

## Allowed and spin-forbidden electric dipole transitions in Ca I

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(Received 19 March 2003; published 22 July 2003)

Energy levels, transition probabilities, and lifetimes have been determined for all levels of the Ca I spectrum up to  $3d4p\ ^1F_3^o$  using the multiconfiguration Hartree-Fock method with lowest-order relativistic effects included through the Breit-Pauli Hamiltonian. The mixing of singlet and triplet configuration states was found to be considerably stronger in  $4s5p\ ^{1,3}P_1^o$  levels than in  $4s4p\ ^{1,3}P_1^o$  levels. The near degeneracy of the nonrelativistic  $3d4p\ ^3F_2^o$  and  $^1D_2^o$  term energies, differing by only  $39.59\text{ cm}^{-1}$  resulted in highly mixed Breit-Pauli levels for  $3d4p\ ^3F_2^o$  and  $^1D_2^o$ . Some intercombination transitions from these levels have transition probabilities of magnitude similar to weaker spin-allowed transitions. The “fine-tuned” transition probability for the  $4s4p\ ^3P_1^o-4s4d\ ^1D_2$  transition was found to be  $1.53\times 10^3\text{ s}^{-1}$ , in agreement with a quenching rate observed in a doppler cooling experiment [Binnewies *et al.*, Phys. Rev. Lett. **87**, 123002 (2001)].

DOI: 10.1103/PhysRevA.68.012507

PACS number(s): 31.10.+z, 31.25.-v, 32.70.Cs

### I. INTRODUCTION

Recently, Binnewies *et al.* [1] presented a novel method for preparing ultracold atoms at temperatures close to the recoil limit by extending Doppler cooling to forbidden transitions using Ca atoms. During their investigation, they found that the transition probability for the  $4s4d\ ^1D_2-4s4p\ ^3P_1$  transition was an order of magnitude smaller than reported in the Kurucz database [2]. The NIST compilation [3], in spite of theoretical efforts, was based entirely on experimental data published prior to 1967. It did not include the above intercombination line, frequently referred to as “forbidden” since it is not allowed in the LS approximation.

From a theoretical point of view, in spite of the same simple structure as Mg (core and two electrons), the accurate determination of energy levels and transition probabilities for Ca I is much more difficult. In Ca, the  $^1S$  core is not a filled shell in that the  $3d$  subshell is missing, resulting in a considerable correlation in the core. At the same time, the presence of outer electrons polarize the core, leading to strong core-valence interactions in addition to valence correlation where often perturbers are embedded in a Rydberg series.

There is extensive literature on theoretical studies of calcium and its energy levels. A common approach has been to assume a potential for the core, define an analytic core-polarization potential as a correction, and then treat the system as a two-electron system. This was the approach taken by Mitroy [4], Brage and Froese Fischer [5], and Laughlin and Hansen [6]. The latter is the most accurate of these nonrelativistic calculations in that both mono-electronic and dielectronic core-polarization terms were included and all parameters optimized to the  $\text{Ca}^+$  spectrum. Valence correlation was treated through a configuration interaction (CI) expansion of the wave function using a  $B$ -spline basis. Brage and Froese Fischer [5] used a simple Hartree-Fock potential together with an analytic mono-electronic core-polarization potential, neglecting the dielectronic term but at the same time

they included Breit-Pauli interactions for a number of Rydberg series.

Early calculations for transitions were concerned primarily with the effect of correlation in the valence shell, but in 1993 Brage *et al.* [7] investigated the effect of core polarization on the allowed and spin-forbidden  $4s^2-4s4p$  transitions in Ca (extensive references to earlier publications can be found in this paper). Later, Hansen *et al.* [8] extended their analytic model potential and  $B$ -spline method to determine also transition probabilities. Weighted oscillator strengths for LS allowed transitions were reported for levels up to  $4s10s$ . But these results were nonrelativistic. Relativistic transition amplitudes using a combination of CI and many-body perturbation theory (CI+MBPT) have recently been reported by Porsev *et al.* [9]. Included in their work were the allowed  $4s^2-4s4p$ ,  $4s4p-3d4s$  transitions, and the spin-forbidden  $4s4p\ ^1P_1-4s5s\ ^3S_1$  and  $4s4p\ ^3P_{1,2}-3d4s\ ^1D_2$  transitions. Omitted were transitions to the  $4s4d\ ^1D_2$  state. Since then Savukov and Johnson [10] have investigated two variants of CI+MBPT, reporting a number of levels in Ca I, but the transition amplitudes were restricted to the  $4s^2-4s4p$  allowed and spin-forbidden transitions.

