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Fine-structure splitting for the 3d and 4d terms in the sodium isoelectronic sequence

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Abstract. — The fine-structure splitting for the 3d and 4d terms of the Na I isoelectronic sequence up to Sn XL are calculated using relativistic wavefunctions obtained by means of the relativistic parametric potential method. Good agreement with experimental data is obtained throughout the sequence. The different contributions to the spin-orbit constant are analysed and their variations along the sequence are discussed. In the Pauli approximation the relativistic effects separate into effective operator contributions and purely relativistic effects associated with relativistic corrections to the wavefunctions; it is shown that the former effect is predominant for high stages of ionization, meanwhile the latter correction corresponds to the most important contributions for the first ions of the sequence and accounts for the fine-structure inversion.

1. Introduction. — The anomalous fine-structures of alkali-like spectra have attracted a renewed interest during the last few years. Strong deviations from hydrogen-like behaviour have been observed for a long time for some low lying levels: indeed many of the doublets are inverted or anomalously narrow [1]. Due to the development of several high-resolution techniques using tunable lasers it has become possible to populate efficiently and selectively highly excited levels and to perform measurements with sub-Doppler resolution. Consequently systematic experimental studies of long Rydberg series have been carried out for the alkali-atoms and for some ions with a moderate stage of ionization. A brief review of the experimental results is given in references [2, 3].

These fine-structure anomalies were attributed long ago to the exchange part of the magnetic interaction between the valence electron and the inner shells [4] or to configuration mixing with doubly excited configurations lying above the first ionization limit and having inverted doublet terms [5]. Nevertheless these contributions are unable to reproduce the experimental data. More elaborate calculations have been performed recently by several groups using different techniques. Most of them start from non-relativistic wavefunctions and introduce relativistic effects perturbatively in the Pauli approximation [6]: in this case, the fine-structure inversions cannot be reproduced in a monoconfigurational study of the magnetic interactions. But these inversions can be explained as due to a crossed second order interaction involving the spin-orbit perturbation and the exchange part of the Coulomb interaction between core and valence electrons [7-12]. In a completely different approach we have used relativistic wavefunctions; then a first order calculation in the central field approximation reproduces very well the experimental data; furthermore we have shown that these different approaches are equivalent to order $\alpha^2$ [13] ($\alpha$ is the fine-structure constant).
The calculations described above deal with neutral atoms or with ions with low stages of ionization (smaller than 4). There exist some calculations of the spin-orbit constant for isoelectronic sequences with one-electron spectra [14-16]; however, these studies introduce the relativistic effects in the Pauli approximation and do not consider the configuration mixing; consequently these methods cannot account for the fine-structure inversions observed for the first ions of the sequence and cannot be used to study highly ionized spectra for which relativistic effects are expected to dominate.

In this paper we present the results of a fully relativistic calculation of the fine-structure intervals for the 3d and 4d terms of the sodium isoelectronic sequence up to Sn XL. Recent works with low-inductance sparks and laser-produced plasmas have greatly extended the knowledge of this sequence up to Mo XXXII [17]; a synthesis of the experimental data was presented by Edlén [18] who derived semi-empirical formulae describing the fine-structure intervals. For the first ions of the sequence the fine-structure intervals are inverted but tend to become normal again with increasing degree of ionization; consequently the fine-structure interval goes through zero for Si IV.

The fully relativistic treatment used to determine the spin-orbit constant in one-electron spectra has already been applied to study the \( n^2 \) D series of Na I and \( n^2 \) Fs series of Cs I [13]; this method corresponds to a frozen-core model and is briefly described in the first part. In the second part the equivalent operator formalism [19] is used to analyse the terms of order \( \alpha^2 \) present in the spin-orbit constant. The results obtained for the Na I isoelectronic sequence are presented in the third part and are compared with previous experimental and theoretical works. In the fourth part we introduce a different fully relativistic approach in the frozen-core approximation and compare it to the first used method.

2. Relativistic calculations of fine-structure intervals. — 2.1 Relativistic spin-orbit constant. —

2.1.1 Relativistic hamiltonian. — The Breit-Dirac hamiltonian [6] is the most commonly used approximation describing the interactions between relativistic electrons. The one-body part of this hamiltonian is the sum of the Dirac hamiltonians describing the kinetic energy and the relativistic interaction of the \( N \) electrons of the atom with the nucleus of charge \( Z \). The two-body part arises from the electron-electron interaction; in addition to the instantaneous Coulomb interaction, it includes the Breit interaction corresponding to the magnetic interaction between Dirac currents \( G \) (the Gaunt term) and the retardation term \( R \). The Breit hamiltonian is an effective operator describing only the leading term (of order \( \alpha^2 Z^2 \)) in the interaction between positive energy electrons; consequently it can only be introduced into the problem as a perturbation and then only to first order.

2.1.2 Equivalent fine-structure operator. — By using the equivalent operator formalism [19], it is possible to write the Breit-Dirac hamiltonian in terms of the one-body double tensors \( \omega^{\text{exn}}_K \) having well defined ranks, \( k \) in the spin space, \( \kappa \) in the orbital space and \( K \) in the total space [20]. This equivalent operator evaluated between non-relativistic wavefunctions produces the same result as obtained by calculating the relativistic operator between relativistic states. In the present paper we consider states with one-electron outside closed shells; consequently by summation over the core orbitals, the two-particle operators reduce to effective one-particle operators.

