Interpretation of the spectrum of Pb(II). Theoretical transition probabilities and lifetimes

C. Colón
A. Alonso Medina

Abstract: Radiative transition probabilities for 190 lines arising from the $ns^2S_{1/2}$, $np^2P_{1/2,3/2}$, $nd^2D_{3/2,5/2}$, $nf^2F_{5/2,7/2}$, and $6p^2$ ($^4P_{1/2,3/2,5/2}$, $^2D_{3/2,5/2}$, $^2P_{1/2,3/2}$, and $^2S_{1/2}$) levels of Pb(II) have been calculated. Lifetimes of the above mentioned levels have been determined from the present transition probabilities. These values were obtained in intermediate coupling (IC) and using ab initio relativistic Hartree–Fock calculations. For the IC calculations, we use the standard method of least-square fitting of experimental energy levels by means of computer codes from Cowan. The results of calculations for radiative transition probabilities and excited states lifetimes are presented and compared with the experimental results present in the literature and with other theoretical values. There is generally good agreement between our values and the experimental data available. Analysis of the interaction shows that the level $^4P_{5/2}$ of the $6s6p^2$ configuration presents a large contribution to the $^2D_{5/2}$ level of the $6s^26d$ configuration. This result explains the good agreement between our result and the experimental values obtained to the observed as the $6s6p^2\ ^4P_{5/2} - 6s^25f^2F_{7/2}$ dipole-forbidden transition.

Résumé : Nous avons calculé les probabilités de transition radiative provenant des niveaux de Pb(II) $ns^2S_{1/2}$, $np^2P_{1/2,3/2}$, $nd^2D_{3/2,5/2}$, $nf^2F_{5/2,7/2}$, et $6p^2$ ($^4P_{1/2,3/2,5/2}$, $^2D_{3/2,5/2}$, $^2P_{1/2,3/2}$ et $^2S_{1/2}$). Les demi-vies sont évaluées à partir de ces probabilités. Les valeurs numériques ont été obtenues de deux façons, utilisant l'approche du couplage intermédiaire (I.C.) et un calcul Hartree–Fock relativiste complet. En I.C., nous utilisons l'approche habituelle d'ajustement moindre carré des niveaux à des valeurs expérimentales en utilisant le programme de Cowan. Les résultats des calculs sont comparés aux valeurs expérimentales trouvées dans la littérature scientifique ainsi qu'à d'autres valeurs théoriques. L'accord est généralement très bon entre nos résultats et les valeurs expérimentales. Une analyse des interactions montre que le niveau $^4P_{5/2}$ de la configuration $6s6p^2$ a une contribution importante du niveau $^2D_{5/2}$ de la configuration $6s^26d$. Ce résultat explique le bon accord entre nos résultats et les valeurs expérimentales pour la transition dipolaire interdite $6s6p^2\ ^4P_{5/2} - 6s^25f^2F_{7/2}$.

1. Introduction

There is an increasing need for reasonably accurate atomic transition probabilities particularly for astrophysical applications. Pb(II) has been detected with the Goddard High Resolution Spectrograph (GHRS) aboard the Hubble Space Telescope (HST) in several stars [1], and lead also presents a large solar abundance [2]. So, reliable Pb(II) transition probabilities are needed to derive different astrophysical parameters. Experimental values may be preferred to theoretical ones but, in the Pb(II) ion, there are several intense lines without any type of value in the literature.

Transition probabilities in Pb(II) have been the subject of few theoretical works [3–6]. The experimental investigations of the spectrum and transition probabilities or radiative lifetimes of Pb(II) are also very sparse [6–10]. Transition probabilities for 30 lines involving S, P, D, and F levels of Pb(II) were determined from hollow cathode discharge by Alonso-Medina [6]. In recent works [8,9] transition probabilities of Pb(II) have been determined from the values of the intensities obtained using the emission of a plasma generated by focusing a laser beam on a Pb target and including the 2203.53 Å line of Pb(II) not previously present in the literature. In 1985, the lifetimes of seven levels of Pb(II) were obtained by Gorshkov and Verolainen [10] using the multichannel method of delayed coincidences.

Calculations, including a potential model to represent the core polarization of Pb(II) were reported by Migdalek [5] and Alonso-Medina [6]. Both works are based on a simple one-electron approach and no calculations about the intense dipole-forbidden transition were presented.

