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Doublet inversions in alkali-metal spectra: Relativistic and correlation effects

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It is shown that in the central-field approximation, a relativistic calculation reproduces the inverted fine structures experimentally observed in the series of excited sodium nd ($3 \leq n \leq 16$) and cesium nf ($4 \leq n \leq 12$) terms. Theoretical results are in good agreement with measured values. In view of the simplicity of the method used, it can easily be applied to all the states of a given Rydberg series. This work brings to light the fact that a complete relativistic treatment (which introduces automatically the relativistic contributions on the large components of the wave functions) is equivalent to a multiconfigurational expansion of nonrelativistic wave functions taking into account relativistic corrections (in the low-Z Pauli limit).

I. INTRODUCTION

Many alkalilike systems exhibit anomalously narrow or inverted fine structures.[1] Such an example is provided by the nd Rydberg states of sodium, or the nf states of cesium. This well-known result is rather strange since these levels have a strong hydrogenlike behavior as far as atomic properties such as energies or polarizabilities[2] are concerned. Recently, Fabre and co-workers,[3] using quantum-beat spectroscopy and a stepwise excitation process, have measured the fine-structure intervals of highly excited sodium nd states ($9 \leqslant n \leqslant 16$). The experimental data agree with an empirical formula giving the fine-structure interval as an expansion in odd powers of n^{-1}; in the asymptotic limit, this empirical function is negative, so that fine-structure anomalies appear even for very highly excited states.

For a long time theoretical studies on this subject have introduced two distinct phenomena. In 1933, Johnson and Breit[4] showed that the exchange term corresponding to magnetic interactions gives a contribution which reduces the doublet separation of the cesium nf terms, but this effect is too small to explain the doublet inversion in this spectrum. In the same year Phillips[5] tried to explain the inversion of the $3d$ levels of the Na I sequence as owing to core polarization; such an effect can be formulated as a third-order contribution from the excited configuration $2p^5\,3p3d$, but this contribution is likewise insufficient.[6]

Recently, several theoretical groups have become interested in the study of the anomalies in the fine structures of the alkali isoelectronic sequences. According to Beck and co-workers[7,8] it is necessary to correlate the wave functions and to include the low-Z Pauli operators, i.e., correction terms to the energy of order $Z^4\alpha^4$ (Z is the nuclear charge and α is the fine-structure constant). As for Lee and co-workers,[9] they introduce the anisotropic exchange core polarization of the non-s core shells.

The usual spin-orbit and other magnetic interactions are in fact effective operators obtained from the nonrelativistic limit of the Breit-Dirac equation. Since the fine structure is essentially a relativistic effect, it can be studied in the framework of a complete relativistic treatment using relativistic wave functions. In a previous work[10] it was shown that a relativistic central-field model is able to reproduce the inversion effect observed in the cesium nf levels and in the $3d$ states of the Na I isoelectronic sequence. In order to study highly excited states it was necessary to improve the numerical accuracy of the method; indeed, the doublet separation is very small compared with the total term energy, and large cancellation effects occur in the study of exchange terms. In the following, a systematic study of excited sodium nd and cesium nf states is described and an analysis of both relativistic and correlation effects is presented.

II. RELATIVISTIC CALCULATION OF ATOMIC FINE STRUCTURES IN THE CENTRAL-FIELD APPROXIMATION

A. Relativistic Hamiltonian for a many-electron atom

The study of two-electron atoms has been extensively reviewed by Bethe and Salpeter,[11] and we shall present here only the main results. A fully Lorentz-invariant Hamiltonian describing two-body interactions between relativistic particles is not available. Nevertheless, it is possible to obtain the correction to the Coulomb repulsion in the form of an expansion in powers of α. The effective Hamiltonian most often used is the Breit operator, which introduces corrections of order $Z^2\alpha^2$ owing to the exchange of a virtual photon between the two electrons. Higher-order terms are omitted and therefore the Breit correction must be treated as a perturbation in first order and must not be included in the Hamiltonian used for generating the eigenfunctions. In the low-Z Pauli limit, the Breit interaction reduces to a part of the spin-spin, spin-other-orbit, and orbit-orbit interactions.[12]

Practically, the evaluation of the Breit correction is tedious, but, in fact, it is possible to simplify the calculations by considering the Gaunt operator[13] H_G only, which is the unretarded interaction between two Dirac currents. Indeed, in computing fine-structure intervals for light atoms, the Breit and Gaunt operators are nearly equivalent.[13] The Gaunt interaction is used in this work to evaluate corrections to the Coulomb repulsion.

B. Relativistic radial wave functions

To compute relativistic radial wave functions we use the relativistic parametric-potential method described in a previous paper.[10] However, this method has been modified to be better adapted to the study of nonpenetrating Rydberg states.