In this paper, we report “spectrum” calculations that include all energy levels up to  $3d4p\ ^1F_3$  and all electric dipole transitions between these levels, both allowed and spin forbidden. The  $3d4p\ ^1P_1^o$  level has been omitted from this work. The  $3d4p\ ^1P_1^o$  configuration is a perturber in the  $4snp\ ^1P_1^o$  series of levels with no member having a predominant  $3d4p$  character (see Ref. [8] for more details). Strong mixing of the  $3d4p\ ^1D_2^o$  and  $^3F_2^o$  configuration states, and to lesser extent also the  $4s5p\ ^3P_2^o$  configuration state, was found for  $3p3d\ ^1D_2^o$  and  $^3F_2^o$  levels. For the  $4s5p\ ^{1,3}P_1^o$  levels, the mixing of  $^1P_1^o$  and  $^3P_1^o$  configuration states was considerably stronger than for  $4s4p$  [25].

### II. COMPUTATIONAL PROCEDURE

The general approach of our method has already been described [11] elsewhere. Briefly, the variational multiconfiguration Hartree-Fock method is used to determine an orbital basis for a Breit-Pauli wave function. These basis func-

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TABLE I. Groups of terms and their eigenvalues that were optimized simultaneously and included in a Breit-Pauli configuration interaction calculation. The eigenvalue is indicated by the dominant configuration state. Independent optimization was performed for all other cases.

Parity	Group	Terms and their eigenvalues
Even	1	$3d4s\ ^1D$ and $\ ^3D$
	2	$4s4d\ ^1D$ and $\ ^3D$ ; $4p^2\ ^3P$
Odd	1	$4s4p\ ^1P^o$ and $\ ^3P^o$
	2	$3d4p\ ^3F^o$ and $\ ^1D^o$ ; $4s5p\ ^1P^o$ and $\ ^3P^o$

tions are optimized simultaneously for groups of nonrelativistic terms that interact in the Breit-Pauli approximation. Transition calculations for electric dipole transitions using the  $J$ -dependent wave functions are done with orbitals that are nonorthogonal between initial and final states. The biorthogonal transformation method was used for this purpose [12]. In calcium, correlation in some cases was found to be more important than term mixing. For the excited states  $3d4p\ ^3D^o$ ,  $\ ^3P^o$ , and  $\ ^1F^o$ , the term separation is sufficiently large compared with fine-structure splitting, that it was deemed more important to consider correlation carefully. The  $3d4p\ ^3D^o$  term is the lowest of its symmetry and presents no particular difficulty when optimized independently. The  $3d4p\ ^3P^o$  term is the third eigenvalue with the  $4s5p$  configuration, a major component, and an orbital basis for this state needs to represent not only  $4s5p$  but also  $4s4p$  reasonably well. At the same time, the  $3d4p\ ^1F^o$  term has a large  $4s4f$  component. As a result, each of these wave functions has a sufficiently different composition that independent optimization was preferred. This has the consequence that our calculation may have neglected some intercombination transitions between the lower members and these more high-lying states. Table I shows the groups for which the optimization process included several terms and also the terms that were allowed to mix in the Breit-Pauli approximation.

The earlier study by Brage *et al.* [7] found core polarization to be important not only for transition energies but also for oscillator strengths. A simple MCHF calculation for  $\text{Ca}^{+2}$  quickly shows that correlation in the core is significant, with a 4% probability of the core having a  $3s^23p^43d^2$  angular distribution compared with a 0.4% probability of either  $3s^23p^54p$  or  $3s^23p^44p^2$ , part of radial correlation. Core correlation affects all states and, to a large extent, will cancel when transition energies are computed, but it also modifies the potential for the valence electrons, and for this reason the most important contributor, namely,  $3s^23p^43d^2$ , was included. Thus, the wave function started with an expansion including  $3s^23p^6nln'l'$  and  $3s^23p^43d^2nln'l'$ , where  $nl, n'l'$  were orbitals in the "valence" set  $\{3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f\}$ . To this, expansion were added configuration states that represent core polarization. An assumption was made that core correlation and core polarization could be treated as being additive with no core-valence contribution arising from the  $3s^23p^43d^2$  core.

