Energy Levels of the $6p_{3/2}n$s, nd, ng Autoionizing Series of Pb I

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Abstract

Based on the weakest bound electron potential model (WBEPM) theory, six energy levels of the autoionizing Rydberg series $6pns$ $3/2[3/2]_1$ (n = 15–25), $6pns$ $3/2[3/2]_2$ (n = 15–25), $6pnd$ $3/2[3/2]_1$ (n = 13–25), $6pnd$ $3/2[5/2]_3$ (n = 13–25), $6pnd$ $3/2[7/2]_3$ (n = 14–25) and $6png$ $3/2[5/2]_2$(n = 5–25) of Pb I are calculated. Foreign level perturbation corrections are taken into account in calculations of four series among them. The theoretical calculated results are in good agreement with the known experimental data, and some energies without experimental values are predicted.

Key Words: WBEPM, Pb atom, Rydberg states, energy levels.
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1. Introduction

The rapid development of spectral measurement techniques is bringing more extensive investigation of atom and ion spectra, especially of energy levels and radiative lifetimes of high Rydberg states, on account of their importance in a variety of areas such as astrophysics, laser physics, physical chemistry and nuclear fusion. There are many theoretical computation methods for studying spectra, such as the multi-channel quantum defect theory (MQDT) [1–3], the fully relativistic Dirac-Hatree-Fock (DHF) method [4], R-matrix [5–6], etc. However, their calculation is sometimes rather complicated, especially for many-valance electron systems, because of the large number of fitted parameters.

Weakest bound electron potential model (WBEPM) theory, developed in recent years, is a simple and effective method to investigate atomic or ionic energy levels, lifetimes, transition probabilities etc [7–12]. The main idea is that, based on the considerations of successive ionization of free particles (atom and molecule), there is choice of zero energy point in quantum mechanics and the separation of the weakest bound electron

(WBE) and non-weakest bound electrons (NWBE). In this paper, based on WBEPM theory plus foreign level perturbation corrections, four Rydberg state energy levels $6 \, pns \, 3/2[3/2]_1$ (n = 15-25), $6 \, pnd \, 3/2[3/2]_1$ (n = 13-25), $6 \, pnd \, 3/2[5/2]_3$(n = 13-25), $6 \, pnd \, 3/2[7/2]_3$(n = 14-25) of Pb I are calculated, and two series $6 \, pns \, 3/2[3/2]_2$ (n = 15-25) and $6 \, png \, 3/2[5/2]_2$(n = 5-25) of Pb I without being considered perturbation are also calculated. The results agree very well with known experimental data.

2. Theory and Method

The concept of the weakest bound electron (WBE) was first represented when defining the concept of the ionization potential of a free particle. WBE in a given system is different from all other electrons in the system and are behaviorally called non-weakest bound electrons (NWBEs). With respect to excitation and ionization process, the WBE is the most active electron in the system, and is the electron that can be most easily excited or ionized. As many properties of the many-electron systems are related with the WBE, it is very useful to treat WBE accurately. Since the WBE is different from NWBEs in behavior, it can be treated separately. By the separation of WBE and NWBEs, the problem of a many-electron system can be simplified to be a single-electron problem by WBEPM theory.

For an N-electron atom, N electrons in the WBE system are successively ionized one-by-one. In sequence are the neutral atom, a unit positive ion, and so on. We label the atoms in each ionized states as WBE_1, WBE_2,... WBE_N, respectively. So an N-electron system can be said capable of N WBEs. The nucleus and NWBEs, together, is considered an ion-core. Considering the effect of penetration, polarization and shielding, we use the WBE potential function as proposed in [11]:

$$V(r_i) = \frac{-Z'}{r_i} + \frac{d(d+1) + 2ld}{2r_i^2}, \tag{1}$$

where Z' is the effective nuclear charge, l is the WBE angular quantum number and d is an undetermined parameter. In this paper, all energy terms are expressed in Hartree units.

The corresponding Schrödinger equation of the WBEi is

$$\left[-\frac{1}{2}\nabla_i^2 + V(r_i) \right] \psi_i = \varepsilon_i \psi_i. \tag{2}$$

By solving the one-electron Schrödinger equation of WBE_i, one can obtain the expression of energy eigenvalue of WBE_i:

$$\varepsilon = -\frac{Z'}{2n'^2}, \tag{3}$$

in which, $n' = n + d$, n' is the effective principal quantum number and n is the principal quantum number of WBE_i.