In the central-field approximation, the Hamiltonian for an N-electron atom can be written as $H=H^0+H^1$, where H^0 is a sum of single-particle Dirac Hamiltonians h,[11] corresponding to the same central potential $U(r)$. H^1, which contains both one- and two-body operators, is treated as a perturbation. A relativistic state $|nljm)$ is a solution of the eigenvalue equation

$$h\,|nljm)=\epsilon_{nlj}\,|nljm) \tag{1}$$

and can be written

$$|nljm)=\begin{bmatrix}[P_{nlj}(r)/r]\,|ljm\rangle\\ i[Q_{nlj}(r)/r]\,|\bar{l}jm\rangle\end{bmatrix}, \tag{2}$$

where $\bar{l}=2j-l$, and where the radial wave functions P_{nlj} and Q_{nlj} (P and Q for short) are solutions of a system of two coupled first-order differential equations[11] (atomic units),

$$\begin{aligned}\frac{dP}{dr}+\kappa\frac{P}{r}&=\frac{1}{\alpha}[1+\epsilon-\alpha^2U]Q\,,\\ \frac{dQ}{dr}-\kappa\frac{Q}{r}&=\frac{1}{\alpha}[1-\epsilon+\alpha^2U]P\,,\end{aligned} \tag{3}$$

where $\kappa=(-1)^{l+j+1/2}(j+\frac{1}{2})$. U (<0) is the central potential. The reduced total energy ϵ is related to the binding energy E (in hartrees) by

$$\epsilon=1+E/mc^2\equiv 1+\alpha^2E$$

(m is the mass of the electron, c the speed of light). For bound states, $\epsilon<1$; for continuum states, $\epsilon>1$.

The nonrelativistic state $|nljm\rangle$ associated with the relativistic state $|nljm)$ is given by

$$|nljm\rangle=[R_{nl}(r)/r]\,|ljm\rangle\,. \tag{4}$$

In the parametric-potential method, the central potential is represented by an analytic function depending on a set of parameters, each parameter describing the distribution of charges in a complete shell $(K,L,\ldots)$ of the atomic core. The optimal potential is determined by minimizing either the total energy of the studied level [variational criterion (VC)] or the root-mean-square deviation between observed and calculated energies of some chosen levels of the spectrum [spectroscopic criterion (SC)]. The potential $U(r)$ being known, it is possible to compute radial functions P and Q by integrating numerically systems of two coupled first-order differential equations.

C. Optimal central potential in the case of nonpenetrating Rydberg states

To study nonpenetrating Rydberg states, neither of the usual criteria (VC and SC) is well adapted for generating simultaneously core and valence orbitals. Indeed, in this case the valence electron is mostly well outside the core, so that the overlap between valence and core charge distributions is very small. The core wave functions are hardly disturbed by the valence electron and the relative values of the energy levels are mainly linked to the direct part of the electrostatic interaction. For all of these reasons the SC criterion applied to nonpenetrating Rydberg states does not reproduce the overlap of core and valence orbitals very well. As it will be shown below, the fine-structure inversions are principally due to this overlap. Moreover, the contribution of the valence electron to the total energy of a level (VC criterion) is weak; thus to obtain the best core wave functions it is preferable to study the core alone and to apply the VC criterion to the ground state of the positive ion. The valence electron moves in the local potential owing to the nucleus and to the direct part of the electrostatic interaction, and in the nonlocal exchange potential. Since the overlap of core and valence orbitals is small, it is possible to treat the exchange potential as a first-order perturbation. In first approximation the central potential for the valence orbital is Coulombic ($V_h=-1/r$). In a more exact way the central potential arises from the complete electrostatic interaction produced by the ground state of the core, which has spherical symmetry; this potential can be written

$$V_d(r)=-\frac{Z}{r}+\sum_{n_cl_cj_c}\frac{(2j_c+1)Y^0(n_cl_cj_c,n_cl_cj_c;\,r)}{r}\,, \tag{5}$$

where the summation concerns the $n_c l_c$ core orbitals and $j_c = l_c \pm \frac{1}{2}$. The Y^K functions[14] are similar to those introduced in the nonrelativistic study.

In the particular case of the sodium *nd* or cesium *nf* states, the orthogonality conditions between core and valence orbitals are automatically satisfied, since these orbitals correspond to different *l* values.