In this effective operator the terms having the same angular dependence as the usual spin-orbit hamiltonian can be identified as the relativistic (i.e. arising from the Breit-Dirac operator) fine-structure interaction \( A_{\text{BD}} \):

\[
A_{\text{BD}}(nl) = \sum_{\ell} [\zeta_{\text{def}}(nl) + \zeta_{\text{R}}(nl)] (s, I) = \sum_{\ell} [\zeta_{\text{D}}(nl) + \zeta_{\text{E}}(nl) + \zeta_{\text{G}}(nl) + \zeta_{\text{R}}(nl)] (s, I) \tag{1}
\]

where the different contributions to the spin-orbit constant \( \zeta_{\text{BD}}(nl) \) are respectively:

\( \zeta_{\text{D}}(nl) \): interaction of the \( nl \) orbital with the nucleus and direct part of the electrostatic interaction with the core orbitals;

\( \zeta_{\text{E}}(nl) \): exchange part of the electrostatic interaction between core and valence orbitals;

\( \zeta_{\text{G}}(nl) \): Gaunt interaction between core and valence orbitals;

\( \zeta_{\text{R}}(nl) \): retardation term between core and valence orbitals.

The expressions for \( \zeta_{\text{D}} \) and \( \zeta_{\text{E}} \) in terms of the radial integrals are given in the Appendix. Similar formulae exist for \( \zeta_{\text{G}} \) and \( \zeta_{\text{R}} \) but they are much more complicated.

2.2 Relativistic radial wavefunctions. — The relativistic radial wavefunctions are obtained from the relativistic parametric potential method RELAC [21, 22] associated with a frozen-core model. This method is an extension of the non-relativistic parametric potential method introduced by Klapisch [40, 41].

2.2.1 Core wavefunctions for the Na II-like ions. — The relativistic wavefunction for an orbital \( c \) of the core is solution of the Dirac hamiltonian corresponding to the central potential \( U_c \). The radial functions \( P_c(r) \) and \( Q_c(r) \) corresponding respectively to the large and small components of the relativistic wavefunction satisfy a system of first-order homogeneous coupled differential equations. In the RELAC method \( U_c \) is represented by an analytic function depending on a set of parameters; in the present case there are three parameters associated respectively with the subshells 1s, 2s and 2p. The optimal set of parameters minimizes the total energy of the ground level of the-
ion 1s^2 2s^2 2p^6 J = 0 calculated in the first order of the perturbation theory.

2.2.2 Valence wavefunction. — In the frozen-core approximation the valence electron e moves in the electrostatic potential \( V_{e+C} \) due to the nucleus and core electrons (direct D and exchange E parts). The radial functions \( P_j(r) \) and \( Q_j(r) \) for the valence orbital are solutions of a system of first order inhomogeneous coupled differential equations similar to the relativistic Hartree-Fock equations [23]. To study the nd states of the sodium isoelectronic sequence a more simple model can be introduced. Indeed core and valence orbitals which are of a different angular symmetry are automatically orthogonal; moreover the overlap between core and valence orbitals is generally small. Consequently it is possible to treat the exchange part of the electrostatic interaction as a perturbation to first order; in this case the valence wavefunctions are determined in the central potential \( V_D \) due to the nucleus and the spherically symmetric charge distribution corresponding to the core electrons (the non-local exchange electrostatic potential is thus not introduced in the determination of the wavefunctions).

3. Non-relativistic limit for the spin-orbit constant \( \xi_{BD}(nl) \). Calculation in the direct potential of the core \( V_D \). — The non-relativistic limit (i.e. terms of order \( a^2 \)) for the spin-orbit constant \( \xi_{BD}(nl) \) is particularly easy to derive by using the equivalent operator formalism. Indeed the non-relativistic limit for the radial integrals present in \( \xi_{BD}(nl) \) is obtained by expanding the relativistic radial functions and \( W \) the energy of the corresponding orbital (not including the rest mass energy) in powers of \( a^2 \):

\[
P = P^{(0)} + a^2 P^{(1)} + \cdots \\
Q = a Q^{(0)} + a^2 Q^{(1)} + \cdots \\
W = W^{(0)} + a^2 W^{(1)} + \cdots
\]  

(2)

The expansion (2) is not unique and depends on the approximation used to determine the wavefunctions. In this part we discuss the simpler case for which the wavefunctions for the valence electron are calculated in the central potential \( V_D \).

3.1 Non-relativistic limit for the radial wavefunctions. Effective operator contributions and "purely relativistic effects". — In order to obtain the non-relativistic limit of \( \xi_{BD} \), only \( P^{(0)} \), \( P^{(1)} \) and \( Q^{(0)} \) are to be studied. The non-relativistic limit for wavefunctions calculated in a central potential \( U \) has been discussed in great details elsewhere [13, 24]; we present only the main results.

The non-relativistic limit for the radial part of the large component \( R_{nlj} \) is identical to the non-relativistic radial function \( R_{nlj} \) determined in the same central potential; \( W_{nlj}^{(0)} \) is equal to the corresponding non-relativistic eigenvalue. \( P_{nlj}^{(0)} \) and \( W_{nlj}^{(0)} \) do not depend on the \( j \)-value.

The leading term in the small component of the wavefunction (term of order \( a \)) can be written in terms of the corresponding non-relativistic wavefunction (Ref. [24], eq. (11)). Consequently in a perturbative treatment of the relativistic effects — i.e. in the Pauli limit — the relativistic contributions arising from the components \( Q^{(0)} \) of the relativistic wavefunctions can be taken into account by the introduction of effective operators: these operators evaluated between non-relativistic functions produce the same effects as the concerned contribution.

The corrections of order \( a^2 \) in the large components of the relativistic wavefunctions cannot be reproduced in the Pauli approximation through the introduction of effective operators. But they can be accounted for by calculating to the first order of the perturbation theory the configuration mixing arising from the one-particle relativistic operators \( q_{1l}^{(U)} \) (relativistic correction to the kinetic energy, Darwin term and spin-orbit interaction corresponding to the central potential \( U \)) (see Ref. [24], eq. (12)):

\[
a^2 P_{nlj}^{(1)}(r) = \sum_{n' * n} \frac{\langle n'ljm | h_{1l}(U) | nljm \rangle}{W_{nl}^{(0)} - W_{n'l}^{(0)}} R_{nlj}(r)
\]  

(3)

where |nljm> = R_{nlj}(r) |jm> is the non-relativistic state with angular part |jm> approaching, in the non-relativistic limit, the relativistic state described by the quantum numbers nljm.

