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Theoretical calculation of energy levels of Pb III

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Abstract

In this paper, the results of theoretical calculation of five Rydberg series energy levels $5d_{3/2} \rightarrow np_{1/2}(n$=6–20), $5d_{3/2} \rightarrow nf_{5/2}(n$=5–20), $5d_{5/2} \rightarrow np_{3/2}(n$=6–20), $5d_{5/2} \rightarrow nf_{7/2}(n$=5-20) and $5d_{5/2} \rightarrow nf_{5/2}(n$=5-20) for Pb III ions are presented using the weakest bound electron potential model (WBEPM) theory, considering foreign level perturbation corrections. The theoretically calculated results agree very well with present known experimental data, and some energy levels without experimental values are predicted.

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

Because of their wide application in astrophysics, laser physics, physical chemistry and nuclear fusion etc, the high Rydberg state energy levels and radiative lifetimes of atoms and ions have been paid extensive attention. Corresponding measurement techniques and theoretical computation methods are developing rapidly, such as the multi-channel quantum defect theory (MQDT) [1–3], the fully relativistic Dirac-Hartree-Fock (DHF) method [4–6], R-matrix [7, 8], etc. However, their calculation work is sometimes rather complicated, especially for many-valance electron systems, due to the large number of fitted parameters. Although their calculation results of highly excited states are very good, the deviations of lower excited states between theoretical values and experimental data are significant. Weakest bound electron potential model (WBEPM) theory [9–14], developed in recent years, is a simple and effective method in calculating Rydberg state energy levels. It is based on the considerations of successive ionization of free particles (atom and molecule), the 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, five Rydberg state energy levels $5d_{3/2} \rightarrow np_{1/2}(n$=6–20), $5d_{3/2} \rightarrow nf_{5/2}(n$=5–20), $5d_{5/2} \rightarrow np_{3/2}(n$=6–20), $5d_{5/2} \rightarrow nf_{7/2}(n$=5-20) and $5d_{5/2} \rightarrow nf_{5/2}(n$=5-20) of Pb III are calculated by

using WBEPM theory plus foreign level perturbation corrections. The results are in good agreement with known experimental data, and some energy levels without experimental values in these five series are predicted.

2. Theory and method

The concept of the weakest bound electron (WBE) was first represented when the concept of the ionization potential of a free particle is defined. WBE in a given system is different from all other electrons in the system and 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 to 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 system as WBE are ionized one by one in successive ionization processes. The ionized species are the neutral atom, a unit positive ion,..., an ion with charge $+(Z-1)$, corresponding to removal of the first, second,..., N^{th} WBE, which is labeled as WBE_1, WBE_2,..., WBE_N, respectively. So N electrons in an N-electron system can be treated as N WBEs. In each ionized species there is only one WBE, and other electrons are not ionized which are called NWBE. The nucleus and NWBEs, together, are considered an ion-core, and the NWB is supposed to move in the central potential field due to the ion-core. Considering the effect of penetrations, polarization and shielding, we use the WBE potential function as proposed in [13]:

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

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 WBE i 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 some spectral terms, and each term splits into several further spectral levels. Thus we can use the concept of spectrum-level-like series to classify the 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):

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

Then we get

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

where Z_{net} refers to net nuclear-charge number of atomic core (for neutral atom: Z_{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 much excellent work on the evaluation of δ_n. In a later investigation of the Ritz formula, Martin [15] 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$g$ =n-δ_0, δ_0 is the quantum defect of the lowest level in a given Rydberg state series, 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 Martin expression. In order to solve the significantly perturbed levels, N. W. Zheng [10] 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

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

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

where $T_{j,per}$ 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 III with perturbation, and equations (6), (7) and (9) to calculate them without considering perturbation.

3. Results and discussion

Five Rydberg state energy level series of Pb III are calculated by equations (6)–(10) Four perturb levels are taken into account in series $5d_{3/2} \rightarrow np_{1/2}$($n$=6–20), $5d_{3/2} \rightarrow nf_{5/2}$($n$=5–20) and $5d_{5/2} \rightarrow nf_{7/2}$($n$=5–20); one perturb level is taken into account in series $5d_{5/2} \rightarrow np_{3/2}$($n$=6–20); two perturb levels are taken into account in series $5d_{5/2} \rightarrow nf_{5/2}$($n$=5-20). The coefficients a_i, δ_0, andb_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}, as well as another calculated values in Ref. [14] namely T_{other} are all listed in Tables 2-3, respectively. The value of Rydberg coefficient R for calculating T_{cal} is 109737.02 cm^{-1}. The ionization limit T_{lim} is 47.1343 eV for Table 2, and 44.4914 eV for Table 3.