In this work, we present transition probabilities for lines, with wavelengths lower than 15 000 Å, arising from the $6s^2ns$ ($n = 7-14$) $^2S_{1/2}$, $6s^2np$ ($n = 7-9$) $^2P_{1/2,3/2}$, $6s^2nd$ ($n = 6-15$) $^2D_{3/2,5/2}$, $6s^2nf$ ($n = 5-7$) $^2F_{5/2,7/2}$, and $6s6p^2$ ($^4P_{1/2,3/2,5/2}$, $^2D_{3/2,5/2}$, $^2P_{1/2,3/2}$, and $^2S_{1/2}$) levels of Pb(II). The values were calculated using the relativistic Hartree–Fock method and configuration interaction in an intermediate coupling scheme. The Cowan [11] code (1981) was selected for this purpose. To provide level energies for our calculations, Moore’s table [12] was used. The theoretical lifetime values of the levels included in the Gorshkov work [10] have been obtained, in this paper, from our transition probabilities.

The system considered is complex, with high Z where both relativistic and correlation effects must be important. Least-square fitting of experimental energy levels partially account for correlation effects not explicitly calculated in our work. The relatively good agreement between experimental and theoretical results shows that our intermediate coupling (IC) mixing accounts for the correlation effects.

In Sect. 2, we describe the theoretical considerations and then in Sect. 3 the results and discussion.

2. Theoretical calculations

Singly ionized lead involves a single optical electron whose energy levels are well separated. This structure allows us to obtain a suitable comparison between experimental and theoretical results with relativistic central field calculations using the LS coupling scheme. Nevertheless, this scheme is not enough to describe the $6s6p^2$ configuration. A more detailed description is necessary to take into account some features of the interaction between the $6s^26d$ and $6s6p^2$ configurations and some experimental results as the existence of intense dipole-forbidden transitions [13–15].

In this work, we have obtained theoretical values of the transition probabilities in IC using *ab initio* quasirelativistic Hartree–Fock (HFR) calculations.

For the IC calculations, we used the standard method of least-square fitting of experimental energy levels by means of computer codes from Cowan [11]. In this way, we obtained the LS composition of each level and the degree of configuration mixing, when we consider their interaction. For the HFR calculations, the Cowan computer codes provide us with the radial parts for the determination of the transition probabilities and initial estimates of the parameters for the IC fittings. The radial integrals for the calculations of the transition probabilities were obtained from the HFR wave functions.

Fig. 1. Effects of $6s6p^2$ – $6s^26d$ configuration interaction.

3. Results and discussion

3.1. $6s6p^2$ – $6s^26d$ configuration interaction

Levels from the Pb(II) $6s6p^2$ configuration present some anomalies whose interpretation will be discussed here. The most obvious effect demanding some theoretical interpretation is the existence of the observed line at 5373.7 Å corresponding to the $6s6p^2$ $^4P_{5/2}$ – $6s^25f^2F_{7/2}$ dipole-forbidden transition.

To account for this fact, a configuration interaction is recognized to be present and the first interacting candidate must be the nearest $6s^26d$ configuration. A similar situation was found for the homologous $5s5p^2$ and $5s^25d$ configurations of Sn(II) [16].

Interaction between these configurations with the $6s^27s$, $6s^27d$, and $6s^28d$ ones are also introduced in our work. Although the effects of these configurations are irrelevant in the energy level position, we introduce them in our calculations. Interaction with $6s^27s$ is introduced to explain the existence of the dipole-forbidden transitions $6s6p^2$ $^4P_{1/2}$ – $6s^27p$ $^2P_{1/2}$ (6043.0 Å), and $6s6p^2$ $^4P_{1/2}$ – $6s^27p$ $^2P_{3/2}$ (5165.0 Å). Ab initio HFR calculations show us that interaction with $6s^27d$ and $6s^28d$ must be relevant. Only these interactions provide us with good agreement between experimental and theoretical values for the transition probabilities corresponding to 3947.8 Å ($6s^26d$ $^2D_{3/2}$ – $6s^28p$ $^2P_{1/2}$) and 3666.5 Å ($6s^26d$ $^2D_{5/2}$ – $6s^28p$ $^2P_{3/2}$) lines.

The energy level positions expected for $6s^26d$ and $6s6p^2$ configurations, in the absence of interactions, can be observed on the left-hand section of Fig. 1. The values of this first diagram come from a theoretical HFR calculation of separated $6s6p^2$ and $6s^26d$ configurations with no consideration of their interaction. A comparison between these results and the experimental values (Moore [12]) (the right-hand section of Fig. 1) shows a large discrepancy.

The second diagram from the left in Fig. 1 shows the effect of allowing for configuration interaction

Table 1. Energy levels and mixing effects in the $6s6p^2$ configuration of Pb(II).