In a monoconfigurational study introducing the relativistic effects perturbatively it is not possible to take into account the relativistic contributions arising from the components \( P^{(1)} \) of the relativistic wavefunctions. These contributions which can only be accounted for in the Pauli approximation by an explicit treatment of the configuration mixing due to the relativistic operators are called purely relativistic effects [13].

Let us remark that \( q_{1l}^{(U)} \) depends on the central potential \( U \). In the present model, the core wavefunctions are calculated in the central potential \( U_C \) and the valence wavefunctions in the central potential \( V_D \). Consequently different configuration mixings occur for core and valence orbitals; it is possible to show that

\[
h_{1l}^{(U)}(U_C) = p^4 \text{ term} + \text{Darwin term} + \frac{1}{r} \frac{dU_C}{dr} (s.l)
\]

\[
h_{1l}^{(V_D)} = p^4 \text{ term} + \text{Darwin term} + \frac{Z}{r^3} (s.l) + H_{500}
\]  

(4)

where \( H_{500} \) represents the direct part of the spin-other-orbit interaction between core and valence
orbits; two-particle relativistic operators appear thus in $h_{1e}(V_D)$.

3.2 Non-relativistic limit for the spin-orbit constant $\xi_{\text{Bo}}(nl)$. — $\xi_{\text{Bo}}(nl)$ is the sum over four different contributions (eq. (1)) which are studied successively.

3.2.1 Contributions from the direct term $\xi_{d}(nl)$. — The valence wavefunctions $nl_{\pm}$ ($j_\pm = l \pm 1/2$) being calculated in the potential $V_0$, the contribution from the direct terms to the spin-orbit constant is directly related to the difference in the energies of the two orbitals (eq. (A.2)). Consequently in the Pauli approximation $\xi_d(nl)$ can be obtained by the treatment of $h_{1e}(V_0)$ to the first order of the perturbation theory; therefore $\xi_d(nl)$ includes the spin-orbit interaction in the potential $-Z/r$ and the direct part of the spin-other-orbit interaction between non-relativistic core and valence orbitals. Consequently to the order $a^2$, $\xi_d(nl)$ is identical to the direct terms present in the Blume and Watson formula [25] given for an electron outside closed shells:

$$\xi_d(nl) \rightarrow \xi_{\text{Bo}}^\text{eff}(nl) \text{ effective operator contribution.} \quad (5)$$

3.2.2 Contributions from the exchange term $\xi_{e}(nl)$. — In the present model, the exchange part of the electrostatic interaction between relativistic core and valence orbitals is treated to the first order of the perturbation theory. The expression for $\xi_{e}(nl)$ is given in the appendix (eq. (A.3)). The non-relativistic limit for $\xi_{e}(nl)$ is obtained by studying the terms of order $a^2$ in the exchange Slater integrals $G^\text{K}(nl_{\pm}, nl_{\mp})$ between core ($n_s l_c j_c = c$) and valence ($nl_{\pm} = v$) orbitals.

The following quantity appears in this integral:

$$\xi_{e}(nl) = \begin{cases} \xi_{\text{Bo}}^\text{eff}(nl) & \text{effective operator contribution;} \\ \sum_{n_s l_c \neq 0} \Delta \xi_{e}(nl'; \leftarrow n_s l_c) & \text{purely relativistic effects}; \\ \Delta \xi_{e}(nl'; \leftarrow nl) & \text{valence orbital: } \Delta \xi_{e}(nl'; \leftarrow nl) = \sum_{n_s l_c \neq 0} \sum_{E \neq 0} \frac{1}{\Delta E} \left| \langle h_{1e}^{\text{rel}}(V_D) \rangle \right|^2 \left| \langle 1/r^2 \rangle \right|^2. \quad (7) \end{cases}$$

The quantity $\Delta \xi_{e}(nl'; \leftarrow n_s l_c)$ has been studied independently by different authors [7, 12] by introducing the relativistic effects perturbatively in the Pauli approximation. They treat explicitly the configuration mixing by determining first order wavefunctions corresponding to the perturbation of the core orbital $\xi_d(nl)$ or to the valence orbital $nl$ (denoted by $\Delta \xi_{e}(nl'; \leftarrow n_s l_c)$ or to the valence orbital $nl$ (denoted by $\Delta \xi_{e}(nl'; \leftarrow nl)$) occur simultaneously and are associated with different relativistic operator $h_{1e}^{\text{rel}}$ (See eq. (4)). In summary it is possible to write:

$$P_e P_v + Q_e Q_v = P_e^{(0)} P_v^{(0)} + P_e^{(1)} P_v^{(1)} P_e^{(0)} + P_v^{(1)} P_v^{(0)} + \cdots. \quad (6)$$

The terms independent of $a$ in the Slater integrals do not contribute to the fine-structure splitting. The contributions arising from the small components of the relativistic wavefunctions $Q_e^{(0)} Q_v^{(0)}$ can be taken into account in the Pauli approximation through the introduction of an effective operator. This operator is equal to $1/3 H_{\text{SDD}}$, one third of the exchange part of the spin-other-orbit interaction between core and valence orbitals and is therefore related to one third of the exchange contribution $\xi_{\text{Bo}}^\text{eff}(nl)$ in the Blume and Watson formula. In fact one third of the exchange term occurring in the Blume and Watson formula arises from the spin-orbit interaction of one electron in the Coulomb field of the other electrons, meanwhile the remaining two thirds are due to the magnetic interaction of the spin of one-electron with the orbits of the other electrons [25].

