not yet clear. One difficulty preventing us to disentangle effects due exchange Coulomb interaction within the $4nf$ configuration from those related to configuration interaction arises from the fact that some modulo one ambiguities remain in the quantum defects.

The agreement between the present $R$--matrix calculation and the experimental values [12] is surprisingly good, accounting for the complexity of the spectra studied compared to previous results [1-7]. As in previous studies in barium, the spectra are affected by strong two-electron correlation and spin-orbit effects; but here, the number of interacting channels is large ($> 33$) and moreover the f-orbitals of Ba are found to be extremely sensitive to centrifugal barrier effects. Of course, the present study concerns only the energy positions of high members of the $4nf$ $J = 5$, 6 series ($n > 8$) and the ability of the method to reproduce the profiles of the $4nf$ spectra recorded in excitation from several $5df$ levels remains to be investigated. Another desirable point is to extend the calculation to low-lying $4nf$ levels with $(n \leq 8)$, which have not yet been observed. Especially attractive are the $4f^2$ levels involving two electrons with circular orbits, in which electron correlations are expected to be dominant. All these extensions of the present work will be considered in a forthcoming paper, which will also deal with the $4nf$ $J = 4$ levels [13].

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