Table 1. Spectral coefficients of five Rydberg state energy level series for Pb III by fitting the experimental values in equations (7)–(9).

Series	a_1	a_2	a_3	a_4	δ_0	b_1	b_2	b_3	b_4
$5d_{3/2} \rightarrow np_{1/2}$ (n= 6–20)	5.53186	195.01	-4388.06	16799.5	3.75465	0.0928731	0.0377966	0.022204	-0.00314823
$5d_{3/2} \rightarrow nf_{5/2}$ (n= 5–20)	6081.14	30404.1	143808	960000	1.21874	1215.45	-4.19079	-0.0165989	0.000937383
$5d_{5/2} \rightarrow np_{3/2}$ (n= 6–20)	2.43060	9.00695	19.6771	9.43069	3.68478	-0.0114792			
$5d_{5/2} \rightarrow nf_{7/2}$ (n= 5–20)	6.56212	269.353	-14937.4	503124	1.18906	0.350303	0.040593	0.00262268	0.000362655
$5d_{5/2} \rightarrow nf_{5/2}$ (n= 5–20)	1.37526	1.20673	-73.7359	-464.332	1.26790	0.00103083	0.000210754		

Table 2. Theoretical and experimental energy values (eV) of series $5d_{3/2} \rightarrow np_{1/2}$ and $5d_{3/2} \rightarrow nf_{5/2}$ for Pb III.

n	$5d_{3/2} \rightarrow np_{1/2}$			$5d_{3/2} \rightarrow nf_{5/2}$		
	T_{exp} [16]	T^a_{cal}	T_{other} [16]	T_{exp} [16]	T^b_{cal}	T_{other} [16]
6	22.846	22.8459	22.8445	38.57	38.5700	38.5928
7	36.32	36.3200	36.299	41.65	41.6500	41.9391
8	40.82	40.8200	40.7109	43.47	43.4700	43.5583
9	42.89	42.8900	42.8781	44.46	44.4600	44.5051
10		44.1348	44.0788	45.12	45.1199	45.0866
11	44.92	44.9200	44.8203	45.55	45.5515	45.4969
12	45.42	45.4200	45.3141	45.86	45.8565	45.7924
13	45.75	45.7500	45.6606	46.08	46.0818	46.0111
14	46.01	46.0100	45.9199	46.25	46.2530	46.1767
15		46.2079		46.39	46.3861	46.3063
16		46.3586		46.49	46.4913	46.4084
17		46.4752			46.5759	
18		46.5669			46.6449	
19		46.6403			46.7018	
20		46.7001			46.7493	

[a] The perturb levels are $5d^9 6s^2 nf[3/2, 5/2]$ (n=5–8) (35.70 eV, 38.92 eV, 40.74 eV, 41.74 eV). [b] The perturb levels are $5d^9 6s^2 n$ p[3/2, 1/2] (n=6–9) (22.846 eV, 36.932 eV, 40.82 eV, 42.89 eV). These levels are all selected from experimental values in Ref. [16].

Tables 2 and 3 show that our calculated energy levels are very close to the experimental data, with an absolute deviation generally less than 0.016 eV and a relative deviation generally less than 0.04%. The much higher energy levels, whose experimental values are unavailable currently, are predicted in the tables mentioned above. Considering the high accuracy of the foregoing calculated values, our forecasted values are reliable.

In conclusion, WBEPM theory plus foreign level perturbation corrections is an effective and suitable method for studying the spectral series of the many-valence electron Pb III, whose computing process is both

compact and accurate and needs fitting few parameters. No matter whether 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 widely applied to investigating the Rydberg spectra of other many-electron systems.