We can further improve the model by introducing core-polarization effects in an effective way. Indeed, in alkalilike atoms the binding energies of nonpenetrating Rydberg states differ from the corresponding hydrogenic values mainly because of core-polarization effects.[15] These interactions also influence oscillator strengths in the alkali atoms.[16] When the ground state of the core has spherical symmetry and when nonpenetrating Rydberg states are concerned, it is possible to obtain perturbed wave functions for valence electrons by adding to the central potential an effective term ΔV_p.[17] This polarization potential takes into account the second-order perturbation owing to the direct part of the electrostatic interaction, and decreases asymptotically as r^{-4}. A suitable cutoff function has to be introduced; in this work we take

$$\Delta V_p(r) = -\tfrac{1}{2}\alpha_d r^{-4}(1 - e^{-(r/r_c)^6}) , \qquad (6)$$

where α_d is the static dipole polarizability of the core and r_c is an effective core radius. For r_c and α_d we use the values given by Weisheit,[18] and we neglect in $\Delta V_p(r)$ higher-order terms such as quadrupole polarizability interaction or nonadiabatic long-range interactions.[17]

In conclusion, in this approximation the radial wave functions for a Rydberg level *nlj* are generated using the potential $V_d(r) + \Delta V_p(r)$, and the total energy is obtained by treating to first order the contributions of the nonlocal exchange potential H_E and of the Gaunt interaction H_G. We note that for an alkalilike spectrum the direct part of the Gaunt interaction between the valence and core electrons vanishes.

D. Numerical procedure

To describe highly excited wave functions which extend far from the nucleus and which have an oscillatory behavior, it is more convenient to use, rather than a logarithmic mesh, a scaled linear mesh similar to that introduced by Herman and Skillman.[19] This mesh is composed of blocks having equally spaced intervals, the interval being doubled when going to the next block. For each radial wave function 3000 points can be computed. The calculations are performed using double precision on a Univac 1110. For example, this method enables one to compute the 10*d* fine-structure interval for hydrogen with a relative accuracy better than 5×10^{-5}, although this fine-structure interval is 10^6 times smaller than the total energy of the term. (We note that the relativistic determination of one fine-structure interval is achieved by calculating independently the total energies of the two levels $j_\pm = l \pm \frac{1}{2}$ belonging to the corresponding *nl* term.)

III. FINE-STRUCTURE INTERVALS OF SODIUM *nd* AND CESIUM *nf* RYDBERG STATES

A. Numerical results

Table I presents various results concerning the fine-structure intervals of sodium *nd* excited states ($3 \leq n \leq 16$). Experimental data are given in column 7. For the lower states ($n = 3-6$) the fine-structure intervals have been determined using classical interferometry. For highly excited states ($n = 9-16$) the results were recently obtained by Fabre and co-workers[3] by means of quantum-beat spectroscopy. An empirical formula giving the fine-structure intervals as an expansion in odd powers of n^{-1} allows these authors to predict the values for the intermediate states $n = 7$ and 8.

The theoretical results correspond to the different approximations described above. The SC approximation is presented in column 2. Here the central potential is determined with the SC criterion applied to the lowest energy levels of the spectrum, and it is used to generate core as well as valence orbitals; moreover, the Gaunt interaction H_G is not taken into account. In the other columns core wave functions correspond to the VC criterion applied to the ground state of the ion Na$^+$. For the valence electrons the central potential is either the pure Coulombic one, V_h (column 3), or the direct potential V_d [Eq. (5)] produced by the Na$^+$ core (columns 4–6). In column 6 the effective polarization potential ΔV_p [Eq. (6)] is added. In these VC approximations the nonlocal exchange potential H_E is treated as a perturbation to first order and the Gaunt interaction H_G is either neglected (columns 3 and 4) or introduced (columns 5 and 6).

In Table II we report in an analogous way similar results concerning the *nf* Rydberg states of cesium ($4 \leq n \leq 12$). For Cs the experimental data were obtained by Eriksson and Wenåker[20] by means of the classical spectrographic method. These experimental results[20] are undoubtedly not as accurate as those obtained for sodium by quantum-beat spectroscopy,[3] but they are better than the experimental values published previously by Moore.[1]

For both cases the conclusions are similar. The SC results reproduce the fine-structure inversion but the absolute values are too large (factor of 3). As mentioned above, the SC approximation is not

TABLE I. Fine-structure intervals of sodium *nd* states (mK). Potentials used to generate the relativistic radial wave functions: SC, spectroscopic criterion for Na I spectrum; VC, variational criterion for Na^+; V_h, Coulombic potential; V_d, direct potential corresponding to Na^+ [see Eq. (5)]; and ΔV_p, effective polarization potential [see Eq. (6)]. Hamiltonian treated as a perturbation to first order: H_E, nonlocal electrostatic exchange potential; H_G, Gaunt interaction. 1 mK$=10^{-3}$ cm^{-1}.