In a model potential, core polarization can be accounted for through the addition of mono-electronic and dielectronic

TABLE II. Selected trends in the line strength  $S$  for the correlation model. The parameter  $n$  is related to the size of the orbital basis and the wave function expansion.

Transition	$n$	$S_l$	$S_v$	Diff. (%)
$4s^2\ ^1S-4s4p\ ^1P^o$	5	23.78	24.11	1.4
	6	24.53	25.06	2.1
	7	24.51	25.19	2.7
$4s4p\ ^1P^o-4s4d\ ^1D$	5	8.53	19.13	55.4
	6	13.17	16.88	22.0
	7	13.05	14.72	11.4
$4s4p\ ^3P^o-4p^2\ ^3P$	5	68.54	72.27	5.2
	6	66.89	68.00	1.6
	7	66.45	67.19	1.1
$3d4s\ ^3D-3d4p\ ^3F^o$	5	128.6	102.1	20.6
	6	123.8	120.7	2.5
	7	120.5	117.4	2.6

analytic corrections to a potential (which then also requires a modification of the dipole operator). In an *ab initio* calculation, core polarization can be represented in a wave function through configuration states that result from an excitation of one core orbital and one valence orbital to either unfilled valence orbitals or to virtual "correlation" orbitals. For transitions involving outer electrons, the importance of this effect decreases as excitations are made from deeper in the core, and so they were restricted to excitations from either  $3s^2$  or  $3p^6$ . The valence orbitals were extended by correlation orbitals to include also  $\{5g, 6s, 6p, 6d, 6f, 6g, 7s, 7p, 7d, 7f, 7g\}$ .

It was convenient to perform a series of calculations in order to monitor convergence. A calculation is considered an  $n=5, 6$ , or  $7$  calculation if the maximum principal quantum number of the orbitals used in generating configuration states is restricted to 5, 6, or 7, respectively. Wave function expansions increase rapidly with  $n$ . In order to restrict the expansion growth, only those states that interact with at least one member of the set of valence configuration states  $3s^23p^6nln'l'$ , where  $nln'l'$  are valence orbitals, were retained in the expansion. Even so, the largest expansion size was 11 165 configuration state functions (CSF's) for  $3d4p\ ^3F^o$ . In the case of expansions for the terms of  $3d4p$ , calculations for  $n=7$  were first done for each term separately and then CSF's with expansion coefficients less than 0.000 05 were eliminated.

MCHF calculations started by determining the  $\{1s, 2s, 2p, 3s, 3p, 3d\}$  orbitals that define our correlated core. These orbitals were then kept fixed, and the series of  $n=5, 6, 7$  calculations performed for each term or group of terms, to determine the remaining orbitals. In this way, correlation in the core was assured to be the same for all states.

Once MCHF wave functions had been obtained, LS transition calculations were performed and the convergence of the line strength monitored. Table II shows some of these trends. In the LS approximation, with the correct model, the line strengths for length and velocity should converge. In many cases, though not all, the preferred length form is the

TABLE III. A comparison of the shifts in the energy levels (computed and observed, in  $\text{cm}^{-1}$ ) between present results and CI + MBPT methods.

Level	Present	CI+MBPT <sup>a</sup>	CI+MBPT <sup>b</sup>
$4s^2\ ^1S_0$			
$4s4p\ ^3P_1^o$	-165	153	385
$3d4s\ ^3D_2$	988	198	
$3d4s\ ^1D_1$	732	435	
$4s4p\ ^1P_1^o$	169	2	145
$4s5s\ ^3S_1$	-2	17	
$3d4p\ ^3F_2^o$	1033		
$4s5p\ ^3P_1^o$	223		205
$4s5p\ ^1P_1^o$	524		185
$3d4p\ ^1D_2^o$	1030		
$4s4d\ ^1D_2$	498		
$4s4d\ ^3D_2$	312		
$3d4p\ ^3D_1^o$	776		
$4p^2\ ^3P_2$	366		233
$3d4p\ ^3P_1^o$	1150		
$3d4p\ ^1F_3^o$	882		

<sup>a</sup>Reference [9].

