Core polarization in Kr VIII

L. Neale
Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT, England

M. Wilson
Department of Physics, Royal Holloway University of London, Egham Surrey TW20 0EX, England
(Received 12 December 1994)

The effect of core polarization on fine-structure splitting for the $nf\ ^2F_J$ levels in Kr^{7+} is investigated in order to explore further the fine-structure inversion of these levels. Core-polarization effects are included via two distinct methods, namely, by performing multiconfigurational Dirac-Fock calculations and single-configuration Dirac-Fock calculations including a core-polarization potential. Both sets of results are compared with presently available experimental values.

PACS number(s): 31.25.−v, 31.50.+w

I. INTRODUCTION

The spectrum of an atom consisting of a single valence electron outside a closed core should qualitatively be similar to that of a hydrogen atom, i.e., the fine-structure splitting should be normal (higher J level above lower J level). However, the fine-structure splitting for the excited states of some alkalilike and copperlike ions shows an inverted, or anomalously narrow fine-structure splitting (see Moore [1]).

Beck and Odabasi [2] successfully calculated inverted fine structure for several alkalilike atoms using a nonrelativistic approach which incorporated relativistic effect via the low-Z Pauli approximation. However, fine structure is a relativistic effect so the problem of doublet inversion has also been treated using relativistic wave functions. Luc-Koenig [3] was able to show that a relativistic central field reproduces inversion effects in alkali-metal spectra, while Cheng and Kim [4] predicted inversions in the $3d^{10}nf$ doublets for a range of Cu-like ions. A possible connection between the nonrelativistic and relativistic theories was postulated later by Detrich and Weiss [5].

Reader *et al.* [6] first drew attention to the fine-structure inversion of the $4f\ ^2F_J$ levels of the Cu-like spectrum of Kr^{7+} and compared their data with the extensive Dirac-Fock calculations of Cheng and Kim [4]. The data of Reader *et al.* [6], see Table I, suggested that while the $4f$ levels were inverted the levels of $5f$ were normal.

Recent experiments (Boduch *et al.* [7] and Jacquet *et al.* [8]) have produced new measurements for the fine structure of the doublets $3d^{10}nf\ ^2F$ ($n=5,6,7$) in Kr^{7+}. A comparison of these recent results with earlier experimental ones and theoretical calculations (see Table I) suggests that the nf inversion may persist beyond $n=4$, a finding already suggested by the results of Cheng and Kim's earlier work.

Although single-configuration Dirac-Fock calculations predict that all the nf $n=4$–7 levels of the Kr^{7+} ion are inverted, these theoretical inversions are so small that correlation effects, especially core polarization, could easily change them. The aim of this work was to undertake a series of more elaborate Dirac-Fock calculations including core polarization in order to explore whether

TABLE I. Fine-structure intervals for Kr^{7+} ion (in cm^{-1}). An asterisk denotes fine-structure intervals obtained via different transitions.

	Expt.[a]	Expt.[b]	Expt.[c]	Dirac-Fock[d]
$4f\ ^2F$	−26±6			−35.14
	(−38±2)*			
$5f\ ^2F$	13±5		−14.4±16.5	−22.19
$6f\ ^2F$		−27±24	−24.4±16.8	−12.62
			(−36.8±16.0)*	
$7f\ ^2F$			−16.0±5.8	−7.66

[a]Reader *et al.* [6].
[b]Boduch *et al.* [7].
[c]Jacquet *et al.* [8].
[d]Table II, this paper.

TABLE II. Dirac-Fock fine-structure intervals (in cm^{-1}).

	Single configuration	Single manifold
$4f\,^2F$	−35.14	−37.07
$5f\,^2F$	−22.19	−22.79
$6f\,^2F$	−12.62	−12.65
$7f\,^2F$	−7.66	−7.65

TABLE III. Fine-structure splittings (in cm^{-1}) using CP potential.

	DF-AL	Fixed core & CP
$4f\,^2F$	−35.14	−44.30
$5f\,^2F$	−22.19	−23.79
$6f\,^2F$	−12.62	−12.15

or not the predicted theoretical inversions remain unchanged.

Core-polarization effects can be included in theoretical calculations in two distinct ways, either by including a core-polarization potential or via a multiconfiguration approximation. Results of calculations using both of these methods are presented, and a comparison is made in order to determine which method is the most effective for incorporating core-polarization effects.