The contributions corresponding to the corrections to the large components of the relativistic wavefunctions $P_e^{(0)} P_v^{(0)} + P_e^{(1)} P_v^{(0)}$ are associated with purely relativistic effects; in the Pauli limit they can be given by a second order cross-interaction involving the one-electron relativistic operator $h_{1e}^{\text{rel}}$ and the exchange part of the non-relativistic electrostatic interaction $1/r^2$. Let us remark that contributions arising from the corrections to the core orbitals $n_s l_c$ with $l_c \neq 0$ (denoted by $\Delta \xi_{e}(nl'; \leftarrow n_s l_c)$) or to the valence orbital $nl$ (denoted by $\Delta \xi_{e}(nl'; \leftarrow nl)$) occur simultaneously and are associated with different relativistic operator $h_{1e}^{\text{rel}}$ (See eq. (4)). In summary it is possible to write:

$$P_e P_v + Q_e Q_v = P_e^{(0)} P_v^{(0)} + P_e^{(1)} P_v^{(1)} P_e^{(0)} + P_v^{(1)} P_v^{(0)} + \cdots. \quad (6)$$
and $P_n Q$ appear in these integrals; in the non-relativistic limit $PQ' \sim x P^{(0)} Q^{(0)}$ and the contributions $\xi_G(nl)$ and $\xi_R(nl)$ can be taken into account in the Pauli approximation through the introduction of effective operators. For alkali-like ions it is possible to show that to the order $x^2$, $\xi_G(nl)$ is identical to two thirds of the exchange terms present in the Blume and Watson formula and that $\xi_R(nl)$ vanishes:

$$\begin{align*}
\xi_G(nl) &\rightarrow \frac{2}{3} \xi_{BW}(nl), \\
\xi_R(nl) &\rightarrow 0
\end{align*}$$

Indeed the reduction of the retardation term to its Pauli limit contributes to the orbit-orbit interaction, to the two-body part of the Darwin term and to the spin-spin interaction [26]. The first and second interactions which are spin-independent do not contribute to the fine-structure splitting; the third term vanishes for a system composed of one-electron outside closed shells [27].

4. Results and discussion. — We have evaluated the fine-structure splitting $\Delta_n$ for the 3d and 4d terms for some ions of the sodium isoelectronic sequence up to Sn XI.

$$\Delta_n = \frac{5}{2} \xi_{BD}(nd).$$

In this section we present the results obtained by a fully relativistic calculation in the first order of the relativistic central field model; the wavefunction for the valence electron is determined in the direct electrostatic potential $V_D$ of the frozen-core.

4.1 Analysis of the different contributions to the fine-structure splitting. — 4.1.1 $Z$-dependence of the contributions $\xi_G(3d)$, $\xi_R(3d)$ and $\xi_{BD}(3d)$. — Figure 1 presents the contributions to the total fine-structure splitting ($T$) for the 3d term arising from the direct ($D$) and exchange ($E$) terms of the electrostatic interaction and from the Gaunt ($G$) and retardation ($R$) terms. The quantities $\Delta/I^4$ are drawn, where $I = Z - 10$. The hydrogen-like value (H) for a nucleus of charge $I$ is also reported.

$$\Delta H (mK) = 36.071x^{33} I^{4} + 0.00033 I^{6} + \cdots \quad (10)$$

For $I$ less than forty terms higher than $I^4$ in the Dirac formula (10) are negligible. For high stages of ionization the direct term $D$ increases approximately as $I^4$ in agreement with the variation along an isoelectronic sequence of the contributions arising from the one-electron relativistic operators. The contributions corresponding to $\xi_{BD}(nl)$ are $20 \%$ greater than the hydrogen-like value, but this discrepancy can be explained by the incomplete screening of the nucleus by the ten core electrons; the screening parameter is $\sigma \sim 8.135$ [18]. The contributions $E$ arising from the exchange part of the electrostatic interaction between core and valence orbitals are always negative; they are particularly large for the first ions of the sequence (before Ca X) and give rise to the fine-structure inversions. The contributions $G$ arising from the Gaunt interaction are always negative and increase as $I^3$ for sufficiently highly charged ions; this variation corresponds to the contributions of the two-electron relativistic operators. The contributions $R$ arising from the retardation term are negligible ($R \sim 2 G/1000$), as can be predicted from the study of the non-relativistic limit; moreover they are negative for the first ions of the sequence and positive for higher stages of ionization.

4.1.2 Effective operator contributions and « purely relativistic effects » on the exchange part of the interaction between core and valence orbitals. — In the previous part we have shown, that there are two types of contributions of order $x^2$ to the spin-orbit constant. The contributions arising from the small components of the relativistic wavefunctions can be accounted for in the Pauli approximation by the introduction of two-particle effective operators in a monoconfigurational treatment. The contributions arising from the relativistic corrections to the large components of the relativistic wavefunctions correspond to purely relativistic effects which can be accounted for in the Pauli approximation only when configuration mixings are explicitly introduced. The variation along the
sequence of the contributions arising from effective operators and from purely relativistic effects are presented in figure 2, where the quantities $\Delta I^3$ are reported.

Fig. 2. — Contributions to the fine-structure splitting $\Delta I$ arising from the exchange part of the two-particles operators involving the core and the 3d valence wavefunctions in the sodium isoelectronic sequence. Total total exchange term. EO effective operator contributions arising from the small components of the relativistic wavefunctions. PRE purely relativistic effects : contributions arising from the relativistic corrections to the large components of the relativistic wavefunctions. PRE(c) relativistic effects on the core orbitals. PRE(v) relativistic effects on the valence orbitals.

The effective operator contributions EO are negative and vary as $I^3$ for highly ionized spectra. We have verified that one third of these contributions arises from the electrostatic interaction and the remaining two thirds from the Gaunt interaction. The purely relativistic contributions PRE are large and negative for the first ions of the sequence ($I < 10$) and positive for high stages of ionization; they consist of two different parts. The first one PRE(c) corresponds to the corrections to the core wavefunctions and is related to $\sum_{n\ell} \Delta \xi_{\ell} (nd \leftarrow n\ell I_\ell)$; this contribution is negative and predominant for low stages of ionization. The second one PRE(v) is associated with the relativistic corrections to the large component of the valence wavefunction; it corresponds to $\Delta \xi_{\ell} (nd \leftarrow nd)$ and is always positive. PRE(v) gives rise to contributions which are almost negligible for $I$ smaller than five, but are larger than PRE(c) for $I$ greater than fifteen.