<sup>b</sup>Reference [10].

more stable. A good example is the  $4s4p\ ^1P^o-4s4d\ ^1D$  transition. The length value is well converged, and the velocity form is decreasing to a similar limit. When the length form is stable but velocity form still varying, the difference greatly over estimates the error in the line strength. It should be remembered that the length form is independent of the transition energy, whereas the velocity form is not. Thus, any inadequacy in the correlation model leading to errors in the transition energy will affect the velocity form directly. The latter is always more unstable when the transition energy is small. Table II also shows that the accuracy and convergence differ greatly from one transition to another.

Using these orbitals, Breit-Pauli calculations were performed for the various groups of terms, and transitions computed in the LSJ approximation. Now length and velocity forms no longer can be expected to agree in that the velocity form of the transition operator neglected some low-order relativistic corrections which are particularly important for spin-changing transitions. Table III reports the shift of selected *ab initio* energy levels from observed levels, in  $\text{cm}^{-1}$ . It is immediately apparent that, though our shifts in some instances are similar to those found in CI+MPBT [9,10], on the whole they are considerably larger. Generally, shifts for  $4snl$  are smaller than those for  $3d4p$ , which suggests that our core with limited correlation is not sufficiently accurate to determine the spectrum reliably to within a few  $100\ \text{cm}^{-1}$ . To bring the spectrum in good agreement with observation, these shifts can be used as “term energy corrections” that can be subtracted from the diagonal energies of the Breit-Pauli interaction matrix, of all CSF’s associated with a given *LS* term, bringing computed and observed energy levels into close agreement. When this shift has a minor effect, the deviation from observed of the recomputed energy

TABLE IV. Breit-Pauli energy levels (in  $\text{cm}^{-1}$ ), splitting of levels relative to the lowest level of a multiplet and lifetimes,  $\tau$  (in seconds). Numbers in brackets indicate powers of ten.

Config.	<i>LS</i>	<i>J</i>	Level	splitting	$\tau$ (s)
$4s^2$	$^1S$	0	0.00		
$4s4p$	$^3P^o$	0	15162.26		
		1	15210.05	47.79	4.768[-4]
		2	15303.53	141.27	
$3d4s$	$^3D$	1	20327.95		1.166[-6]
		2	20349.36	21.41	1.182[-6]
		3	20378.80	50.85	1.208[-6]
$3d4s$	$^1D$	2	21849.56		1.947[-3]
$4s4p$	$^1P^o$	1	23652.32		4.568[-9]
$4s5s$	$^3S$	1	31539.49		1.170[-8]
$4s5s$	$^1S$	0	33317.26		4.514[-8]
$3d4p$	$^3F^o$	2	35731.74		2.342[-8]
		3	35814.52	82.78	2.370[-8]
		4	35887.20	155.46	2.349[-8]
$3d4p$	$^1D^o$	2	35842.71		2.141[-8]
$4s5p$	$^3P^o$	0	36544.83		5.519[-8]
		1	36553.86	9.03	5.520[-8]
		2	36571.22	26.39	5.510[-8]
$4s5p$	$^1P^o$	1	36732.53		6.594[-8]
$4s4d$	$^1D$	2	37298.33		6.279[-8]
$4s4d$	$^3D$	1	37746.53		1.190[-8]
		2	37751.85	5.31	1.191[-8]
		3	37762.07	15.53	1.191[-8]
$3d4p$	$^3D^o$	1	38183.13		1.402[-8]
		2	38219.13	36.00	1.398[-8]
		3	38262.18	79.05	1.394[-8]
$4p^2(^3P)$	$^3D$	0	38434.75		5.291[-9]
		1	38477.16	42.40	5.282[-9]
		2	38551.53	116.78	5.272[-9]
$3d4p$	$^3P^o$	0	39321.90		1.172[-8]
		1	39335.34	13.44	1.172[-8]
		2	39352.95	31.06	1.173[-8]
$3d4p$	$^1F^o$	3	40537.90		6.887[-8]

level for the selected *J* is essentially zero. Because of the incorrect position of the  $4s5p$  levels (between  $3d4p\ ^3F^o$  and  $^1D^o$  rather than below the latter), the *ab initio* calculation produced an unphysical eigenvalue. The correction needed for  $^1D_2^o$  was determined iteratively with the final value close to the shift for  $^3F_2^o$ . This shift is reported in Table III.