Levels (Moore)	Energy (cm ⁻¹)		Lande factor		J	Composition		
	Expt.	Calc.	Expt.	Calc.		% 1st comp	% 2nd comp	% 3rd comp
$6p^{24}P_{1/2}$	57 911	57 701			1/2	87 $6s6p^2\ ^4P$	10 $6s6p^2\ ^2S$	2 $6s6p^2\ ^2P$
$7s\ ^2S_{1/2}$	59 448	59 450	2.01	2.00	1/2	99 $6s^27s\ ^2S$	1 $6s6p^2\ ^4P$	—
$6p^{22}P_{1/2}$	88 248	88 072			1/2	71 $6s6p^2\ ^2P$	20 $6s6p^2\ ^2S$	8 $6s6p^2\ ^4P$
$6p^{22}S_{1/2}$	104 297	104 424			1/2	70 $6s6p^2\ ^2S$	25 $6s6p^2\ ^2P$	4 $6s6p^2\ ^4P$
$6p^{24}P_{3/2}$	66 124	66 291	1.64	1.66	3/2	92 $6s6p^2\ ^4P$	4 $6s6p^2\ ^2D$	3 $6s^26d\ ^2D$
$6d\ ^2D_{3/2}$	69 740	69 700	0.81	0.85	3/2	83 $6s^26d\ ^2D$	10 $6s6p^2\ ^2D$	6 $6s6p^2\ ^4P$
$6p^{22}D_{3/2}$	83 083	83 310			3/2	76 $6s6p^2\ ^2D$	13 $6s^26d\ ^2D$	10 $6s6p^2\ ^2P$
$7d\ ^2D_{3/2}$	94 284	94 281	0.80	0.86	3/2	98 $6s^27d\ ^2D$	1 $6s6p^2\ ^2D$	1 $6s6p^2\ ^2P$
$8d\ ^2D_{3/2}$	103 394	103 374	0.76	0.80	3/2	82 $6s^28d\ ^2D$	16 $6s6p^2\ ^2P$	1 $6s6p^2\ ^2D$
$6p^{22}P_{3/2}$	104 669	104 762			3/2	72 $6s6p^2\ ^2P$	16 $6s^28d\ ^2D$	10 $6s6p^2\ ^2D$
$6d\ ^2D_{5/2}$	68 964	69 002	1.29	1.31	5/2	46 $6s^26d\ ^2D$	29 $6s6p^2\ ^4P$	24 $6s6p^2\ ^2D$
$6p^{24}P_{5/2}$	73 905	73 845	1.52	1.40	5/2	49 $6s6p^2\ ^4P$	48 $6s^26d\ ^2D$	2 $6s6p^2\ ^2D$
$6p^{22}D_{5/2}$	88 972	88 775			5/2	72 $6s6p^2\ ^2D$	20 $6s6p^2\ ^4P$	6 $6s^26d\ ^2D$
$7d\ ^2D_{5/2}$	95 304	95 315	1.18	1.20	5/2	96 $6s^27d\ ^2D$	3 $6s6p^2\ ^2D$	1 $6s6p^2\ ^4P$
$8d\ ^2D_{5/2}$	104 190	104 192	1.21	1.20	5/2	98 $6s^27d\ ^2D$	1 $6s6p^2\ ^2D$	1 $6s6p^2\ ^4P$

Table 2. Parameters resulting from the least-square fitting of the intermediate coupling calculations.

Configuration	Parameters (cm ⁻¹)	
6s ² 7s	$E_{av} = 59.440$	
6s ² 6d	$E_{av} = 72\ 149$	$\zeta_{6d} = 508\ (203)$
6s ² 7d	$E_{av} = 94\ 694$	$\zeta_{7d} = 365\ (83)$
6s ² 8d	$E_{av} = 103\ 829$	$\zeta_{8d} = 221\ (43)$
6s6p ²	$E_{av} = 82\ 161$	$\zeta_{6p} = 10\ 151\ (9353)$
	$F^2 = 26\ 001\ (35\ 976)$	
	$G^1 = 27\ 922(45\ 208)$	
	$\alpha = -564$	
<hr/>		
$R^1\ (6s^2\ 7s, 6s6p^2) = 916\ (-4902).$		
$R^1\ (6s^2\ 6d, 6s6p^2) = 13\ 375\ (22\ 942).$		
$R^1\ (6s^2\ 7d, 6s6p^2) = 3960\ (12\ 360).$		
$R^1\ (6s^2\ 8d, 6s6p^2) = 4340\ (8340).$		
Values in parentheses are ab initio HFR results.		

in the HFR calculation. The effect of “energy level repulsion” is clearly significant between $6s6p^2\ ^2D$ levels and $6s^26d\ ^2D$.

Finally, the fitting of the experimental energy levels in the IC calculations confirms this situation providing the results that can be seen at the right-hand side of Fig. 1 and in Table 1. The effects of interaction with the $6s^27s$, $6s^27d$, and $6s^28d$ configurations in the energy level scheme are very small and are not explicitly presented in Fig. 1.