4.1.3 Detailed analysis for low (Na I) and moderate (Mo XXXII) stages of ionization. — Table 1 presents an analysis of the contributions to the fine-structure splitting of the 3d terms of Na I and Mo XXXII, the heaviest ion of the sequence for which a comparison with experimental data is possible [17]. The different interactions present in a fully relativistic calculation to the first order of the central field model (not introducing configuration mixing) are presented, as well as the corresponding interactions occurring in a perturbative treatment of the relativistic effects.

For the studied stages of ionization ($I < 40$), terms greater than $\alpha^4$ in the fine-structure interval are almost negligible; consequently the Pauli approximation can be used successfully to determine the corresponding fine-structure constant.

For light ions, the purely relativistic effects correspond to negative contributions which are predominant. Consequently in the Pauli limit, only a multi-configurational treatment can give reliable results. For moderate stages of ionization ($I \sim 30$) the effective operator contributions are preponderant. Indeed the purely relativistic effects either on the core wavefunctions or on the valence wavefunction cancel almost exactly in the present model; this cancellation property which is mainly related to the chosen zeroth order non-relativistic wavefunctions depends probably on the selected model.

To reproduce the experimentally observed fine-structure splittings, it is necessary to take into account of the two-body relativistic interactions (the spin-other-orbit interaction) even for ions as heavy as Mo XXXII.

4.2 Comparison with previous experimental and theoretical works. — 4.2.1 Comparison with experimental data. — The results obtained by using the present method for the fine-structure splitting of the 3d and 4d terms of the sodium isoelectronic sequence are presented in figure 3, where they are compared with the experimental data. The agreement between theory and experiment is very good, throughout the sequence pointing out that the present model is well suited to study a complete isoelectronic sequence. For the first four spectra the discrepancy is more important, but nevertheless the present method allows us to interpret the fine-structure inversion. In order to improve the results for these light ions it is probably necessary to introduce explicitly the mixing between relativistic configurations, in particular to take into account the perturbation of the relativistic core orbitals by the presence of the valence electron (relativistic core-polarization effect).

4.2.2 Comparison with calculations in the Pauli approximation neglecting configuration mixing. — The previous systematic calculations of the fine-structure splittings of the nd terms of the Na I sequence had been carried out in the Pauli approximation neglecting configuration mixing. These results are reported in figure 3. Froese [14] calculated the fine-structure splitting for the 3d term by using the Blume
Table I. — *Contributions to the fine-structure splitting (cm⁻¹) of the 3d terms for Na I and Mo XXXII.* $x \pm y = x \times 10^{±3}$.

<table>
<thead>
<tr>
<th>Relativistic Interaction</th>
<th>Pauli approximation</th>
<th>Effective Contributions (cm⁻¹)</th>
<th>Na I</th>
<th>Mo XXXII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic Interaction</td>
<td>$\xi_{BW}^D$</td>
<td>$(\xi_{BW}^E)$</td>
<td>$3.90 - 2$</td>
<td>$4.77 + 4$</td>
</tr>
<tr>
<td>Direct term</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrostatic Interaction</td>
<td>$\frac{1}{3} \xi_{BW}^E$</td>
<td>$(\xi_{BW}^E)$</td>
<td>$-2.08 - 3$</td>
<td>$-1.18 + 3$</td>
</tr>
<tr>
<td>Exchange term</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gaunt Interaction</td>
<td>$\frac{2}{3} \xi_{BW}^E$</td>
<td></td>
<td>$-4.21 - 3$</td>
<td>$-2.39 + 3$</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>$3.27 - 2$</td>
<td>$4.41 + 4$</td>
</tr>
<tr>
<td>Electrostatic Interaction</td>
<td>$\Delta \xi_{BW}^E (3d; \rightarrow 2p)$</td>
<td>$\Delta \xi_{BW}^E (3d; \rightarrow 3d)$</td>
<td>$-7.51 - 2$</td>
<td>$-2.81 + 3$</td>
</tr>
<tr>
<td>Exchange term</td>
<td></td>
<td></td>
<td>$+2.21 - 3$</td>
<td>$+3.05 + 3$</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>$-7.29 - 2$</td>
<td>$2.47 + 2$</td>
</tr>
<tr>
<td>Retardation term</td>
<td>0</td>
<td></td>
<td>$-9.38 - 6$</td>
<td>$4.38 + 0$</td>
</tr>
<tr>
<td>Calculated value</td>
<td></td>
<td></td>
<td>$-4.02 - 2$</td>
<td>$4.44 + 4$</td>
</tr>
<tr>
<td>Experimental value</td>
<td></td>
<td></td>
<td>$-4.94 - 2$</td>
<td>$4.49 + 4$</td>
</tr>
</tbody>
</table>

a) Ref. [28].
b) Ref. [17].
c) $\xi_{BW}$ Blume and Watson formula (Ref. [25]). $D$: direct terms; $E$: exchange terms.
d) $\Delta \xi_{BW}^E$ second order crossed interaction involving the spin-orbit and the exchange part of the electrostatic interaction. Perturbation of the core orbital ($\rightarrow 2p$) and valence orbital ($\rightarrow 3d$).

and Watson formula [25] and Hartree-Fock wavefunctions. Without the configuration mixing, Froese’s method cannot reproduce the fine-structure inversions for the first ions of the sequence and corresponds to values which are always greater than the experimental data, even for highly ionized spectra (10% for Cu XIX). Jones [15] calculated the fine-structure splitting in the Pauli approximation by using the non-relativistic wavefunctions obtained from a scaled Thomas-Fermi-Dirac potential; the agreement with experiment is not satisfactory since explicit configuration mixing is neglected. Kastner [16] introduced corrections of order $x^2$ compared to the spin-orbit interaction, by using the first two terms in the Dirac formula (cf. eq. (10)) for hydrogen-like ions; the screening parameters are obtained from Hartree-Fock calculations [29]. The predicted values obtained for $Z \geq 25$ (Mn XV) agree very well with the experimental data taking into account the simplicity of the method; this agreement is related to the fact that, for high stages of ionization, the contributions arising from the direct part of the electrostatic interaction are predominant, and these contributions are taken into account with a good approximation through the screening factors.