Table IV reports the energy levels, their splitting relative to the lowest member of a multiplet, and the lifetime of the level. The table shows that the  $3d4p\ ^3F_2^o$  and  $^1D_2^o$  levels are separated by only  $109.97\ \text{cm}^{-1}$ . In fact, the nonrelativistic *LS* terms are nearly degenerate, differing by only  $39.59\ \text{cm}^{-1}$ , and the Breit-Pauli interactions have increased this separation. As a result, both levels are highly mixed with the wave function composition being 81.5%  $^3F_2^o$  and 18.5%  $^1D_2^o$  for the  $3d4p\ ^3F_2^o$  level, and a similar  $^1D_2^o$  and  $^3F_2^o$  composition for the  $3d4p\ ^1D_2^o$  level. No other term mixing reached the 1% level in the composition of a wave function.

TABLE V. Breit-Pauli  $gf$  values for singlet transitions compared with theory and experiment.

Initial state	Final state	Present		MP <sup>a</sup>	Other Theory		Experiment
		$gf_l$	$gf_v$		$gf_l$	$gf_v$	
$4s^2\ ^1S_0$	$4s4p\ ^1P_1^o$	1.760	1.827	1.7458	1.732 <sup>b</sup>	1.746 <sup>b</sup>	1.754(10) <sup>c</sup> , 1.79(3) <sup>d</sup>
					1.717 <sup>e</sup>	1.685 <sup>e</sup>	
					1.64 <sup>f</sup>	1.70 <sup>f</sup>	
$4s4p\ ^1P_1^o$	$4s5p\ ^1P_1^o$	0.0059	0.0051	0.00195			0.00091(19) <sup>g</sup>
	$4s5s\ ^1S_0$	0.356	0.369				
$3d4s\ ^1D_2$	$4s4d\ ^1D_2$	0.640	0.762	0.6188			0.62(2) <sup>h</sup>
	$4s4p\ ^1P_1^o$	0.0045	0.0092	0.0073	0.00737 <sup>b</sup>		0.0046(12) <sup>i</sup> , 0.0051(12) <sup>j</sup>
	$3d4p\ ^1D_2^o$	1.495	1.590	1.84			1.37(4) <sup>k</sup>
	$4s5p\ ^1P_1^o$	0.219	0.270	0.2925			0.299(7) <sup>k</sup>
$4s5s\ ^1S_0$	$3d4p\ ^1F_3^o$	0.416	0.376	0.357			0.499(24) <sup>l</sup>
	$4s5p\ ^1P_1^o$	0.965	1.467				
$3d4p\ ^1D_2^o$	$4s4d\ ^1D_2$	0.010	0.022				
$4s5p\ ^1P_1^o$	$4s4d\ ^1D_2$	0.309	0.496				
$4s4d\ ^1D_2$	$3d4p\ ^1F_3^o$	0.660	0.848	0.9733			0.65(24) <sup>l</sup>

<sup>a</sup>Reference [8].  
<sup>b</sup>Reference [9].  
<sup>c</sup>Reference [13].  
<sup>d</sup>Reference [14].  
<sup>e</sup>Reference [10].  
<sup>f</sup>Reference [7].

<sup>g</sup>Reference [15].  
<sup>h</sup>Reference [16].  
<sup>i</sup>Reference [17].  
<sup>j</sup>Reference [18].  
<sup>k</sup>Reference [19].  
<sup>l</sup>Reference [20].

Transition probabilities for the intercombination  $4s^2\ ^1S_0$ - $4snp\ ^3P_1^o$  transition depend on the mixing of the  $4snp$  singlet and triplet configuration states. An inspection of the wave function showed that the mixing coefficient of the  $4snp\ ^1P_1^o$  configuration state is 0.0056 for the  $4s4p\ ^3P_1^o$  level and 0.0735 for the  $4s5p\ ^3P_1^o$  level. Since transition probabilities often depend, at least in part, on the square of this coefficient, intercombination lines to  $4s5p\ ^3P_1^o$  will be larger than might be expected.