These calculations can be considered successful and some conclusions must be made at this point. In the first place, the values quoted in Table 1 show the strong mixing of $^2D_{5/2}$ levels of both configurations with the $^4P_{5/2}$ of $6s6p^2$ configuration. The contribution of $6s^26d\ ^2D_{5/2}$ in the $6s6p^2\ ^4P_{5/2}$ is more important in the IC fitting calculations than in the ab initio HFR calculation. This result can be used

Table 3. Transition probabilities of lines arising from $6s^2ns$ configurations of Pb(II).

Transition Levels		Transition probabilities (10^6 s^{-1})				
		Wavelength		Theoretical		
Upper	Lower	λ (Å)	This work	Ref. 6	Ref. 5	Experimental
$7s^2S_{1/2}$	$6p^2P_{1/2}$	1682.1	546.5		325.4	
	$6p^2P_{3/2}$	2204.2	485.6		552.0	493±74 ^{Ref.9}
	$6s^2S_{1/2}$	11213	166.1		111.4	
	$6p^2P_{3/2}$	1331.6	198.4		176.8	
$9s^2S_{1/2}$	$7p^2P_{1/2}$	6793.0	51.30	52.20	38.45	44.7±4.5
	$7p^2P_{3/2}$	8397.7	54.30		222.1	
	$6p^2P_{1/2}$	986.7	78.0		51.18	
	$6p^2P_{3/2}$	1145.9	99.60		78.24	
$10s^2S_{1/2}$	$7p^2P_{1/2}$	3719.3	16.35	16.30	14.18	17.5±2.8
	$7p^2P_{3/2}$	4153.9	23.47	23.46	29.96	22.6±3.6
	$6p^2P_{1/2}$	926.5	43.65		30.00	24±10 ^{Ref.7}
	$6p^2P_{3/2}$	1065.5	57.40		24.38	
$11s^2S_{1/2}$	$7p^2P_{1/2}$	2987.7	8.63	7.32	8.14	8.4±1.2
	$7p^2P_{3/2}$	3261.8	13.27	11.27	12.41	10.4±1.5
	$8p^2P_{1/2}$	7780.3	4.69			
	$8p^2P_{3/2}$	8552.9	7.07		18.18	
$12s^2S_{1/2}$	$6p^2P_{1/2}$	896.3	26.75		29.29	
	$6p^2P_{3/2}$	1025.7	35.69		4.82	5.3±0.7
	$7p^2P_{1/2}$	2694.3	5.11	3.78	7.22	4.8±0.7
	$7p^2P_{3/2}$	2915.3	8.07	5.98		
$13s^2S_{1/2}$	$8p^2P_{1/2}$	6061.7	2.51			
	$8p^2P_{3/2}$	6520.6	4.03			
	$9p^2P_{1/2}$	13982.1	1.76			
	$6p^2P_{1/2}$	877.9	17.60			
$14s^2S_{1/2}$	$6p^2P_{3/2}$	1001.7	23.69			
	$7p^2P_{1/2}$	2534.7	3.31			
	$7p^2P_{3/2}$	2729.3	5.30			
	$8p^2P_{1/2}$	5309.3	1.56			
$15s^2S_{1/2}$	$8p^2P_{3/2}$	5658.0	2.58			
	$9p^2P_{1/2}$	10537.4	0.99			
	$9p^2P_{3/2}$	11246.1	1.63			
	$6p^2P_{1/2}$	865.8	12.20			
$16s^2S_{1/2}$	$6p^2P_{3/2}$	986.0	16.52			
	$7p^2P_{1/2}$	2436.8	2.27			
	$7p^2P_{3/2}$	2616.2	3.67			
	$8p^2P_{1/2}$	4897.4	1.05			
$17s^2S_{1/2}$	$8p^2P_{3/2}$	5192.6	1.76			
	$9p^2P_{1/2}$	9030.2	0.64			
	$9p^2P_{3/2}$	9545.6	1.08			
	$6p^2P_{1/2}$	857.5	8.80			
$18s^2S_{1/2}$	$6p^2P_{3/2}$	975.3	11.97			
	$7p^2P_{1/2}$	2372.1	1.63			
	$7p^2P_{3/2}$	2541.7	2.65			
	$8p^2P_{1/2}$	4643.0	0.74			
$19s^2S_{1/2}$	$8p^2P_{3/2}$	4907.5	1.26			
	$9p^2P_{1/2}$	8201.4	0.44			
	$9p^2P_{3/2}$	8624.4	0.76			
	$10p^2P_{1/2}$	14054.8	0.30			
$20s^2S_{1/2}$	$10p^2P_{3/2}$	14784.2	0.52			

Table 4. Transition probabilities of lines arising from $6s^2np$ configurations of Pb(II).