n	Theory: core potential	SC	VC	VC	VC	VC	
	nd potential	SC	V_h	V_d	V_d	$V_d+\Delta V_p$	
	Hamiltonian	H_E	H_E	H_E	H_E+H_G	H_E+H_G	Experiment[a]
3		−174.79	−32.33	−36.05	−40.26	−43.79	−49.43 ±1.67
4		−101.91	−23.75	−25.97	−28.45	−30.49	−34.31 ±0.10
5		−58.56	−14.54	−15.84	−17.28	−18.43	−20.61 ±0.40
6		−35.85	−9.16	−9.96	−10.85	−11.55	−12.41 ±1.67
7		−23.31	−6.05	−6.57	−7.16	−7.61	(−8.44)
8		−15.93	−4.18	−4.54	−4.93	−5.24	(−5.81)
9		−11.39	−3.01	−3.27	−3.55	−3.75	− 4.15 ±0.05
10		−8.34	−2.21	−2.40	−2.61	−2.77	− 3.05 ±0.03
11		−6.31	−1.68	−1.82	−1.98	−2.10	− 2.33 ±0.02
12		−4.89	−1.30	−1.41	−1.54	−1.63	− 1.80 ±0.02
13		−3.86	−1.03	−1.12	−1.22	−1.29	− 1.43 ±0.02
14		−3.10	−0.83	−0.90	−0.98	−1.04	− 1.14 ±0.03
15		−2.53	−0.68	−0.74	−0.80	−0.85	− 0.93 ±0.03
16		−2.09	−0.56	−0.61	−0.66	−0.71	− 0.77 ±0.03

[a] See Ref. 3.

well adapted to the study of fine-structure intervals for nonpenetrating Rydberg states.

On the contrary, if one supposes that the valence electron moves in the Coulombic potential V_h and if only the contribution of the exchange potential H_E is considered (V_h+H_E approximation), the theoretical results are already in reasonable agreement with the experimental data, in spite of the rough approximation used in this treatment. The departure from hydrogenic behavior for the valence orbital, the Gaunt interaction, and the core-polarization effects contribute to the increase in the fine-structure inversion, but they are only secondary effects which, if introduced alone, are not large enough to explain the inversions. In the sodium case these last three effects are of the same order of magnitude and give rise to corrections which are ten times smaller than the contribution of the V_h+H_E approximation. Eventually the results of the complete treatment ($V_d+\Delta V_p+H_E+H_G$ approximation) reproduce very well the evolution of the fine-structure intervals along the Rydberg series, and the discrepancy between the theoretical and experimental data does not exceed 10%. For cesium the departure from hydrogenic behavior for the *f* valence electron is significant, but

TABLE II. Fine-structure intervals of cesium *nf* states (mK). Same notation as in Table I.

n	Theory: core potential	SC	VC	VC	VC	
	nf potential	SC	V_h	V_d	V_d	
	Hamiltonian	H_E	H_E	H_E	H_E+H_G	Experiment[a]
4		−529.94	−203.46	−223.53	−223.86	−181.3
5		−434.81	−165.28	−182.52	−182.79	−146.6
6		−307.62	−116.19	−128.70	−128.90	−103.7
7		−215.82	−81.22	−90.13	−90.28	−69.2
8		−154.37	−57.98	−64.41	−64.52	−46.4
9		−113.18	−42.46	−47.21	−47.28	−34.0
10		−85.00	−31.86	−35.45	−35.50	−23.8
11		−65.25	−24.45	−27.21	−27.25	−24.6
12		−51.08	−19.13	−21.30	−21.33	−13.5

[a] See Ref. 20. Uncertainty ±2 mK.

the contribution of the Gaunt interaction is almost negligible; the effect of core polarization cannot be neglected. Indeed, the static polarizability of the core increases by a factor of 20 from sodium to cesium,[18] so that in the case of heavy alkali atoms the distortion of the core wave functions by the valence electron could be appreciable and the introduction of an effective polarization potential may be insufficient. For this reason core-polarization effects are not included in the cesium case; in order to improve the agreement between experimental and theoretical results one would have to introduce a more elaborate model.

A more detailed analysis of the sodium $3d$ levels is presented in Table III. The core orbitals are VC wave functions of the Na^+ ion and the valence orbital is either hydrogenic (column 1) or calculated in the potential V_d [Eq. (5)] (columns 2 and 3). When the hydrogenic wave function is used it is necessary to introduce as a perturbation to first order the central part of the perturbing potential, but the corresponding contribution $[-Z/r - V_h + \sum (1/r)Y^0]$ is small (2 mK). It can be recalled that this contribution vanishes when the valence orbital moves in the potential V_d, since the one-body part $(-Z/r - V_d)$ cancels exactly the two-body part $[\sum (1/r)Y^0]$ which is the direct electrostatic interaction between the core and valence electrons. By numerical calculation this cancellation is verified with a relative accuracy of 10^{-12}. In column 3 of Table III we report the average contributions to the total energy of the $3d$ term. These values show that the main contribution to the total energy comes from the eigenvalue ϵ of the Dirac equation. The small overlap of the core and valence orbitals gives rise to the weak value of the contribution of the nonlocal exchange potential H_E. The contribution of the Gaunt interaction H_G is of order $Z^2\alpha^2$ smaller than the electrostatic exchange interaction H_E.