In an electronic configuration series, each electronic configuration usually splits into spectral terms, and each term further splits into more spectral levels. Thus we use the concept of spectrum-level-like series to classify energy levels. A spectrum-level-like series is a series that is composed of energy levels with the same spectral level symbol in a given electronic configuration series of a system. The energy of a level in spectrum-level-like

series can be written as

$$T(n) \approx T_{\lim} - \frac{Z'^2}{2n'^2} = T_{\lim} - \frac{Z'^2}{2(n+d)^2}. \tag{4}$$

Here $T_{\lim}$ is the ionization limit corresponding to a given spectrum series. In order to simplify our calculation process, we can employ the following transformation by employing the representation of energy in quantum defect theory (QDT):

$$\frac{Z'}{n+d} = \frac{Z_{\text{net}}}{n-\delta_n}. \tag{5}$$

Then we get

$$T(n) = T_{\lim} - \frac{Z_{\text{net}}^2}{2(n-\delta_n)^2}, \tag{6}$$

where Z_{net} refers to net nuclear-charge number of atomic core (for neutral atom: $Z_{\text{net}} = 1$). The reasons for doing the above are that the WBE moving in the field of the ion-core is somewhat analogous to the valence electron in alkali metals, and the QDT provides a feasible way to study levels in high Rydberg states and Ritz et al. have done many excellent works on the evaluation of δ_n. In a later investigation of the Ritz formula, Martin [13] found an expression to determine δ_n:

$$\delta_n(\varepsilon_n) = a_1 + a_2 m^{-2} + a_3 m^{-4} + a_4 m^{-6}, \tag{7}$$

where $m = n\text{-}\delta_0$, δ_0 is the quantum defect of the lowest level in a given Rydberg state series, and a_1, a_2, a_3 and a_4 are the fitted spectral coefficients.

Many level series are perturbed by foreign levels, while perturbations are not involved in the Martin expression. In order to solve the significantly perturbed levels, Zhang [9] suggested those levels can be expressed as

$$\delta_n(\varepsilon_n) = \sum_{i=1}^{4} a_i m^{-2(i-1)} + \sum_{j=1}^{N} \frac{b_j}{m^{-2} - \varepsilon_j}, \tag{8}$$

in which

$$m = n - \delta_0, \tag{9}$$

$$\varepsilon_j = \frac{2(T_{\lim} - T_{j,\text{per}})}{Z_{\text{net}}^2}, \tag{10}$$

where $T_{j,\text{per}}$ is the foreign perturbing level which possesses the same parity and total angular quantum number J as the perturbed energy level in a spectrum series, N is the number of foreign perturbing levels, a_i and b_j are the parameters obtained from fitting equation (8) through experimental data. So we will use equations (6) and (8)–(10) to calculate the energy levels of Pb I with perturbation, and use equations (6)–(7) and (9) to calculate them without considering perturbation.

3. Results and discussion

Six Rydberg state energy level series of Pb I are calculated by equations (6)–(10). Perturbations are taken into account in four series: the spectrum series of 6pns 3/2[3/2]$_1$ (n = 15–25) is perturbed by 6p13d

$3/2[3/2]_1$ (72759.3 cm^{-1}) and 6p14d $3/2[3/2]_1$ (72964.5 cm^{-1}), 6pnd $3/2[3/2]_1$ ($n = 13$–25) is perturbed by 6p15s $3/2[3/2]_1$ (72849.2 cm^{-1}) and 6p16s $3/2[3/2]_1$ (73027.9 cm^{-1}), 6pnd $3/2[5/2]_3$($n = 13$–25) is perturbed by 6p14d $3/2[7/2]_3$ (72977.4 cm^{-1}), and 6pnd $3/2[7/2]_3$($n = 14$–25) is perturbed by 6p13d $3/2[5/2]_3$ (72736.7 cm^{-1}) and 6p14d $3/2[5/2]_3$ (72941.8 cm^{-1}). Due to lack of the experimental data of foreign perturbing levels, perturbations are not taken into account in another two series: 6pns $3/2[3/2]_2$ ($n = 15$–25) and 6png $3/2[5/2]_2$($n = 5$–25). The coefficients a_i, δ_0, and b_i, in equations (7)–(9) fitted with experiment data from Ref. [14] are listed in Table 1; the calculated values using WBEPM and the experimental data of each energy series namely T_{cal} and T_{exp} are all listed in Tables 2–4, respectively. The values for calculating T_{cal} are 109737.02 cm^{-1} for R and 73900.65 cm^{-1} for T_{lim} [14].

Table 1. Spectral coefficients of the six energy level series for Pb I by fitting the experimental values in equations (7)–(9).