Transition			Transition probabilities (10 ⁶ s ⁻¹)					
Levels		Wavelength λ (Å)	Theoretical				Experimental	
Upper	Lower		This work	Ref. 6	Ref. 5	Ref. 6	Ref. 7	Ref. 8
7p ² P _{1/2}	7s ² S _{1/2}	6661.8	70.40	56.3	73.8	59.1±5.9	62±21	57.2±5.4
	6p ² ⁴ P _{1/2}	6043.0	0.90			0.62±0.06		0.54±0.07
	6p ² ⁴ P _{3/2}	11997.6	0.52					
7p ² P _{3/2}	7s ² S _{1/2}	5610.4	117.8	94.4	124.9	83.1±8.3	124±43	84.8±8.5
	6d ² ² D _{3/2}	13276.7	1.19					
	6d ² ² D _{5/2}	12036.6	6.99					
	6p ² ⁴ P _{1/2}	5165.0	1.43			1.6±0.2		1.1±0.2
	6p ² ⁴ P _{3/2}	8970.2	0.13					
8p ² P _{1/2}	7s ² S _{1/2}	2806.7	9.69	4.4	1.8			5.6±0.6
	6d ² ² D _{3/2}	3947.8	0.50	0.44				0.51±0.06
	6p ² ⁴ P _{3/2}	3453.8	0.01					
8p ² P _{3/2}	7s ² S _{1/2}	2718.1	10.67	4.9	14.0			7.3±0.8
	8s ² S _{1/2}	14168.3	23.48					
	6d ² ² D _{3/2}	3773.9	0.01					
	6d ² ² D _{5/2}	3666.5	0.60	0.46				0.56±0.06
	6p ² ⁴ P _{5/2}	4477.7	0.04					
9p ² P _{1/2}	7s ² S _{1/2}	2223.5	3.34					
	8s ² S _{1/2}	6560.8	2.44					
	6d ² ² D _{3/2}	2883.3	0.15					
	7d ² ² D _{3/2}	9863.9	0.08					
9p ² P _{3/2}	7s ² S _{1/2}	2194.3	3.53					
	8s ² S _{1/2}	6313.1	2.74					
	6d ² ² D _{3/2}	2834.5	0.01					
	6d ² ² D _{5/2}	2773.5	0.08					
	7d ² ² D _{3/2}	9314.5	0.01					
	7d ² ² D _{5/2}	10292.3	0.06					
6p ² ⁴ P _{1/2}	6p ² ² P _{1/2}	1726.8	112.6					
	6p ² ² P _{3/2}	2281.5	4.37					
6p ² ⁴ P _{3/2}	6p ² ² P _{1/2}	1512.3	7.32					
	6p ² ² P _{3/2}	1921.5	4.64					
6p ² ⁴ P _{5/2}	6p ² ² P _{3/2}	1671.6	889.8					
6p ² ² D _{3/2}	6p ² ² P _{1/2}	1203.6	4655					
	6p ² ² P _{3/2}	1449.2	1.05					
	7p ² ² P _{1/2}	11595.5	1.51					
6p ² ² D _{5/2}	6p ² ² P _{3/2}	1335.3	2237					
	7p ² ² P _{3/2}	8547.0	2.07					
6p ² ² P _{1/2}	6p ² ² P _{3/2}	1133.2	5770					
	6p ² ² P _{3/2}	1348.3	363.4					
6p ² ² P _{3/2}	6p ² ² P _{1/2}	955.4	476.0					
	6p ² ² P _{3/2}	1103.9	7903					
6p ² ² S _{1/2}	6p ² ² P _{1/2}	958.8	273.2					
	6p ² ² P _{3/2}	1108.4	4154					

to explain the intense dipole-forbidden transitions corresponding to 5369.4 and 5373.4 Å. $6s^27d$ and $6s^28d$ configuration mixing effects in the $6s^26d^2D_{5/2}$ level is less than 1%. Nevertheless, it induces an important effect in the $6s^26d^2D_{5/2}$ – $6s^28p^2P_{3/2}$ transition-probability values.

Table 5. Transition probabilities of lines arising from $6s^2nd$ configurations of Pb(II).