TABLE III. Fine-structure interval of the sodium $3d$ term. Experimental value $\Delta\nu_{exp} = -49.43 \pm 1.67$ mK. The core wave functions are VC functions of Na^+. The $3d$ electron moves in the potential U which is either the hydrogenic potential V_h or the direct potential V_d of Na^+ [see Eq. (5)]. H_D: direct electrostatic interaction plus cinetic energy; H_E: exchange electrostatic interaction; H_G: Gaunt interaction.

		Fine-structure interval (mK)		Average total energy for $3d$ (cm^{-1})
		V_h	V_d	V_d
H_D	ϵ	36.07	39.00	−12 200
	$-Z/r-U$	+1442.87	1633.41	−244 282
	$\sum (1/r)Y^0$	−1440.94	−1633.41	+244 282
H_E		−70.33	−75.05	−16
H_G		−3.47	−4.21	9.2×10^{-3}
Total		−35.80	−40.26	−12 216

The operator H_D, which contains the kinetic energy and the direct part of the electrostatic potential, gives rise to a positive contribution to the fine-structure interval (+39 mK). This was already shown by Blume and Watson[21] using the low-Z Pauli limit, and is demonstrated in the Appendix in the framework of a fully relativistic treatment. The negative contribution of the Gaunt interaction H_G (−4 mK) is too small to explain the inverted fine structure. The inversion comes from the large negative contribution of the nonlocal exchange potential H_E (−75 mK).

B. Negative contribution of the nonlocal exchange potential: A purely relativistic effect

To aid us in understanding the origin of the negative contribution of the exchange potential H_E, it is possible to expand the relativistic radial wave functions in powers of α^2, so that

$$\begin{aligned} P_{nlj} &\rightarrow R_{nl} + \alpha^2 \Delta R_{nlj} + \cdots , \\ Q_{nlj} &\rightarrow \alpha\left(\frac{d}{dr} + \frac{\kappa}{r}\right) R_{nl} + \cdots , \end{aligned} \tag{7}$$

where $\kappa = (-1)^{j+l+1/2}(j+\frac{1}{2})$ and R_{nl} is the corresponding nonrelativistic radial wave function.

In the Appendix we show that $\alpha^2\Delta R_{nlj}$, the correction of order α^2 to the large component P, can be interpreted as a shift of the large component P_{nlj} towards the nucleus with respect to the nonrelativistic function R_{nl}. This displacement is larger for $j_- = l - \frac{1}{2}$ than for $j_+ = l + \frac{1}{2}$ and, with a good approximation, depends only on j.

The low-Z Pauli limit neglects all terms but the first in the large component and thus introduces relativistic corrections coming from the small component only; moreover, the nonrelativistic limit of both the electrostatic and Breit interactions is introduced. The expression $(P_aP_b + Q_aQ_b)$ occurs in the study of the electrostatic interaction, and the product P_aQ_b occurs in the evaluation of the Breit interaction. When the relativistic effects associated with the product P_aP_b are not small—i.e., when the quantities $\alpha^2 R_a \Delta R_b$ or $\alpha^2 R_b \Delta R_a$ are not negligible compared to Q_aQ_b—the low-Z Pauli limit of the electrostatic interaction is not sufficient. The Breit interaction is of order α^2 compared to the nonrelativistic electrostatic interaction; consequently, the terms $\alpha^2\Delta R_{nlj}$ give rise to contributions to the energy of order α^4 and are therefore negligible.

It has been shown previously that the hydrogenic approximation $V_h + H_E$ is sufficient to reproduce the essential characters of the doublet inversion, and this shows, in particular, that the inversion is due mainly to the exchange potential H_E. Consequently, this approximation can be used to evaluate the respective influences of the relativistic effects from the large and small components. A simple way to do this is to neglect completely the small component of the hydrogenic *nd* wave function. The value obtained in this way for H_E is reported in column 2 of Table IV; it does not differ much from the result of the complete treatment (column 1). We may note that H_E gives the same contribution for both fine-structure levels when terms $\alpha^2 \Delta R_{nlj}$ are neglected, since the matrix element is then independent of j. Thus any difference seen is due directly to relativistic corrections to the large components. The contribution to the exchange potential H_E is negative and large enough (−68.57 mK) to explain the doublet inversion.

