Large-Scale Relativistic Correlation Calculations: Levels of Pr $^{+3}$

Ziyong Cai, Verena Meiser Umar, and Charlotte Froese Fischer
Department of Computer Science, Vanderbilt University, P.O. Box 6035B, Nashville, Tennessee 37235

(Received 13 September 1991)

The multiconfiguration Dirac-Fock program GRASP has been modified for large-scale, relativistic correlation studies requiring wave-function expansions with several thousand configuration state functions. As a test case, the program was used to study the effects of relativistic correlation on the levels of Pr^{+3}. Our results are in reasonable agreement with experimental data, the lower ^3H and ^3F levels being in good agreement. The previously controversial $^1S_0$ term is confirmed by theory for the first time.

PACS numbers: 31.20.Tz, 32.30.−r

Most studies of correlation in relativistic atomic systems generally have been restricted to highly ionized atoms where the effect of correlation is well described by the complex. The multiconfiguration Dirac-Fock (MCDF) method is well suited to such an approach and the MCDF [1,2] program has frequently been used for this purpose. This program was not originally designed with large wave-function expansions in mind. For example, in their interpretation of the electronic structure of neutral and ionized states of uranium where the lowest configuration is $5f^36d7s^2$, Pyper and Grant [3] (in 1978) restricted the calculation for the $J=6$ state to wave-function expansions with no more than 30 configuration states. With the supercomputers available today it is possible to overcome such limitations by taking advantage of their speed and large memory capacity.

In large-scale atomic structure calculations, the number of configuration states (NCF) determines the size of the large arrays: The more recent version of the MCDF program, GRASP [3], has three arrays of dimension NCF×NCF. In our study all such arrays were eliminated. The interaction matrix was represented in sparse matrix form requiring the storage of only the nonzero matrix elements; the transformation matrix (transforming from *jj* coupling to *LSJ* coupling) was deleted, since for our correlation studies (described later) the transformation could not be performed; and the array representing the complete set of eigenvectors of the interaction matrix was replaced by one that contained only the eigenvectors of interest. These were determined using an in-core version of Davidson's algorithm for vector processors [4]. Furthermore, dynamic memory allocation was used in declaring these arrays as well as the list of coefficients and radial integrals defining the interaction matrix so that the sizes of the arrays were automatically adapted to the size of the problem. With these modifications, many of the calculations described here could also be performed on a Sun workstation.

Energy-level data are readily available for many excited states of neutral atoms and positive ions. Rare-earth elements are an exception where significant gaps or uncertainties still exist [5]. The energy structures of most of the triply ionized lanthanides have been derived from absorption and fluorescence spectra of crystals (mainly LaCl$_3$ crystals) containing these ions as impurities. The energy spectra obtained for $4f^N$ configurations in this way may well differ from that of free ions because the crystal field distorts the relative positions of the terms and splits energy levels into their Stark components.

In 1965, Sugar [6] and Crosswhite, Dieke, and Carter [7] each published free ion spectra of Pr^{+3}. Crosswhite, Dieke, and Carter identified all 49 levels of the four lowest configurations, namely, the $4f^2$, $4f5d$, $4f6s$, and $4f6p$ configurations. Sugar also identified these levels except for the $^1S_0$ term of $4f^2$. In 1971, Morrison and Rajnak [8] studied the effect of configuration interaction on the levels of $4f^2$ as represented by effective two-body operators which were evaluated using many-body perturbation theory (MBPT). They suggested that the $^1S_0$ might not have been identified correctly. As a result, Martin, Zalubas, and Hagan [5] omitted the term in their compilation of energy levels of the rare-earth elements.

As a first attempt in the study of correlation outside the complex in relativistic atoms, we selected the $4f^2$ levels of Pr^{+3} since most of the levels are well established and can serve as a check on the calculation. Also, this system is similar to the $5f^2$ levels of U^{+4} where relativistic correlation effects are likely to explain the difference between the observed energy-level structure [9] and simple relativistic calculations neglecting correlation [10].