### 4.2.3 Comparison with multiconfigurational treatments in the Pauli approximation.

Holmgren et al. [11] and Mårtensson [12] calculated the fine-structure intervals for the 4d-state of the first five ions of the sodium sequence by introducing the relativistic effects perturbatively in a multiconfigurational model. They include to all orders the non-relativistic polarization of the core wavefunctions by the valence electron. From the perturbed wavefunctions they calculated the contributions of the spin-orbit and
spin-other-orbit interactions. The results obtained by Mårtensson with and without the spin-other-orbit interaction are reported in table II. The values obtained by Holmgren et al. are also presented; the differences between the results from references [11] and [12] arise from a number of errors in the computer program used by Holmgren [12]. For Na I and Mg II Mårtensson’s results are in better agreement with experimental data than our values. Indeed, as it is shown by Holmgren et al., a calculation of the non-relativistic core-polarization effects to the second order of the perturbation theory is insufficient and the convergence of the perturbation series is rather slow. To improve our results it would be necessary to study explicitly the relativistic core-polarization effects. For Al III, Si IV and P V the values obtained by Mårtensson do not agree completely with the experimental data; moreover there is a large difference between the values obtained with or without the spin-other-orbit interaction. In such cases, where the fine-structure splitting results from large cancellation effects between different contributions, relativistic effects of order higher than $a^2$ can be significant; consequently the Pauli approximation can be insufficient.

5. Calculation of the valence wavefunctions in the total electrostatic potential $V_{D+E}$ of the frozen-core. — The method described above cannot be used when the valence orbital has the same angular symmetry as some core orbitals. In this case it is necessary to determine the valence orbital in the total potential of the core $V_{D+E}$ (local direct potential and non-local exchange potential); then the orthogonality of wavefunctions with the same angular symmetry is ensured by the introduction of Lagrange multipliers. In this section we compare briefly this new method to the method presented in the previous sections.

5.1 NON-RELATIVISTIC LIMIT FOR THE SPIN-ORBIT CONSTANT FOR A CALCULATION IN $V_{D+E}$. — When the wavefunction for the valence orbital ($v \equiv nlj$) is determined in the total potential $V_{D+E}$ of the frozen-core, the large $P'_{v}$ and small $Q''_{v}$ components of the relativistic wavefunction are solution of an inhomogeneous system of two coupled first order differential equations; this system involves the wavefunctions

Table II. — Fine-structure intervals (in cm$^{-1}$) for the 4d state in the Na isoelectronic sequence.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na I</td>
<td>0.034 3</td>
<td>0.026 9</td>
<td>0.031 58</td>
<td>0.028 5</td>
</tr>
<tr>
<td>Mg II</td>
<td>0.52</td>
<td>0.405</td>
<td>0.572</td>
<td>0.409</td>
</tr>
<tr>
<td>Al III</td>
<td>1.19</td>
<td>0.532</td>
<td>1.629</td>
<td>1.097</td>
</tr>
<tr>
<td>Si IV</td>
<td>0.12</td>
<td>2.082</td>
<td>1.420 0.387</td>
<td>0.194</td>
</tr>
<tr>
<td>P V</td>
<td>5.13</td>
<td>10.532</td>
<td>2.736 6.866</td>
<td>4.514</td>
</tr>
</tbody>
</table>
for the frozen-core orbitals. The non-relativistic limit for the wavefunctions and for the energies is obtained by expanding the two equations of this system, the energy $W'$ as well as the radial wavefunctions, in powers of $a^2$ (cf. eq. (2)). In this section, quantities with a prime ' correspond to results where the valence wavefunction is determined in $V_{D+E}$; unprimed quantities are associated with the calculation in $V_D$.

5.1.1 Non-relativistic limit for the valence wavefunction $v \equiv nl$. — The non-relativistic limit for the large component of the valence wavefunction, $P_{nl}^{(0)}$ is identical to the non-relativistic wavefunction $R_{nl}$ obtained in the corresponding Hartree-Fock frozen-core model; compared to $P_{nl}^{(0)}$, this function $P_{nl}^{(0)}$ takes into account the configuration mixing corresponding to the exchange part of the non-relativistic electrostatic interaction, between core and valence orbitals.

The relativistic correction to the large component $P_{nl}^{(1)}$ introduces implicitly the configuration mixing (cf. eq. (3)) arising from the relativistic operator $h_{rel}(V_D)$

$$h_{rel}^{nl}(V_D, E) = p^4 \text{ term } + \text{ Darwin term } + \frac{Z}{\alpha^3} (s \cdot l) + H_{900}^{D} + \frac{1}{3} H_{900}^{E}.$$  

In addition to the relativistic operators present in $h_{rel}^{nl}(V_D)$ (eq. (4)), $h_{rel}^{nl}(V_{D+E})$ includes one third of the exchange part of the spin-other-orbit interaction $H_{900}$ between core and valence orbitals.

5.1.2 Non-relativistic limit for $\xi_D(nl) + \xi_E(nl)$. — For a calculation in the total potential of the core $V_{D+E}$, the contributions to the spin-orbit constant arising from the electrostatic interaction (direct and exchange terms) are directly related to the difference between the eigenvalues for the $nlj_+ = l + 1/2$ and $nlj_- = l - 1/2$ orbitals. To the order $a^2$

$$\xi_D(nl) + \xi_E(nl) \rightarrow \frac{2}{2l + 1} (W_{nlj_+}^{D} - W_{nlj_-}^{D}).$$  

Consequently $\xi_D(nl) + \xi_E(nl)$ is directly determined to the zero order of the present model. Furthermore it is possible to show that this quantity introduces the effective operators contributions present in eq. (11) and the purely relativistic effects corresponding to the relativistic corrections to the core wavefunctions $\Delta \xi_D(nl)$ and $\Delta \xi_E(nl)$; indeed since the valence wavefunction is determined in the total electrostatic potential, the contributions arising from the direct part and from the exchange part of the potential cancel exactly.