The contributions from the small components of the wave functions are equal to the differences between the values in columns 1 and 2 of Table IV (ϵ excepted), and are reported in column 3. The direct part of the electrostatic potential gives rise to a positive contribution (+1.47 mK) which is the two-body part of the spin-orbit interaction,[22] and the exchange potential is associated with the small negative contribution (−1.76 mK) to the spin-other-orbit interaction. In order to obtain the low-Z Pauli limit it is necessary to add the spin-orbit splitting of an hydrogenic $3d$ state—i.e., the value 36.07 mK, which is equal to the difference between the two eigenvalues $3d_+$ and $3d_-$. It can be noted that the spin-orbit interaction is an effective operator which introduces only the difference between the small components Q_{nlj+} and Q_{nlj-}. The total fine-structure interval is positive (+31.30 mK) and therefore it is impossible to interpret the anomalies observed in the Rydberg states of alkalilike spectra in the framework of the lowest Pauli limit without configuration interactions. Nevertheless, it is possible to account for this phenomenon in a first-order central-field model provided that this treatment introduces higher relativistic corrections; accordingly it is possible to say that these anomalies are "purely relativistic" effects. Another way to describe these inversions is to say that the nonlocal exchange potential is not the same for the two levels belonging to the same term, and that it is more attractive for the j_+ level than for the other one. In the Appendix we show how this result can be interpreted in terms of shifts of the large components of the wave functions.

IV. CONFIGURATION INTERACTION AND RELATIVISTIC EFFECTS IN ATOMIC STRUCTURE

A. Fine-structure study in the framework of a nonrelativistic description of the atomic states

In Sec. III we have shown that it is possible to interpret the anomalies in the fine structure of alkali atoms in a first-order relativistic central-field approximation without configuration interaction. A different way to study this problem is to correlate the nonrelativistic wave functions and to include the low-Z Pauli operators simultaneously.

Lee and co-workers[9] have studied the fine structure of the rubidium $4d$ term using a method similar to the following, introduced by Sternheimer[23] in the study of quadrupole shielding: First-order core wave functions are obtained which take into account the spin-orbit interaction. These perturbed wave functions are used to evaluate the exchange electrostatic energy between core and va-

TABLE IV. Respective contributions of relativistic corrections from the small and large components of the sodium $3d$ wave functions. The core wave functions are VC functions of Na^+. The $3d$ wave function is hydrogenic.

	Total	Large components	Small components or low-Z Pauli limit
ϵ	36.07	36.07	36.07[a]
$-(Z-1)/r$	+1442.87	+1082.15	360.72[b]
$\sum (1/r) Y^0$	−1440.94	−1081.69	−359.25[b]
$-(Z-1)/r + \sum (1/r) Y^0$	1.93	0.46	1.47[b]
H_E	−70.33	−68.57	−1.76[b]
H_G	−3.47	0	−3.47[b]
total	−35.80	−32.04	+32.31

[a] Spin-orbit splitting for a $3d$ hydrogenic term.

[b] Magnetic interactions.

lence electrons. These energies include the exchange core polarization contributions to the spin-orbit splitting, but the calculated value is larger than the experimental data by a factor of 25.

Beck and Odabasi[7] used a multiconfigurational wave function and introduced the low-Z Pauli operators to interpret the fine structure of the Na I and Mg II $3d$ terms. To generate all of the radial wave functions these authors introduced a central potential similar to the Hartree-Fock-Slater potential modified by Lindgren.[24] The exchange part of the potential depends on three parameters which are chosen to minimize the $2p^6\,3d - 2p^6\,4d$ configuration interaction, the Hamiltonian introducing the one-electron Pauli operators. In this sense the wave functions are relativistic ones and the central potential partially incorporates relativistic effects. In this approach, to reproduce the doublet inversion it is necessary to introduce both the $2p^6\,3d - 2p^5\,np3d$ configuration interactions and the two-body Pauli operators. For sodium $3d$, Beck and Odabasi[7] obtained the value $\nu_B = -38$ mK, which can be compared with the experimental data $\nu_{\rm exp} = -49.4$ mK and with the result of our fully relativistic treatment, $\nu = -43.8$ mK.

B. Discussion

In the treatments[7-9] using nonrelativistic wave functions, relativistic and correlation effects are very much mixed, and these studies show that correlation effects cannot be neglected. On the contrary, the first-order relativistic-central-field approach, which is used in the present work, does not introduce explicitly correlation effects. It may appear very strange that both models lead to similar results; however (see the Appendix), to order α^2 the large component P_{nlj} can be obtained by solving a Schrödinger equation which takes into account the one-electron Pauli operators[11] (spin orbit, Darwin term, and variation of electron mass with velocity). Consequently, the $\alpha^2 \Delta R_{nlj}$ corrections can be obtained in the framework of a first-order perturbation theory, which introduces a multiconfigurational expansion of the wave functions. This study shows likewise that relativistic-central-field wave functions introduce in an effective way configuration interactions coming from the one-electron Pauli operators.