MCDF calculations can be performed according to different schemes [1,2]. The single-configuration, average-level (AL) calculation, in which all orbitals of all levels are the same, is the starting point for this calculation. However, the optimized-level (OL) scheme is preferred for most cases [11]. Single-configuration OL calculations were performed leading to only minor differences in the energies, indicating that there is not much term dependence in the orbitals. The quantum electrodynamic (QED) corrections were also shown to be negligible. These single-configuration OL orbitals were used in subsequent multiconfiguration calculations. Figure 1 shows that the level structure is too expanded in an AL calculation and that the $^1I_6$ level is too low relative to ^3P.

In our search for configurations with a differential correlation effect on the term energy separation and fine-structure splitting, a series of two-configuration (in nonrelativistic notation) calculations were performed, where the second configuration was obtained by replacing one or two occupied orbitals by other occupied or virtual orbitals. If the replacement is only to $4f$, the calculation was performed as a configuration-interaction (CI) calculation; if virtual orbitals are present, the MCDF calculation was carried out in OL mode, but with the occupied orbitals frozen. These calculations give us a good idea of the magnitude of the correlation effect and the extent to which there is a differential effect on the energy levels—a large effect that is the same for all levels would not contribute towards an improvement in term energy separation. In all, 38 replacements were considered (sets are given in order of decreasing importance):

$$\{4d^2,4p^2,5p^2,4s4d,5s^2,4s^2,4p5p,4s5s,4s5s\} \rightarrow 4f^2\,,$$

$$\{4p,5p\} \rightarrow 4f \text{ and } 4f \rightarrow \{5f,6h,6p,8k\}\,,$$

$$4f^2 \rightarrow \{5f^2,5g^2,5d5g,6p^2,6s^2,6h^2,6p5f,5f6h,6s5d,6p6h,6s5g,5d7i,7i^2,6s7i\}\,,$$

$$5s \rightarrow 5d,\ 4d \rightarrow 7i,\ 5p \rightarrow \{5f,6p,8k,6h\},\ \{4s,5s\} \rightarrow 7i\,.$$

Next, a large OL calculation was performed for each level combining 16 of the larger contributors. Again, only the virtual orbitals were optimized. This calculation led to (354, 858, 1386, 1579, 1708, 1535, 1344) configuration states in the wave-function expansions for $J=0$ to $J=6$, respectively. To within about 100 cm^{-1} the effects are additive. To these large-scale OL results are added, as a first-order correction, those contributions from the set of 38 configurations that were omitted in the combined sum.

In 1982, Huang *et al.* [12] noticed that when fine-structure splitting is calculated using the MCDF method, the spin-orbit splittings are distorted by "spurious correlation." The splitting between two levels of the same term should approach zero as the speed of light goes to infinity. Under these conditions, instead of degenerate states for a term, a nonphysical splitting is introduced by the correlation calculation. These false corrections were calculated following the method suggested by Huang *et al.* The corrections were small and could have been neglected in this case. The final energies are reported in Table I.

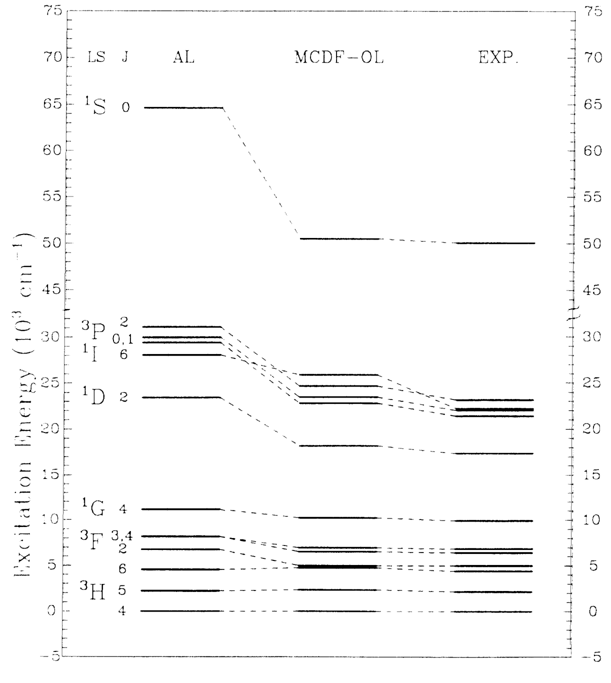

FIG. 1. Comparison of the single-configuration AL energy-level structure with the MCDF-OL structure including correlation and with experiment.