Series	a_1	a_2	a_3	a_4	δ_0	b_1	b_2
6pns $3/2[3/2]_1$ ($n = 15$–25)	169404	-32.0456	$9.79853\times10^{+6}$	$1.07152\times10^{+7}$	4.78397	0.207197	2890.41
6pns $3/2[3/2]_2$ ($n = 15$–25)	4.66756	71.8532	-9115.55	375,315	4.84940		
6pnd $3/2[3/2]_1$ ($n = 13$–25)	$1.54932\times10^{+6}$	1997.22	$8.00693\times10^{+7}$	$8.32504\times10^{+7}$	3.20155	0.19883	29,689.9
6pnd $3/2[5/2]_3$ ($n = 13$–25)	2.68218	-591.914	333040	$-5.03353\times10^{+6}$	3.29027	-0.0275189	
6pnd $3/2[7/2]_3$ ($n = 14$–25)	-70.4901	-10157.7	$6.86873\times10^{+7}$	$-18,354.3$	3.09773	-3.15832	1.22465
6png $3/2[5/2]_2$ ($n = 5$–25)	-0.0782659	45.8275	-5211.41	102,590	0.0179399		

Table 2. Theoretical and experimental energy values (cm^{-1}) of 6pns $3/2[3/2]_{1,2}$ for Pb I.

n	6pns $3/2[3/2]_1$			6pns $3/2[3/2]_2$		
	T_{exp} [14]	T_{cal}	Difference	T_{exp} [14]	T_{cal}	Difference
15	72849.2	72849.199	-0.001	72835.6	72835.600	0.000
16	73027.9	73027.899	-0.001	73017.8	73017.800	0.000
17	73164.9	73164.899	-0.001		73156.961	
18	73271.9	73271.900	0.000		73265.969	
19	73357.3	73357.300	0.000	73352.9	73352.900	0.000
20	73426.7	73426.669	-0.001		73423.257	
21		73483.883			73480.945	
22		73531.523			73528.799	
23		73571.580			73568.915	
24		73605.542			73602.866	
25		73634.553			73631.850	

Tables 2–4 show that our calculated energy levels are very close to experimental data, with an absolute deviation generally less than 2 cm^{-1} and relative deviation generally less than 3×10^{-5}%. The much higher energy levels, in comparison experimental values unavailable, are predicted in the tables mentioned above. Considering the high accuracy of the foregoing calculated values, our forecasted values are reliable.

Table 3. Theoretical and experimental energy values (cm^{-1}) of 6pnd 3/2[3/2]$_1$, 6pnd 3/2[5/2]$_3$, 6pnd 3/2[7/2]$_3$ for Pb I.

n	6pnd 3/2[3/2]$_1$			6pnd 3/2[5/2]$_3$			6pnd 3/2[7/2]$_3$		
	$T_{\exp}$ [14]	T_{cal}	Difference	$T_{\exp}$ [14]	T_{cal}	Difference	$T_{\exp}$ [14]	T_{cal}	Difference
13	72759.3	72757.671	−1.629	72736.7	72736.688	−0.012			
14	72964.5	72964.610	0.110	72941.8	72941.899	0.099	72977.4	72977.400	0.000
15	73115.3	73115.280	−0.020	73098.9	73098.596	−0.304	73126.2	73126.199	-0.001
16	73233.4	73233.406	0.006	73220.3	73220.732	0.432	73241.7	73241.700	0.000
17	73325.9	73325.909	0.009	73316.5	73316.210	−0.290	73334.3	73334.300	0.000
18	73400.9	73400.888	−0.012	73391.9	73391.975	0.075	73406.7	73406.700	0.000
19		73463.327			73453.236			73463.429	
20		73516.033			73503.652			73508.747	
21		73560.772			73545.790			73545.867	
22		73598.841			73581.464			73577.028	
23		73631.299			73611.992			73603.749	
24		73659.045			73638.351			73627.060	
25		73682.845			73661.286			73647.669	

Table 4. Theoretical and experimental energy values (cm^{-1}) of 6png 3/2[5/2]$_2$ for Pb I.

n	$T_{\exp}$[14]	T_{cal}	Difference
5	69479.5	69479.500	0.000
6		71403.064	
7		71921.147	
8		72286.837	
9		72579.996	
10		72811.906	
11	72993.5	72993.417	-0.083
12	73135.2	73135.687	0.487
13	73249.1	73248.149	-0.951
14	73337.3	73338.076	0.776
15	73411.1	73410.873	-0.227
16		73470.516	
17		73519.941	
18		73561.328	
19		73596.318	
20		73626.158	
21		73651.810	
22		73674.020	
23		73693.379	
24		73710.353	
25		73725.320	

In conclusion, WBEPM theory plus foreign level perturbation corrections is an effective and suitable method for study the spectral series of the many-valence electron Pb I , whose computing process is both compact and accurate and needs fitting few parameters. No matter how the principal quantum number n is

large or small, the calculated results are in good agreement with the experimental data. So this method can be applied to study the Rydberg spectra for other many-valence electron atoms or ions.

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