Transition		Transition probabilities (10^6 s^{-1})						
Levels		Wavelength	Theoretical			Experimental		
Upper	Lower	λ (Å)	This work	Ref. 6	Ref. 5	Ref. 6	Ref. 7	Ref. 8
6d $^2D_{3/2}$	6p $^2P_{1/2}$	1433.9	603.3		1409.7			
	6p $^2P_{3/2}$	1796.7	153.6		206.6			
	6d $^2D_{5/2}$	1822.1	72.72		1178.8			
7d $^2D_{3/2}$	6p $^2P_{1/2}$	1060.6	477.5		424.0			
	6p $^2P_{3/2}$	1246.8	58.78		54.9			
	7p $^2P_{1/2}$	5044.1	136.4	106.7		101.7±15.2	77±23	90.0±8.9
7d $^2D_{5/2}$	7p $^2P_{3/2}$	5878.2	17.23	13.5		16.8±2.5		13.8±1.0
	6p $^2P_{3/2}$	1231.2	366.3					
	7p $^2P_{3/2}$	5545.7	123.1					
8d $^2D_{3/2}$	6p $^2P_{1/2}$	967.2	208.1	96.6		104±31		102.8±10.6
	6p $^2P_{3/2}$	1129.7	26.83					
	7p $^2P_{1/2}$	3456.0	38.10	42.9				42.1±6.1
8d $^2D_{5/2}$	7p $^2P_{3/2}$	3828.2	6.78	6.3		43.7±7.0		6.3±0.7
	8p $^2P_{1/2}$	12023.6	24.22					
	8p $^2P_{3/2}$	13974.3	3.09		152.56			
8d $^2D_{3/2}$	6p $^2P_{3/2}$	1109.8	165.3					
	7p $^2P_{3/2}$	3715.0	44.48	42.2				41.9±6.2
	8p $^2P_{3/2}$	12575.5	25.10					
9d $^2D_{3/2}$	6p $^2P_{1/2}$	915.3	114.9			103.91		
	6p $^2P_{3/2}$	1050.7	15.19			12.15		
	7p $^2P_{1/2}$	2873.7	24.91					
9d $^2D_{5/2}$	7p $^2P_{3/2}$	3126.5	3.87					
	8p $^2P_{1/2}$	7052.2	12.78					
	8p $^2P_{3/2}$	7681.1	1.98					
10d $^2D_{3/2}$	6p $^2P_{3/2}$	1049.8	91.33			78.69		
	7p $^2P_{3/2}$	3118.8	23.38					
	8p $^2P_{3/2}$	7634.8	12.09					
10d $^2D_{5/2}$	6p $^2P_{1/2}$	889.6	69.83			61.96		
	6p $^2P_{3/2}$	1017.0	9.35			7.30		
	7p $^2P_{1/2}$	2635.0	14.66	10.2			10.4±1.5	
10d $^2D_{3/2}$	7p $^2P_{3/2}$	2846.0	2.33	1.6			1.5±0.2	
	8p $^2P_{1/2}$	5769.7	7.12					
	8p $^2P_{3/2}$	6183.9	1.16					
11d $^2D_{3/2}$	9p $^2P_{1/2}$	12520.3	4.53					
	9p $^2P_{3/2}$	13533.6	0.72					
	6p $^2P_{3/2}$	1016.4	56.18			46.92		
11d $^2D_{5/2}$	7p $^2P_{3/2}$	2841.3	14.03					
	8p $^2P_{3/2}$	6161.8	7.02					
	9p $^2P_{3/2}$	13428.2	4.41					
11d $^2D_{3/2}$	6p $^2P_{1/2}$	873.6	45.80					
	6p $^2P_{3/2}$	996.2	6.18					
	7p $^2P_{1/2}$	2499.6	9.45					
11d $^2D_{5/2}$	7p $^2P_{3/2}$	2688.6	1.52					
	6p $^2P_{3/2}$	995.8	37.12					
	7p $^2P_{3/2}$	2685.6	9.14					

(Table 5 concluded on next page.)

Table 5. (*concluded.*)

Transition		Wavelength	Transition probabilities (10^6 s^{-1})					
Levels			Theoretical			Experimental		
Upper	Lower	λ (Å)	This work	Ref. 6	Ref. 5	Ref. 6	Ref. 7	Ref. 8
12d $^2\text{D}_{3/2}$	6p $^2\text{P}_{1/2}$	862.9	31.75					
	6p $^2\text{P}_{3/2}$	982.3	4.31					
	7p $^2\text{P}_{1/2}$	2413.9	6.48					
	7p $^2\text{P}_{3/2}$	2589.8	1.05					
12d $^2\text{D}_{5/2}$	6p $^2\text{P}_{3/2}$	982.0	25.85					
	7p $^2\text{P}_{3/2}$	2587.9	6.31					
13d $^2\text{D}_{3/2}$	6p $^2\text{P}_{1/2}$	855.4	22.92					
	6p $^2\text{P}_{3/2}$	972.6	3.12					
	7p $^2\text{P}_{1/2}$	2356.3	4.64					
	7p $^2\text{P}_{3/2}$	2523.5	0.76					
13d $^2\text{D}_{5/2}$	6p $^2\text{P}_{3/2}$	972.4	1.87					
	7p $^2\text{P}_{3/2}$	2522.2	4.54					
14d $^2\text{D}_{3/2}$	6p $^2\text{P}_{1/2}$	849.9	17.11					
	6p $^2\text{P}_{3/2}$	965.5	2.34					
15d $^2\text{D}_{3/2}$	6p $^2\text{P}_{1/2}$	845.8	13.12					
	6p $^2\text{P}_{3/2}$	960.2	1.79					
15d $^2\text{D}_{5/2}$	6p $^2\text{P}_{3/2}$	960.1	10.77					