II. RESULTS AND CALCULATIONS

The first stage of these calculations involved performing both single-configuration and single-manifold average level (AL)–type calculations using the GRASP[2] MDCF package (Grant *et al.* [9]). In the single-configuration calculations a separate calculation was performed for each J value, while in the single-manifold calculation both J values were included in the same calculation. The results of these calculations are shown in Table II.

The difference between the single-manifold and single-configuration calculations arises from the use of a common set of orbitals in the single-manifold calculation for both J levels; clearly this effect becomes less important as the mean radius of the valence electron becomes much larger than that of the core electrons.

These Dirac-Fock calculations predict a doublet inversion for all the nf, $n=4-7$ doublets of Kr^{7+}, even though core polarization has not been included explicitly. The fact that the Dirac-Fock approximation predicts doublet inversion can be ascribed to the use of different wave functions for l and $\bar{l}$ electrons (Detrich and Weiss [5]), which leads to implicit inclusion of the exchange polarization of the valence electron due to the $np \rightarrow p$ and $nd \rightarrow d$ excitations of the core, which is known to cause doublet inversion.

III. CORE-POLARIZATION EFFECTS

The second stage of these calculations involved the inclusion of core-polarization effects by two different methods, i.e., a core-polarization potential and a multiconfiguration approximation explicitly including the most important core excitations.

A. Core-polarization potential

Core-polarization effects can be introduced explicitly into the Dirac-Fock approximations by including a core-polarization potential of the form

$$V_{\mathrm{CP}}(r)=\frac{\alpha_d}{r^4}(1-e^{(r/r_c)^6})+\frac{\alpha_q-3\beta}{2r^6}(1-e^{(r/r_c)^{10}}),$$

where α_d and α_q are, respectively, the dipole and quadrupole polarizabilities of the core, r_c is the cutoff radius for the potential, and β is a dynamical parameter.

In the first set of calculations a core-polarization potential of the form described above was included in single-configuration AL calculations of the fine-structure splitting in $4f\,^2F$, $5f\,^2F$, and $6f\,^2F$. The calculations were carried out in the following manner. First, Dirac-Fock orbitals were obtained for the core electrons $1s, 2s, \ldots, 3d$; these orbitals were then kept fixed while the outer valence electron orbital was calculated. At this stage the core-polarization potential of the valence electron was included, the values of $\alpha_d(Kr^{8+})$ and r_c used being 0.307 and 0.54 a.u., respectively (Migdalek and Bayliss [10]); the second term was neglected as its contribution to the potential is negligibly small. The results of these calculations are shown in Table III.

It can be seen from the results in Table III that the explicit inclusion of core-polarization effects via a core-polarization potential does not change the sign of the fine-structure interval, i.e., an inversion is still predicted, but in the cases of $4f\,^2F$ and $5f\,^2F$ the magnitude of the inversion is somewhat increased.

B. The multiconfiguration approximation

Core-polarization effects can also be included in Dirac-Fock calculations through the multiconfigurational

TABLE IV. Fine-structure splittings (in cm^{-1}) from MCDF calculations.

MCDF configurations	$4f\,^2F$	$5f\,^2F$	$6f\,^2F$	$7f\,^2F$
$3d^{10}nf$	−37.07	−22.79	−12.65	−7.65
$3d^{10}nf \times 3d^9nsnp$	−32.08	−18.24	−10.54	−6.44
$3d^{10}nf \times 3d^9nsnf$	−29.81	−20.64	−12.87	−8.23
$3d^{10}nf \times 3d^9ndnf$	−39.26	−25.42	−15.67	−10.02
$3d^{10}nf \times 3d^9nsnp \times 3d^9nsnf \times 3d^9ndnf$	−31.34	−20.65	−16.58	−13.45

approximation which allows the inclusion of the most important core excited states. Therefore a series of multiconfigurational Dirac-Fock calculations were performed which included the major core-polarizing configurations.

The most important correlation effects arise from one-electron core excitations such as $3d^9nsnp$, $3d^9nsnf$, and of course $3d^9ndnf$. A series of calculations were performed including each of these one-electron core excited states in turn, and then a full MCDF calculation including all of these configurations was performed. When performing these MCDF calculations care had to be taken to correct for errors arising from the fact that the radial parts of the l and $\bar{l}$ may not always converge to the same nonrelativistic limit (Wood and Pyper [11]). The results are shown in Table IV.

The MCDF fine-structure calculations in Table IV show a different trend from those obtained by including an explicit core-polarization potential. Although n inversion is still predicted for all the $nf\,^2F$ doublets, the $4f$ and $5f$ inversions have now decreased.