Table 3. Theoretical and experimental energy values (eV) of series $5d_{5/2} \rightarrow np_{3/2}$, $5d_{5/2} \rightarrow nf_{7/2}$, and $5d_{5/2} \rightarrow nf_{5/2}$ for Pb III.

n	$5d_{5/2} \rightarrow np_{3/2}$			$5d_{5/2} \rightarrow nf_{7/2}$			$5d_{5/2} \rightarrow nf_{5/2}$		
	T_{exp} [16]	T^a_{cal}	T_{other} [16]	T_{exp} [16]	T^b_{cal}	T_{other} [16]	T_{exp} [16]	T^c_{cal}	T_{other} [16]
5				36.06	36.06	36.0844	35.70	35.7000	35.7084
6	21.647	21.6469	21.5754	39.25	39.2500	39.304	38.92	38.9200	38.9057
7	34.18	34.1800	34.1168	40.94	40.9400	40.833	40.74	40.7400	40.6071
8		39.4619	38.3002	41.91	41.9100	42.4294	41.74	41.7400	41.6096
9		41.2479	40.3349	42.47	42.4692	42.8170		42.4019	42.3009
10		42.1652	41.4877	42.89	42.8912	43.1095		42.8542	42.7479
11		42.7231	42.209	43.19	43.1922	43.4369		43.1751	43.0657
12		43.0950			43.4208	43.6686		43.4105	43.2951
13		43.3579		43.61	43.5975	43.7326		43.5881	43.4768
14		43.5481		43.72	43.7356	43.8480		43.7253	43.6129
15		43.6989		43.85	43.8447	43.9303		43.8335	43.7191
16		43.8137			43.9320			43.9203	
17		43.9051			44.0028			43.9910	
18		43.9790			44.0609			44.0493	
19		44.0397			44.1092			44.0980	
20		44.0902			44.1496			44.1391	

[a] The perturb level is $5d^9 6s^2 6p[3/2, 1/2]$ (22.846 eV). [b] The perturb levels are $5d^9 6s^2 nf[5/2, 5/2]$ (n = 5–8) (35.70 eV, 38.92 eV, 40.74 eV, 41.74 eV). [c] The perturb levels are $5d^9 6s^2 nf[5/2, 7/2]$(n = 5–6) (30.06 eV, 39.25 eV). These levels are all selected from experimental values in Ref. [16].

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References

[1] F. Leyvraz, R. A. Méndez-Sánchez, M. Lombardi, and T. H. Seligman, *Phys. Lett. A*, **268,** (2000), 309.

[2] C. J. Dai, *Journal of Electron Spectroscopy and Related Phenomena*, **74**, (1995), 167.

[3] L. Liang, Y. C. Wang, and C. Zhou, *Phys. Lett. A*, **339**, (2005), 89.

[4] H. Ray, *J. Phys. B: At. Mol. Opt. Phys.*, **35**, (2002), L299.

[5] K. Blagoev, R. Roussev, A. Morozov, K. Iskra, and L. Windholz, *Eur. Phys. J.D*, **13**, (2001), 159.

[6] H. L. Xu, A. Persson, S. Svanberg, K. Blagoev, G. Malcheva, V. Pentchev, E. Biémont, J. Campos, M.Ortiz, and R. Mayo, *Phys. Rew. A*, **70,** (2004), 042508.

[7] A. Belhout, S. Ouichaoui, H. Beaumevieille, A. Boughrara, S. Fortier, J. Kiener, J. M. Maison, S. K. Mehdi, L. Rosier, J. P. Thibaud, A. Trabelsi, and J. Vernotte, *Nucl. Phys. A*, **793**, (2007), 178.

[8] L. Liang, Y. C. Wang, and C. Zhou, *Phys. Lett. A***, 360**, (2007), 599.

[9] N. W. Zheng, and Y. J. Sun, *Sci. Chin. (Ser.B)*, **43**, (2000), 113.

[10] N. W. Zheng, D. Ma, R. Yang, T. Zhou, T. Wang, and S. Han, *J. Chem. Phys.* **113**, (2000), 1681.

[11] N. W. Zheng, and T. Wang, *Astrophys. J. Suppl. Ser.* **143**, (2002), 231.

[12] D. X. Ma, N. W. Zheng, and J. Fan, *J. Phys. Chem. Ref. Data*, **33**, (2004), 1013.

[13] T. Zhang, N. Zheng, and D. Ma, *Phys. Scr.*, **75**, (2007), 763.

[14] C. Zhou, L. Liang, and L. Zhang, *Chin. Opt. Lett.*, **6**, (2008), 161.

[15] W. C. Martin, *J. Opt. Soc. Am.*, **70, (**1980**),** 784.

[16] C. Banahan, C. McGuinness, J. T. Costello, D. Kilbane, J-P. Monsnier, E. T. Kennedy, G. O'Sunllivan, and P. van Kampen, *J. Phys. B: At. Mol. Opt. Phys.*, **41**, (2008), 205001.