Secondly, as is predicted in the ab initio HFR calculations no relevant amount of $6s^2 6d \text{ } ^2\text{D}_{3/2}$ is derived for the $6s6p^2 \text{ } ^4\text{P}_{3/2}$ composition in the IC fitting calculations. Nevertheless, the small contribution of $6s6p^2 \text{ } ^2\text{D}_{3/2}$ and $6s^2 6d \text{ } ^2\text{D}_{3/2}$ in the $6s6p^2 \text{ } ^4\text{P}_{3/2}$ are important in accounting for the existence of the observed doublet–quadruplet forbidden transitions (1512.3 and 1921.5 Å). The presence of the $6s^2 8d \text{ } ^2\text{D}_{3/2}$ level (16%) in the $6s6p^2 \text{ } ^2\text{P}_{3/2}$ level composition is noticeable.

A similar situation can be found for the $J = 1/2$ family where the contribution of $6s6p^2 \text{ } ^2\text{P}$ and $6s6p^2 \text{ } ^2\text{S}$ in the $6s6p^2 \text{ } ^4\text{P}$ account for the same type of forbidden transitions (1726.8, 2281.5, and 1512.3 Å).

The values found for the different parameters involved in the IC calculations are shown in Table 2.

Finally, two questions should be raised. There remains a discrepancy of 300 cm^{-1} between the experimental value of the $6s6p^2 \text{ } ^2\text{D}_{5/2}$ level energy and the calculated one. We think that it must have its origin in an interaction with other configurations. The $6s^2 nd$ ($n = 9\text{--}15$) IC set cannot remove these discrepancies, and there is no appreciable variation in the calculated transition probabilities. Considerations of other candidates with no experimentally observed energy levels were also analysed. The ab initio HFR calculations show that the interaction must be weak. The IC fitting was unfruitful owing to the increase in the number of parameters above the number of experimental energy levels.

Ab initio HFR calculations show small energy splitting between the $6s^2 nf^2 \text{ } ^2\text{F}_{5/2}$ and $6s^2 nf^2 \text{ } ^2\text{F}_{7/2}$ doublet ($\sim 5 \text{ cm}^{-1}$). Experimental data also present a small energy splitting but the doublets are inverted. We have not made an interaction-configuration study of this discrepancy because the final numeric discrepancies between experimental and theoretical data are very small versus the accuracy of the IC fitting techniques. Also, no configuration candidates with experimentally observed energy levels mix with the $6s^2 nf$ configurations to enable us to study this question. We think that, although more detailed calculations are necessary to decide this open question, our calculations of the transition probabilities where a $6s^2 nf^2 \text{ } ^2\text{F}$ level is present show that the interaction with other configurations will be very weak.

Table 6. Transition probabilities of lines arising from $6s^2nf$ configurations of Pb(II).

Transition		Wavelength	Transition probabilities (10^6 s^{-1})				
Levels			Theoretical		Experimental		
Upper	Lower	λ (Å)	This work	Ref. 6	Ref. 6	Ref. 7	Ref. 8
5f $^2\text{F}_{5/2}$	6d $^2\text{D}_{3/2}$	4388.1	243.3	167.7	147.1±14.4	44±15	155.7±15.6
	6d $^2\text{D}_{5/2}$	4243.6	10.38	12.6	9.3±0.9		9.8±1.0
	6p 2 $^4\text{P}_{3/2}$	3787.2	15.08		9.6±1.4	3.3±1.4	10.1±1.0
	6p 2 $^4\text{P}_{5/2}$	5369.4	5.44		3.0±0.3		3.1±0.3
	6p 2 $^2\text{D}_{3/2}$	10586.5	2.51				
5f $^2\text{F}_{7/2}$	6d $^2\text{D}_{5/2}$	4246.3	155.8	133.7	112.1±16.8	29±10	115.0±11.6
	6p 2 $^4\text{P}_{5/2}$	5373.7	81.66		60.0±6.1	128±38	62.1±6.2
6f $^2\text{F}_{5/2}$	6d $^2\text{D}_{3/2}$	3017.4	48.07	41.8	41.1±6.2		40.9±5.0
	6d $^2\text{D}_{5/2}$	2948.4	2.00	3.1	3.5±0.5		3.3±0.4
	7d $^2\text{D}_{3/2}$	11631.9	41.16				
	7d $^2\text{D}_{5/2}$	13198.8	1.97				
	6p 2 $^4\text{P}_{3/2}$	2720.6	2.64				1.7±0.2
	6p 2 $^4\text{P}_{5/2}$	3451.1	1.32				
	6p 2 $^2\text{D}_{3/2}$	5051.0	1.56				
	6p 2 $^2\text{D}_{5/2}$	7189.6	0.02				
	6d $^2\text{D}_{5/2}$	2949.5	29.94	47.0			44.8±4.9
	7d $^2\text{D}_{5/2}$	13220.5	29.48				
6f $^2\text{F}_{7/2}$	6p 2 $^4\text{P}_{5/2}$	3452.7	19.74				5.5±0.6
	6p 2 $^2\text{D}_{5/2}$	7196.6	0.31				
	6d $^2\text{D}_{3/2}$	2557.4	17.03	12.8	12.8±1.9		
	6d $^2\text{D}_{5/2}$	2526.9	0.70	0.9	0.96±0.14		
7f $^2\text{F}_{5/2}$	7d $^2\text{D}_{3/2}$	7015.6	14.03				
	7d $^2\text{D}_{5/2}$	7556.3	0.80				
	6d $^2\text{D}_{5/2}$	2527.5	10.51				
	7d $^2\text{D}_{5/2}$	7561.4	12.04				
7f $^2\text{F}_{7/2}$	6p 2 $^4\text{P}_{5/2}$	2887.4	7.44				
	6p 2 $^2\text{D}_{5/2}$	5113.2	0.19				