5.2 COMPARISON BETWEEN THE CALCULATIONS $V_D$ AND $V_{D+E}$. — In table III we present the values obtained for the fine-structure splitting $A$ for the 3d and 4d terms for some ions of the sequence. The calculations are performed either in the direct $V_D$ or in the total potential $V_{D+E}$ of the frozen-core model and are compared to the experimental data. The difference between the values $V_D$ and $V_{D+E}$ decreases with increasing stages of ionization and is not very significant for $Z$ greater than twenty. Indeed for highly ionized spectra the contributions arising from the direct part of the relativistic operators are predominant compared to the contributions corresponding to the exchange part; therefore in the study of purely relativistic effects the configuration mixing arising from the exchange part of the spin-other-orbit interaction is almost negligible.

For the first ions of the sequence, important cancellation effects appear, involving the direct part of the electrostatic interaction and the purely relativistic effects in the exchange part of the electrostatic

<table>
<thead>
<tr>
<th>Ion</th>
<th>$A_{D}$</th>
<th>$A_{D+E}$</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na I</td>
<td>-0.04025</td>
<td>-0.05316</td>
<td>-0.0508 (*)</td>
</tr>
<tr>
<td>Mg II</td>
<td>-0.6505</td>
<td>-0.9931</td>
<td>-0.875 (*)</td>
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<td>Al III</td>
<td>-1.760</td>
<td>-3.445</td>
<td>-2.29 (*)</td>
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<td>Si IV</td>
<td>-0.4283</td>
<td>-4.463</td>
<td>-1.19 (*)</td>
</tr>
<tr>
<td>P V</td>
<td>+8.273</td>
<td>1.090</td>
<td>7.05 (*)</td>
</tr>
<tr>
<td>S VI</td>
<td>30.06</td>
<td>19.23</td>
<td>32.5 (*)</td>
</tr>
<tr>
<td>Cl VII</td>
<td>71.79</td>
<td>56.99</td>
<td>73.3 (*)</td>
</tr>
<tr>
<td>Ar VIII</td>
<td>141.3</td>
<td>122.3</td>
<td>151.7 (*)</td>
</tr>
<tr>
<td>K IX</td>
<td>246.3</td>
<td>222.8</td>
<td>255.0 (*)</td>
</tr>
<tr>
<td>Ca X</td>
<td>396.5</td>
<td>368.3</td>
<td>410.0 (*)</td>
</tr>
<tr>
<td>Mn XV</td>
<td>2195</td>
<td>2139</td>
<td>2217.4 (*)</td>
</tr>
<tr>
<td>Zn XX</td>
<td>6965</td>
<td>6873</td>
<td>720.0 (*)</td>
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<tr>
<td>Zr XXX</td>
<td>34400</td>
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<td>15120</td>
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<tr>
<td>Mo XXXII</td>
<td>44320</td>
<td>44110</td>
<td>44900.7 (*)</td>
</tr>
<tr>
<td>Sn XL</td>
<td>106500</td>
<td>106100</td>
<td>19430</td>
</tr>
</tbody>
</table>

(*) Refs. [28, 30] ; (t) Ref. [31] ; (v) Ref. [32] ; (w) Ref. [33] ; (x) Ref. [34] ; (y) Ref. [35] ; (z) Ref. [36] ; (a) Ref. [37] ; (b) Ref. [18].
interaction; these cancellations give rise to small fine-structure splitting. In such a case, the contributions arising from the spin-other-orbit interaction cannot be neglected. In a calculation in the total potential V_p+E, one third of the exchange part of the spin-other-orbit interaction appears in the zero order and the remainder in the study of the Gaunt interaction to the first order of the perturbation theory. Owing to this asymmetry, it may be asked whether it is better to introduce the Gaunt interaction in the inhomogeneous equations used to generate the wavefunctions for the valence orbitals; in such a treatment the purely relativistic effects corresponding to the whole spin-other-orbit interaction occur in the first order of the perturbation theory. Let us recall that this procedure is not theoretically justified, since the Breit interaction must be treated only as a perturbation in first order.

6. Conclusion. — The theoretical results obtained from the Relativistic Parametric Potential Method describe well the experimentally observed fine-structure splitting for the 3d and 4d terms of the sodium isoelectronic sequence. In particular the anomalies in the fine-structure of alkali-like spectra can be interpreted in a first order relativistic central field approximation without introducing explicitly configuration mixing. In fact the purely relativistic effects, which in the Pauli limit correspond to configuration interaction through the relativistic operators, are automatically introduced in the single configuration approach provided that the relativistic corrections of order α^2 on the large components of the wavefunctions are kept. For the first ions of the sequence (up to Ca X) the purely relativistic effects are predominant and account for the fine-structure anomalies; for higher stages of ionization the contributions arising from the small components of the relativistic wavefunctions — i.e. the effective operator contributions — are the most important. For the first ions apart from relativistic effects, the correlation effects are also important, as reflected in the discrepancy between the values obtained by using different methods for generating the valence wavefunctions (V_p and V_p+E calculations). For such cases, a treatment to the first order in a frozen-core model is insufficient. It would be particularly interesting to develop a relativistic treatment of the polarization effects induced in the core by the presence of the valence electron; such a treatment could be used to study the fine-structure anomalies observed in the nd series of rubidium for which the correlation effects cannot be neglected [38].

APPENDIX A

1. Effective spin-orbit constant for a system with one-electron outside closed shells. — Let us consider a system with one-electron nlj outside closed shells n, ij.