Figure 1 shows the improvement in the prediction of the level structure as correlation has been included. For the controversial $^1S_0$ level, our calculated result agrees extremely well with the experimental data of Crosswhite, Dieke, and Carter [7]. This suggests that the question raised by Morrison and Rajnak [8] about this level is not supported by adequate evidence.

Our calculations were guided by two nonrelativistic studies. Morrison and Rajnak report the effect of various replacements on effective operators describing the level structure, namely, the Slater integrals F^2, F^4, and F^6, and the parameters α, β, and γ, where the latter two are associated with Casimir operators [13] for the group used to classify the states of the $4f^N$ subshell. These energy levels are compared with the results of our two-configuration runs in Table II for some of the major correlation contributors. (For this comparison our relativistic results were converted to LS coupling by averaging the triplet terms which has the effect of shifting the reference

TABLE I. Comparison of the final MCDF-OL results with experiment (Refs. [5,7]) relative to $^3H_4$ (in cm^{-1}).

Level	Expt.	MCDF-OL	Level	Expt.	MCDF-OL
$^1S_0$	50 090.29	50 517.0	$^1G_4$	9921.24	10 207.9
$^3P_2$	23 160.61	24 653.4	$^3F_4$	6854.75	6950.6
$^1I_6$	22 211.54	25 854.1	$^3F_3$	6415.24	6517.7
$^3P_1$	22 007.46	23 450.5	$^3F_2$	4996.61	4984.3
$^3P_0$	21 389.81	22 776.1	$^3H_6$	4389.09	4733.0
$^1D_2$	17 334.39	18 153.0	$^3H_5$	2152.09	2337.6

TABLE II. Comparison of energy levels predicted by the three major replacements from MCDF-OL calculations and many-body perturbation theory (MBPT) [8] relative to ^3H (in cm^{-1}).

	$4d^2 \rightarrow 4f^2$		$4p^2 \rightarrow 4f^2$		$5p^2 \rightarrow 4f^2$	
Level	MCDF-OL	MBPT	MCDF-OL	MBPT	MCDF-OL	MBPT
^1S	59631.1	57778.1	59949.5	62760.0	60525.6	62402.8
^3P	27834.6	27063.0	27907.6	29051.2	27684.8	29052.7
^1I	26791.7	26760.5	25538.9	26760.5	25304.2	26760.5
^1D	20705.3	20389.9	20826.1	21947.1	20687.6	21892.2
^1G	8651.1	6433.0	8710.1	7220.7	8609.5	7220.7
^3F	5142.5	5612.5	5375.3	6314.3	5330.1	6314.3

energy.) Clearly, there are similarities and some significant differences.

Jankowski and Sokolowski [14] reported nonrelativistic, *ab initio* studies of intrasubshell electron correlation for $4f^2$ in Pr^{+3} and tabulated the contribution from the most important contributors. Their results show that for $4f^2$ intrasubshell correlation, a single virtual orbital can represent the pair-correlation contribution to within about 100 cm^{-1}. Thus our MCDF-OL calculation is expected to have similar accuracy for this effect. One big difference is the $4f5f$ configuration (represented by the $4f \rightarrow 5f$ replacement). Morrison, Rajnak, and Wilson [15] had identified this configuration as a large contributor but this was revised later to a much smaller value [8]. Jankowski and Sokolowski [14] designate $4f5f$ as the largest contributor to intrasubshell correlation (they do not include intersubshell correlation and hence neglect the $4d^2 \rightarrow 4f^2$ replacement). This is in disagreement with the present results. For Hartree-Fock solutions, this effect should be zero to first order. One possible explanation is that the authors neglected the contribution from the one-electron part of the Hamiltonian in their calculation. This matrix element is not zero when the $4f$ orbital is a Hartree-Fock orbital from the $4f^2$ configuration. A simple multiconfiguration Hartree-Fock calculation confirmed that, indeed, the effect of $4f5f$ would be large if this nondiagonal matrix element were neglected.

In Table III, the experimental term energies (similarly converted to LS coupling) and those from the three theories are presented. Included are the terms computed using effective operators obtained from second-order perturbation theory as well as an experimental fit to the data and the values predicted by Jankowski and Sokolowski, both with and without the contribution from $4f5f$.