**III. RESULTS AND DISCUSSION**

In Table V, we report  $gf$  values for the LS-allowed singlet transitions. Our values are compared with model potential (MP) results of Hansen *et al.* [8], other theory, and experimental values with the smaller errorbars. An extensive list of experimental values going back to the 1960s can be found in the Hansen *et al.* paper. The resonance transition has received a lot of attention, both experimentally and theoretically. In Table V, we have included only the more recent results. Our  $gf$  value is slightly higher (but well within errorbars) of the most accurate recent experiment, whereas the CI+MBPT are slightly lower. The earlier result by Brage *et al.* [7] was determined including only core polarization, and the difference with the present result shows the effect of including also some correlation in the core. Since these are spin-allowed transitions, we assume that the comparison of length and velocity values could be of significance even though the velocity form has omitted some relativistic corrections. In many instances, such as the  $4s4d\ ^1D_2$ - $3d4p\ ^1F_3^o$  transition, the length value agrees well with experiment while the velocity form deviates significantly.

Similarly, triplet transitions are compared in Table VI. Here, we compare multiplet values obtained from a weighted sum of transitions in the multiplet, with nonrelativistic  $gf$  values and similar experimental values. The error we report is an average of the deviation in the length and velocity form of the line strength of the individual lines of the multiplet, in

TABLE VI. Present multiplet  $gf$  values for transitions among the triplet terms compared with nonrelativistic model potential values and experiment.

Initial	Final	Present	MP <sup>a</sup>	Experiment
$4s4p\ ^3P^o$	$3d4s\ ^3D$	0.725(218)		
	$4s5s\ ^3S$	1.451(145)	1.374	1.46(22) <sup>b</sup>
	$4s4d\ ^3D$	3.722(19)	3.411	3.86(53) <sup>b</sup>
$3d4s\ ^3D$	$4p^2\ ^3P$	4.727(236)	4.527	5(1) <sup>c</sup>
	$3d4p\ ^3F^o$	5.322(160)	5.066	5.42(13) <sup>d</sup>
	$4s5p\ ^3P^o$	0.556(19)	0.7031	0.67(2) <sup>d</sup>
	$3d4p\ ^3D^o$	5.040(136)	4.980	5.47(14) <sup>d</sup>
$4s5s\ ^3S$	$3d4p\ ^3P^o$	3.171(270)	2.848	3.11(8) <sup>d</sup>
	$4s5p\ ^3P^o$	3.891(428)		
	$3d4p\ ^3P^o$	0.117(50)		
$3d4p\ ^3F^o$	$4s4d\ ^3D$	0.025(3)		
$4s5p\ ^3P^o$	$4s4d\ ^3D$	2.41(108)		

<sup>a</sup>Reference [8].  
<sup>b</sup>Reference [21].  
<sup>c</sup>Reference [22].  
<sup>d</sup>Reference [19].

TABLE VII. Some transition probabilities (in  $s^{-1}$ ) for intercombination transitions.

Lower	Upper	$A_{ki}$
$4s^2\ ^1S_0$	$4s4p\ ^3P_1^o$	$2.098 \times 10^3$
	$4s5p\ ^3P_1^o$	$4.098 \times 10^3$
$4s4p\ ^3P_1$	$4s5s\ ^1S_0$	$5.201 \times 10^2$
	$4s4d\ ^1D_2$	$1.222 \times 10^3$
$4s4p\ ^3P_2$	$4s4d\ ^1D_2$	$1.709 \times 10^4$
$3d4s\ ^3D_3$	$3d4p\ ^1D_2$	$7.160 \times 10^4$
$3d4s\ ^3D_2$	$3d4p\ ^1D_2$	$9.061 \times 10^5$
$3d4s\ ^3D_1$	$3d4p\ ^1D_2$	$6.680 \times 10^6$
$3d4s\ ^3D_2$	$4s5p\ ^1P_1$	$2.884 \times 10^4$
$3d4s\ ^1D_2$	$3d4p\ ^3F_2$	$8.431 \times 10^6$
	$3d4p\ ^3F_3$	$7.257 \times 10^3$
	$4s5p\ ^3P_1^o$	$6.208 \times 10^4$
	$4s5p\ ^3P_2^o$	$1.454 \times 10^4$

percentage. Our results agree well with those of Hansen *et al.*, and sometimes are in better agreement with experiment, as in the  $3d4s\ ^3D-3d4p\ ^3F^o$  multiplet.