In conclusion, correlation and relativistic effects are strongly connected and some phenomena can be described as either relativistic effects or configuration-interaction effects according to the chosen approximation. Furthermore, as shown by Feneuille and Armstrong,[25] when correlations and relativistic effects are separately calculated, it is necessary to add corrections to such an additive approach.

A great advantage of the relativistic-central-field approximation comes from its great simplicity. Indeed, in the case of alkalilike spectra it is easier to use directly the Gaunt operator than to introduce all of the operators appearing in the low-Z Pauli limit. Moreover, the relativistic treatment takes into account automatically the configuration-interaction effects owing to the one-electron Pauli operators. Furthermore, the relativistic-central-field approximation enables one to study all states of a given Rydberg series; on the contrary, in the approach of Beck and Odabasi[7] it is necessary to generate a multiconfigurational wave function for each state of the series. In the relativistic-central-field approximation it is possible to interpret the anomalies in the fine structure in term of shifts of the large components P_{nlj} with respect to the nonrelativistic wave function R_{nl}.

V. CONCLUSION

In this work we have been able to reproduce the inversion effect in the fine structure of sodium *nd* and cesium *nf* Rydberg states, in the framework of a relativistic-central-field approximation. This phenomenon is related to a purely relativistic effect, which can be accounted for in the single-configuration approach, provided that the relativistic corrections of order α^2 on the large components of the wave functions are kept. An equivalent method involves the use of multiconfiguration nonrelativistic wave functions together with the low-Z Pauli operators. In fact, relativistic and correlation effects are closely related and in the present problem the distinction between the two phenomena is somewhat arbitrary.

The advantages of the relativistic-central-field approximation come from the simplicity of the method, which allows one to study through a single calculation all states of a Rydberg series. The very good agreement between experimental and calculated values of the sodium *nd* and cesium *nf* fine-structure intervals shows that this method might give relevant results for many alkalilike spectra.

The introduction of the concept associated with the shift of a large component of a relativistic wave function allows one to predict where purely relativistic effects can occur. First, they appear only when the overlap of two different orbitals appears; for this reason, highly excited sodium *nd* states behave as almost perfect hydrogen states as far as total energies or polarizabilities[2] are concerned. Secondly, purely relativistic effects are not negligible when large cancellation effects occur; indeed, in this case the calculated radial integrals are very sensitive to a small relative shift of the corresponding orbitals. A well-known example of this concerns the nonzero minimum in the photoionization cross sections of the ground states of the Na, K, Rb, and Cs atoms.[26] Purely relativistic effects can also explain the line-strength anomalies in the doublet resonance lines $n^2P \rightarrow 6\,^2S$ of cesium.[27] In the relativistic-central-field approximation we have shown[28] that the two integrals $\int_0^\infty P_{npj}Q_{6s_{1/2}}\,dr$ ($j=\frac{1}{2}$ and $\frac{3}{2}$ and $8 \leq n \leq 11$), which are equal in the nonrelativistic limit, differ by a factor of 2, and that the value when $j=\frac{1}{2}$ is equal to the nonrelativistic one. This result can be easily understood by remembering that the shifts of the $6s_{1/2}$ and $np_{1/2}$ orbitals are almost equal but are much larger than the shift of the $np_{3/2}$ orbitals. Fine-structure anomalies in alkalilike spectra obey both of the following conditions: The nonlocal exchange potential introduces two different orbitals and is in this sense a nondiagonal quantity; and cancellation effects are important owing to the small overlap of core and valence orbitals.

In conclusion, in the framework of a relativistic central potential, various anomalies observed in alkalilike spectra can be related; they are due to the relativistic terms in the large components of the wave functions. These corrections give rise to a shift of the orbital towards the nucleus, the displacement being different for the j_+ and j_- functions.

APPENDIX: RELATIVISTIC TERMS $\alpha^2\Delta R_{nlj}$ IN THE LARGE COMPONENT OF A RADIAL WAVE FUNCTION

Effective Dirac potential

In the central-field approximation the radial wave functions, for an orbital nlj, are the solutions of system (3).