Since only a small number of configurations are included in the MCDF calculation, this difference in behavior could arise from the fact that the core-polarization potential models the effects of many more correlation configurations. Therefore as a final test of the use of multiconfiguration wave functions for calculating fine structure, calculations were made including nine manifolds, i.e., $3d^{10}nf \times 3d^{10}np \times 3^97^2$ complex. [The complex 3^9m^2 includes all configurations with nine electrons in $n=3$ subshells and two electrons in $m=n$ subshells (Layzer [12]).] The results of these calculations are shown in Table V. The nine manifold calculations shown in Table V show a marked decrease in the fine-structure interval compared with the single-configuration and single-manifold calculations. This indicates the strong effect of electron correlation on the nf levels. However, a fine-structure inversion is still predicted. The estimate for the $5f$ interval is in close agreement (perhaps fortuitously) with the experimental result of Jacquet *et al.* [8].

IV. CONCLUSION AND DISCUSSION

It has been shown that single-configuration Dirac-Fock calculations predict fine-structure inversion for the $nf\,^2F$ ($n=4,5,6,7$) doublets in Kr^{7+}. The Dirac-Fock procedure is able to do so because it includes the effect of core-valence correlation on the atomic wave function. These calculations confirm explicitly the conjecture of Detrich and Weiss [5] that the Dirac-Fock procedure automatically includes the major core-polarizing configurations.

Core-polarization effects (i.e., core-valence correlation) are strong but their inclusion via multiconfiguration Dirac-Fock calculations or by the inclusion of a core-polarization potential leads only to a change in magnitude of the inversion and does not affect its sign.

The present results lend good qualitative support to the inversions suggested by the work of Jacquet *et al.* [8] but as yet there is insufficient accuracy in the experimental data to make worthwhile any further attempts to reconcile them with theory.

ACKNOWLEDGMENTS

Thanks are due to Dr. F. A. Parpia and Dr. W. P. Wijesundera for helpful discussions and correspondence concerning GRASP[2] and Dr. Y-K. Kim and Dr. J. Reader for helpful correspondence concerning their own work on Kr^{7+}. This work was supported in part by a grant from the UK SERC for a postgraduate studentship and a grant to use the Cray YMP8 at the Rutherford Appleton Laboratory.

TABLE V. Results of FS (in cm^{-1}) from nine manifold MCDF.

	AL (each J)	Nonrel. limit	Corrected fs
$3d^{10}4f \times 3d^{10}4p \times 3^94^2$	88.87	121.08	−32.21
$3d^{10}5f \times 3d^{10}5p \times 3^95^2$	−25.31	−10.68	−14.63
$3d^{10}6f \times 3d^{10}6p \times 3^96^2$	−110.11	−101.85	−8.26
$3d^{10}7f \times 3d^{10}7p \times 3^97^2$	−136.38	−131.81	−4.57

[1] C. E. Moore, *Atomic Energy Levels,* Nat. Bur. Stand Circ. No. 467 (U.S. GPO, Washington, D.C., 1971).
[2] D. R. Beck and H. Odabasi, Ann. Phys. (NY) **67**, 274 (1971).
[3] E. Luc-Koenig, Physica **62**, 393 (1972); Phys. Rev. A **13**, 2114 (1976).
[4] K-T. Cheng and Y-K. Kim, At. Data Nucl. Data Tables **22**, 547 (1978).
[5] J. Detrich and A. W. Weiss, Phys. Rev. A **25**, 1203 (1982).
[6] J. Reader, N. Acquista, and V. Kaufman, J. Opt. Soc. Am. B **8**, 538 (1991).
[7] P. Boduch, M. Chantepie, D. Hennecart, X. Husson, D. Lecler, M. Druetta, and M. Wilson, Phys. Scr. **46**, 337 (1992).
[8] E. Jacquet, P. Boduch, M. Chantepie, M. Druetta, D. Hennecart, X. Husson, D. Lecler, F. Martin-Brunetiere, R. E. Olson, J. Pascale, and M. Wilson, Phys. Scr. **49**, 154 (1994).
[9] I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Mayers, and N. C. Pyper, Comput. Phys. Commun. **21**, 207 (1980).
[10] J. Migdalek and W. E. Bayliss, J. Phys. B **12**, 113 (1979).
[11] C. P. Wood and N. C. Pyper, Mol. Phys. **41**, 149 (1980).
[12] D. Layzer, Ann. Phys. **8**, 27 (1959).