The contribution ξ_D(nl) to the spin-orbit constant ξ_{BD}(nl) arising from the one-particle Dirac operators and from the direct part of the electrostatic interaction between core and valence orbitals is given by

$$\xi_D(nl) = \frac{2}{[l]} \left[ R(nlj+) - R(nlj-) \right] + \frac{6}{\sqrt{l(l+1)(2l+1)}} \sum_{n,l,j} (-1)^{l+j+1/2} \times$$

$$\times \left[ jj_1 \right] \left[ 1/2 \right. \left. l \right] \left[ j \right] \left[ 1/2 \right. \left. 1 \right] \times F^0(n, l, j, nlj) \quad (A.1)$$

where j± = l ± 1/2, [ll'] = (2l + 1)(2l' + 1), and \{\} = 6j symbol.

Explicit expressions for the one-electron integral I and the direct Slater integral F^0 are given in reference [23].

When the wavefunctions for the valence orbitals are calculated in the direct potential of the frozen-core and correspond to energy W

$$\xi_D(nl) = \frac{2}{[l]} [W_{nlj+} - W_{nlj-}] \quad (A.2)$$

The contribution ξ_E(nl) arising from the exchange part of the electrostatic interaction between core and valence orbitals is given by

$$\xi_E(nl) = \frac{6}{\sqrt{l(l+1)(2l+1)}} \sum_{j,k} (-1)^{l+j+3/2} \left[ jj_2 \right] \times$$

$$\times \left\{ 1/2 \right. \left. l \right\} \left\{ j \right. K \left. j \right\} \left[ l \right. \left. 1/2 \right. \left. 1 \right] \times \left\{ l \right. \left. 1/2 \right. \left. l \right\} \times G^K(n, l, j, nlj) \quad (A.3)$$

Expressions for the exchange Slater integral G^K and the reduced matrix element (l || C^(K) || l) are given in reference [23].
The direct part of the Breit interaction between core and valence orbitals does not contribute to the spin-orbit constant. The contributions arising from the exchange part of the Gaunt interaction $\xi_G(nl)$ and of the retardation term $\xi_R(nl)$ can be expressed in terms of exchange magnetic integrals $H^K$ [39]

$$H^K(a, b, c, d) = \int_{r_1 < r_2} \frac{r_1^K}{r_2^{l+1}} P_a(1) Q_b(1) P_{a'}(2) Q_{a'}(2) \, dr_1 \, dr_2. \quad (A.4)$$

2. Purely relativistic contributions to $\xi_E(nl)$. — The contribution arising from the corrections to the core orbital $n_c l_c$ determined in the central potential $U_C$ are given by

$$\Delta \xi_E(nl'; \leftarrow n_c l_c) = 2 \sqrt{l_c(l_c + 1)(2l_c + 1)} \sum_K (l \parallel C^K \parallel l_c)^2 \left\{ \begin{array}{ccc} l & l_c & 1 \\ l & 1 & K \end{array} \right\} \times$$

$$\times \sum_{n'_c \neq n_c} \sum_{n_{l_c} \neq n_{l_c}} R^K(n_c l_c nl; n'_c l'_c) \frac{1}{W^{(0)}_{n_c l_c} - W^{(0)}_{n'_c l'_c}} \xi(U_C)_{nl l_c n'_c l'_c} R^K(n_c l_c nl; nl, n'_c l'_c) \quad (A.5)$$

$\xi(U_C)_{nl l_c n'_c l'_c}$ is the non-diagonal radial integral of the spin-orbit interaction in the potential $U_C$ (see eq. (4)); $R^K$ is an electrostatic radial integral and the denominator is equal to the difference in the energies of the non-relativistic orbitals $n_c l_c$ and $n'_c l'_c$. Due to the $6j$ symbol the relativistic contributions to the s-orbitals of the core ($l_c = 0$) do not contribute to the purely relativistic effects.

The corrections to the wavefunction of the valence orbital determined in $V_D$ contribute to $\Delta \xi_E(nl'; \leftarrow nl)$

$$\Delta \xi_E(nl'; \leftarrow nl) = \frac{1}{[l]} \sum_{n_{l_c} \neq n_c} \sum_K (l \parallel C^K \parallel l_c)^2 \times \sum_{n_{l_c} \neq n_c} R^K(n_l l_c nl; n_l, n'_c l'_c) \frac{1}{W^{(0)}_{n_l l_c} - W^{(0)}_{n_l l_c}}$$

$$\xi(V_D)_{nl n'_c l'_c} R^K(n_l l_c nl; nl, n'_c l'_c) \quad (A.6)$$

$\xi(V_D)_{nl n'_c l'_c}$ is the non-diagonal radial integral of the spin-orbit interaction in the potential $V_D$; it includes the spin-orbit interaction in the potential of the nucleus and the direct part of the spin-other-orbit interaction between core and valence orbitals (see eq. (4)). All core wavefunctions, even $l_c = 0$ contribute to $\Delta \xi_E(nl'; \leftarrow nl)$.

If one supposes that not too far from the nucleus $R_{nl'}$ and $R_{nl'}$ (or $R_{nl'}$ and $R_{nl'}$) differ only through a normalization factor, then the quantities $\xi \times R^K \times \frac{1}{W^{(0)}_{nl} - W^{(0)}_{nl'}}$ are positive. Consequently $\Delta \xi_E(nl'; \leftarrow nl)$ is positive; the different contributions (for different $K$ values) in $\Delta \xi_E(nl'; \leftarrow n_l l_c)$ depend on the sign of the $6j$ symbol: they are positive for $K(K + 1) > [l(l + 1) + l_c(l_c + 1)$, negative otherwise. We have verified these results for the $nd$ terms of Na I sequences; $\Delta \xi_E(nd; \leftarrow nd)$ is always positive; the term $K = 1$ in $\Delta \xi_E(nd; \leftarrow 2p)$ is negative and in absolute value four times greater than the term $K = 3$, this latter being positive. Consequently our analysis agrees completely with the conclusion of Foley and Sternheimer [7], which explain the observed inversion in the fine-structure as due to a crossed second order effect involving the electrostatic dipole exchange interaction ($K = 1$) and the magnetic spin-orbit interaction acting on the np electrons of the core.

References