Though our results are the best *ab initio* results to date, one level still differs significantly from the experimental value. In this work, as well as the *ab initio* nonrelativistic results reported by Morrison and Rajnak, the $^1I_6$ level is above the ^3P term, as shown in Table III. Only in their experimental fit is the position of this level changed significantly. It is interesting to note that this level was identified by Crosswhite, Dieke, and Carter [7] using two transitions, one weak and one strong. The same supposedly strong transition was also used by Sugar [6] in identifying the $^1I_6$ level, except that it appeared as a weak transition in his data. Further theoretical and experimental studies are needed to explain this discrepancy.

In heavy systems, correlation and relativistic effects are not additive. In the present study, the inner orbitals are clearly relativistic, but the correlation in the unfilled $4f^2$ shell may well be nonrelativistic except for the indirect core effects. At the same time, the largest correlation contributor comes from the $4d^2 \rightarrow 4f^2$ replacement, leading to a $4d^84f^4$ configuration that is best dealt with in jj coupling. Thus we refer to the present calculation as a "relativistic correlation" study. Though it has been demonstrated that large-scale relativistic correlation studies are possible, problems remain. We were unable to simultaneously vary occupied and virtual orbitals, which remains a barrier for reliable studies for neutral and near-neutral systems.

We would like to thank Dr. Jefferey R. Fuhr at the

TABLE III. Comparison of experimental LS term energies relative to ^3H with MCDF-OL results and other theories (in cm^{-1}).

			CI [15]		Six parameters [8]	
LS term	Expt.	MCDF-OL	With $4f5f$	Without	*Ab initio*	Expt. fit
^1S	47643.6	47874.7	48644.4	55926.5	54794.2	47312.5
^3P	20132.4	21401.5	23927.1	26736.4	25789.2	19828.9
^1I	19765.9	23211.9	23130.4	25838.7	26725.2	19640.2
^1D	14887.0	15510.7	17744.5	19871.2	18418.7	14987.7
^1G	7475.3	7565.6	5539.5	6248.4	6622.8	6107.8
^3F	3818.9	3695.8	5021.6	5557.1	5114.9	4254.1

National Institute of Standards for his help with the literature search. Thanks are also due to Tomas Brage for his many helpful suggestions. Finally, we are grateful to Farid Parpia for providing us with GRASP2, the most recent unpublished version of GRASP. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

[1] I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Myers, and N. C. Pyper, Comput. Phys. Commun. **21**, 207 (1980).

[2] K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia, and E. P. Plummer, Comput. Phys. Commun. **55**, 425 (1989).

[3] N. C. Pyper and I. P. Grant, J. Chem. Soc. Faraday Trans. 2 **74**, 1885 (1978).

[4] V. M. Umar and C. Froese Fischer, Int. J. Supercomputer Appl. **3**, 28 (1989); (unpublished).

[5] W. C. Martin, R. Zalubas, and L. Hagan, *Atomic Energy Levels—The Rare-Earth Elements*, U.S. National Bureau of Standards, National Standards Reference Data Series—NBS 60 (U.S. GPO, Washington, DC, 1978).

[6] J. Sugar, J. Opt. Soc. Am. **55**, 1058 (1965).

[7] H. M. Crosswhite, G. H. Dieke, and Wm. J. Carter, J. Chem. Phys. **43**, 2047 (1965).

[8] J. Morrison and K. Rajnak, Phys. Rev. A **4**, 536 (1971).

[9] J. F. Wyart, V. Kaufman, and J. Sugar, Phys. Scr. **22**, 389 (1980).

[10] C. Froese Fischer (unpublished).

[11] J. Migdalek and M. Stanek, Phys. Rev. A **41**, 2869 (1990).

[12] K. N. Huang, Y. K. Kim, K. T. Cheng, and J. P. Desclaux, Phys. Rev. Lett. **48**, 1245 (1982).

[13] B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).

[14] K. Jankowski and A. Sokolowski, J. Phys. B **14**, 3345 (1981).

[15] J. Morrison, K. Rajnak, and M. Wilson, J. Phys. (Paris), Colloq. **31**, C4-167 (1970).