The multiplet values to a large extent obscure the effect of term mixing. In Table VII, we report some of the larger intercombination transition probabilities found in these calculations. Some of the values for lower levels are of interest in astrophysics and the value for the  $4s4d\ ^1D_2-4s4p\ ^3P_1^o$  transition has recently been important in studies of doppler cooling and trapping on forbidden transitions [1]. Generally, anomalies of all sorts are of interest in spectroscopy. The transition probabilities in Table VII reflect the strong term mixing in  $3d4p\ ^3F_2^o$  and  $^1D_2^o$  levels and, to a lesser extent, the mixing in  $4s5p\ ^{1,3}P_1^o$  levels. The best example is the transition probability for the  $3d4s\ ^1D_2-3d4p\ ^3F_2^o$  transition which is three orders of magnitude larger than the one between the same lower level and the  $^3F_3^o$  level.

In Table VIII, we compare transition amplitudes with other theory and a recent experiment. For the  $4s^2\ ^1S_0-4s4p\ ^3P_1^o$  intercombination transition, the present calculation has underestimated the relativistic effects. This was evidenced by the fact that the spread of the  $^3P$  fine-structure splitting was too small, a result that can be attributed, in part, to the omission of core polarization from the correlation component of the core. The spread for a fixed-core Hartree-Fock (HF) wave function is only  $84.23\text{ cm}^{-1}$  for  $4s4p\ ^3P^o$ , whereas the observed value is  $158.04\text{ cm}^{-1}$ . Core polarization alone results in a spread of  $150.5\text{ cm}^{-1}$  (Brage *et al.* [7]), compared with the present value of

 TABLE VIII. Comparison of intercombination transition amplitudes ( $\times 10^2$ ) with other theory and experiment.

Initial	Final	Present	Other theory		
			Length	velocity	Expt.
$4s^2\ ^1S_0$	$4s4p\ ^3P_1^o$	2.97(3.32 <sup>a</sup> )	3.4 <sup>b</sup>	3.2 <sup>b</sup>	3.57(4) <sup>c</sup>
			3.23 <sup>d</sup>	3.34 <sup>d</sup>	
			3.36 <sup>e</sup>		
$4s4p\ ^1P_1^o$	$4s5s\ ^3S_1$	3.51(3.92 <sup>a</sup> )	4.3 <sup>b</sup>	4.5 <sup>b</sup>	
$4s4p\ ^3P_1^o$	$3d4s\ ^1D_2$	5.66(6.33 <sup>a</sup> )	5.9 <sup>b</sup>	6.1 <sup>b</sup>	
$4s4p\ ^3P_2^o$	$3d4s\ ^1D_2$	3.43	2.8 <sup>b</sup>	2.4 <sup>b</sup>	

<sup>a</sup>Fine-tuned result (see text): recommended value.

<sup>b</sup>Reference [9].

<sup>c</sup>Reference [23].

<sup>d</sup>Reference [10].

<sup>e</sup>Reference [7].

$141.27\text{ cm}^{-1}$ . According to Hibbert [24], a theoretical result can be fine tuned for this discrepancy by multiplying by the factor needed to bring the spread into agreement with observed. Such values are shown in parentheses in Table VIII and, indeed, are in much better agreement with other theory and experiment. Only transitions involving  $4s4p\ J=1$  have been adjusted through fine tuning.

#### IV. CONCLUSION

The calcium spectrum presents many challenges to theory. In this work, we have attempted to extend earlier nonrelativistic calculations, such as those by Hansen *et al.*, to include relativistic effects through the Breit-Pauli Hamiltonian. A computational model was defined that included the major correlation effects in the core. It was designed not only for the resonance transitions but also for transitions to higher members in the spectrum where near degeneracies may occur. The length value for allowed transitions was often in better agreement with experiment than the corresponding nonrelativistic value. Strong intercombination lines were observed for transitions to  $3d4p\ ^1D_2^o$  or  $^3F_2^o$  because of the strong term mixing in these levels. In particular, the adjusted transition probability for spontaneous emission from  $4s4d\ ^1D_2$  to  $4s4p\ ^3P_1^o$  was found to be  $1.53 \times 10^3\text{ s}^{-1}$ , in agreement with recent observation in a doppler cooling and trapping experiment [1].

#### ACKNOWLEDGMENTS

This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

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