3.2. Transition probabilities and lifetimes

Transition probabilities calculated for 190 lines of Pb(II) with wavelengths less than 15000 Å are displayed in column three of Tables 3–6, while columns one and two give the transitions and corresponding wavelengths, respectively. The remaining columns give the theoretical (Alonso-Medina [6] and Migdalek [5]) and experimental (Miller et al. [7], Alonso-Medina [6,8], and Alonso-Medina et al. [9]) transition-probability values to be found in the bibliography.

These values, although in relative good agreement with the rare experimental data, present some noticeable discrepancies.

In Table 3, the theoretical transition-probability value of the 2915.3 Å line is 60% higher than the experimental one. A similar numeric situation can be found in the 2806.7 Å line in Table 4. In Table 6, the theoretical transition-probability value of the 4388.1 Å line is 57% higher than the experimental one. We think that in all these cases the discrepancies can be analyzed from residual interactions. Levels of $J = 1/2$ for the $6s6p^2$ configuration can be mixed with the ns^2S and very weak energy effects can produce relatively large effects in the transition-probability values (2806.7 and 2915.3 Å lines). In the case of the 4388.1 Å line, a similar situation can be derived from other candidates: $6s^2nd$ configurations or other configurations with no levels experimentally observed.

Table 7. Lifetimes (in ns) of some excited levels of Pb(II).

Level	Theory		Experiment
	This work	Ref. 5	Ref. 10
$6s^2 7s^2 S_{1/2}$	0.97	1.14	7.2 ± 0.9
$6s^2 7p^2 P_{1/2}$	13.9		15.2 ± 1.7
$6s^2 7p^2 P_{3/2}$	7.85		10.2 ± 1.2
$6s^2 7d^2 D_{3/2}$	1.46		3.4 ± 0.4
$6s^2 5f^2 F_{5/2}$	3.63		5.9 ± 0.6
$6s^2 5f^2 F_{7/2}$	4.20		5.8 ± 0.6
$6s^2 6f^2 F_{5/2}$	10.1		11.6 ± 1.5

As mentioned above, the system considered is complex, since at high Z , both relativistic and correlation effects are important. Dirac–Fock and core polarization effect calculations could be justified [17]. The relativistic wave functions obtained using this method could explain the residual discrepancies. It would be well worth the effort in future works. Nevertheless, the relatively good agreement between the experimental data available in the bibliography and the theoretical values in our work shows that our IC mixing accounts for the fundamental results of the correlation and relativistic effects.

In Table 7, a comparison between the lifetimes deduced from our transition-probability calculations and the experimental values available in the literature is presented. There is good agreement. The experimental value of the $6s^2 7s^2 S_{1/2}$ lifetime is in contradiction with the experimental value of the $6s^2 6p^2 P_{1/2} - 6s^2 7s^2 S_{1/2}$ transition probability [9]. From this value we can deduce that this lifetime must be lesser than 2.4 ns. We cannot explain the 7.2 ns present in the literature [10].

4. Conclusions

This work provides theoretical transition probabilities for 190 transitions of Pb(II) including some dipole-forbidden lines arising from the $6s6p^2$ configuration, which is of astrophysical interest, and for which no previous values theoretical or experimental were known. Theoretical lifetime values of seven levels, which have experimental values in the literature have been calculated from our transition probabilities. We have also studied the interaction of $^2D_{3/2,5/5}$ levels from the $6s^2 7s + 6s^2 6d + 6s^2 7d + 6s^2 8d + 6s6p^2$ configurations.

Acknowledgments

The authors acknowledge the financial support from the Spanish CYCIT project No. MAT97-0697-C02-02.