The small component Q may be eliminated by introducing the H function[29] defined by

$$P=\eta^{1/2}H, \quad \text{where } \eta=(1/\alpha)\,(1+\epsilon-\alpha^2U);$$

H is a solution of a linear second-order equation which is formally equivalent to the Schrödinger equation

$$-\frac{1}{2}\frac{d^2H}{dr^2}+H\left(+\frac{1}{2\alpha^2}(1-\epsilon^2)+\frac{l(l+1)}{2r^2}+U_\kappa\right)=0\,, \qquad (8)$$

in which the "effective Dirac potential" U_κ depends on the energy and on κ,

$$U_\kappa=-\frac{1}{4}\frac{\eta''}{\eta}+\frac{3}{8}\frac{\eta'^2}{\eta^2}+\frac{\kappa}{2r}\frac{\eta'}{\eta}-\tfrac{1}{2}\alpha^2U^2+\epsilon\,U\,. \qquad (9)$$

At large values of r, since η becomes constant, H is proportional to P.

It is possible to expend U_κ and $\alpha^{-2}(1-\epsilon^2)$ in powers of α^2. To the first order in α^2 it can be easily shown that H is a solution of a Schrödinger equation in which the term $\alpha^2\Delta U_\kappa$ appears in addition to the potential term U; $\alpha^2\Delta U_\kappa$ contains the following interactions, which are the one-electron Pauli operators[11]:

$$\begin{aligned}&\text{relativistic correction to kinetic energy,}\\ &\qquad -\tfrac{1}{2}\alpha^2[E^2-2EU+U^2]=-\tfrac{1}{8}\alpha^2p^4;\\ &\text{spin orbit,}\quad -\tfrac{1}{4}\alpha^2(\kappa+1)(1/r)U'; \qquad (10)\\ &\text{Darwin term,}\quad \tfrac{1}{8}\alpha^2[+U''+(2/r)U'+Z\delta(r)]\,.\end{aligned}$$

Shift of the radial wave function

In order to study the highest terms of a Rydberg series it is possible to consider the limiting case $\epsilon=1$ (or $n\rightarrow\infty$) which represents the continuum wave function at threshold. At large values of r, where α^2U is negligible, it is possible to take into account the contribution of the relativistic corrections by introducing in the oscillatory part of the $P_{n\rightarrow\infty,\,lj}$ wave function a phase shift $\delta_{n\rightarrow\infty,\,lj}$ with respect to the nonrelativistic $R_{n\rightarrow\infty,\,l}$ wave function. As in scattering theory an approximate value of this phase shift is given by[30]

$$\delta_{n\rightarrow\infty,\,lj}=\alpha^2\int_0^\infty R^2_{n\rightarrow\infty,\,l}(r)\Delta U_\kappa(r)\,dr\,. \qquad (11)$$

For the hydrogenic potential, the phase shift depends not on l but only on j and n. At threshold this value is given by

$$\delta_{n\rightarrow\infty,\,j}=\pi Z^2\alpha^2/2\,|\kappa|\,. \qquad (12)$$

As it is well known, the relativistic effects shift the wave functions towards the nucleus, and this displacement is greater for $j_-=l-\frac{1}{2}$ than for $j_+=l+\frac{1}{2}$.

At large values of r, ΔU_κ is negligible, so that the main part of the phase shift comes from the region near the nucleus where the potential is Coulombic. Therefore in first approximation, even for nonhydrogenlike spectra, the phase shift depends only on j. This assumption was numerically verified in the Cs I case.

Fine-structure intervals

The direct local part U_D of the electrostatic potential always gives rise to a positive contribution to the fine-structure intervals. Indeed, U_D is a negative function which increases with r; consequently, the contribution of the small components, which is equal to

$$\alpha^2\frac{(2l+1)}{4}\int_0^\infty\frac{1}{r}\frac{dU_D(r)}{dr}R^2_{nl}(r)\,dr\,, \qquad (13)$$

is positive. As for the large components, since the j_- orbital is closer to the nucleus than the j_+ orbital, the j_- electron moves in a potential which is more attractive than the potential acting on the j_+ electron; therefore the corresponding contribution to the fine-structure interval is positive. In conclusion, as shown by Blume and Watson[21] in the framework of a nonrelativistic treatment, the contribution of the direct part of the electrostatic potential can only be positive.

Consequently, to observe an inverted fine structure, the contribution of the exchange nonlocal potential must be negative and large enough to cancel the first part. For example, in the Na isoelectronic sequence, the exchange potential for the $3d$ orbital is essentially related to the $G^K(2p3d)$ Slater integrals ($K=1,3$). In a relativistic study several exchange integrals occur whose values are mainly linked to the overlap of $2p_j$ and $3d_{j'}$ relativistic orbitals. Since the $3d_{j'}$ orbitals are more external than the $2p_j$ orbitals, it is easy to predict from relative shifts of the wave functions that, for example,

$$G^K(2p_j3d_{3/2}) > G^K(2p_j3d_{5/2})\,, \quad j=\tfrac{1}{2} \text{ or } \tfrac{3}{2}\,.$$

Consequently, the nonlocal exchange potential is not the same for both $3d_{j'}$ levels and the fine-structure interval can be negative.

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