Theoretical calculation of energy levels and radiative lifetimes of Tl I

Chao Zhou (周 超), Liang Liang (梁 良), and Ling Zhang (张 玲)

Department of Physics, Xi'an University of Architecture and Technology, Xi'an 710055

Received September 21, 2007

Considering the perturbation, the results of theoretical calculation of five Rydberg series energy levels $6s^2ns^2S_{1/2}$ ($n=7-20$), $6s^2nd^2D_{3/2}$ ($n=6-20$), $6s^2nd^2D_{5/2}$ ($n=6-20$), $6s^2np^2P^0_{1/2}$ ($n=7-20$), and $6s^2np^2P^0_{3/2}$ ($n=7-20$) for Tl I are presented using the weakest bound electron potential model (WBEPM) theory. Furthermore, the radiative lifetimes of this five series are also calculated. The calculated values of energy levels and lifetimes are in good agreement with the experimental results.

OCIS codes: 020.0020, 020.5780.

Owing to extensive use 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 more and more attention. Corresponding measurement techniques and theoretical computation methods are also developing quickly, 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, in the theoretical methods mentioned above, calculation work is sometimes rather complicated, especially for many-valance electron systems on account of a large number of parameters to be fitted. While the results of highly excited states are very good, the deviations of lower ones are significant. The weakest bound electron potential model (WBEPM) theory[7−11] 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 of energy in quantum mechanics, and the separation of the weakest bound electron (WBE) and non-weakest bound electrons (NWBEs). In this paper, based on WBEPM theory, the Rydberg state energy levels $6s^2ns^2S_{1/2}$ ($n=7-20$), $6s^2nd^2D_{3/2}$ ($n=6-20$), $6s^2nd^2D_{5/2}$ ($n=6-20$), $6s^2np^2P^0_{1/2}$ ($n=7-20$) and $6s^2np^2P^0_{3/2}$ ($n=7-20$) for Tl I are calculated, and the results agree very well with experimental values. In addition, the radiative lifetimes for the five series mentioned above are also calculated, whose results are in good agreement with the experimental values.

For an N-electron atom, N electrons in the system as WBE are ionized one by one in successive ionization processes. In these processes species ionized are the neutral atom, unit positive ion, $\cdots$, ion with charge $+(Z-1)$, and WBEs removed are WBE1, WBE2, $\cdots$, WBEN respectively. So N electrons in an N-electron system can be treated as N WBEs. In each species ionized there is only one WBE, and other electrons are not ionized which are called NWBE. The nucleus and NWBEs can be regarded as an ion-core, and the WBE is supposed to move in the central potential field due to the ion-core. Considering the effect of penetrations, polarization and shielding, the potential function of WBE is presented as (in this paper, all the energy terms in expressions are in Hartree units)[10]

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

where Z' is the effective nuclear charge, l is the angular quantum number of the WBE and d is the parameter.

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 WBEi, one can obtain the expression of energy eigenvalue of WBEi:

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

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

As we know, in an electronic configuration series, each electronic configuration usually splits into some spectral terms, and each term splits into several further spectral levels. So 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

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

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

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

Table 1. Spectral Coefficients of the Five Energy Level Series for Tl I by Fitting the Experimental Values in Eq. (8)

Series	a_1	a_2	a_3	a_4	b_1
$6s^2ns^2S_{1/2}$ $(n=7-20)$	4.74335	0.247864	0.308823	−0.285106	−0.000002
$6s^2nd^2D_{3/2}$ $(n=6-20)$	3.11657	−0.0285184	−1.90791	14.7082	−0.000003
$6s^2nd^2D_{5/2}$ $(n=6-20)$	3.12700	−1.36740	20.7985	−93.1322	0.000008
$6s^2np^2P^0_{1/2}$ $(n=7-20)$	4.25563	−0.183652	7.60464	−26.7257	−0.0000006
$6s^2np^2P^0_{3/2}$ $(n=7-20)$	4.244937	−6.79801	154.8506	−809.18	−0.000041

Then we get

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

where $Z_{\rm net}$ refers to net nuclear-charge number of atomic core (for neutral atom: $Z_{\rm net}=1$). The reasons for doing 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. Later a development of Ritz formula was made by Martin[12], he founded Martin 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 $m = n - \delta_0$ and δ_0 is the quantum defect of the lowest level in a given series.

Many level series are perturbed by foreign levels, while perturbations are not involved in Martin expression. In order to solve the significantly perturbed levels, Zhang[10] consider those levels as follows

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

in which

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

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

where $T_{j,\rm per}$ is the energy of perturbing levels, and j is the number of the foreign perturbing levels. So we will use Eqs. (4), (8)—(10) to calculate the energy levels of TI I with perturbation.

In addition, by means of the calculative formula of radiative lifetime for a many-valance electron atomic (or ionic) system[13]

$$\tau = \tau_0 (n-\delta_n)^{\alpha}, \tag{11}$$

where τ_0 and α are the coefficients of a given series, which can be fitted from Eqs. (4), (9) and (11) using the experimental values of energy level and lifetime, the theoretical values of lifetime will be obtained.

Five Rydberg spectral series energy levels of Tl I $6s^2ns^2S_{1/2}$ $(n=7-20)$, $6s^2nd^2D_{3/2}$ $(n=6-20)$, $6s^2nd^2D_{5/2}$ $(n=6-20)$, $6s^2np^2P^0_{1/2}$ $(n=7-20)$ and $6s^2np^2P^0_{3/2}$ $(n=7-20)$ are calculated by Eqs. (4), (8)—(10) with the consideration of perturbation coming from $6s6p^2\ ^4P_{1/2}$ (45220 cm^{-1})[14]. The coefficients a_1, a_2, a_3, a_4 and b_1 in Eq.(8) fitted with experiment data from Ref. [14] are listed in Table 1; the coefficients τ_0 and α in Eq. (11) are listed in Table 2; the calculated values using WBEPM and the experimental values of each energy series namely $T_{\rm cal}$ and $T_{\rm exp}$ are all listed in Tables 3 − 5, respectively. In order to compare with other theoretical calculations, the energy values $T_{\rm DHF}$ calculated by Biémont[14] using fully relativistic Dirac-Hatree-Fock (DHF) method are also listed in Tables 3 − 5, respectively. Meanwhile, our calculated values, the experimental values and the theoretical values using DHF of radiative lifetime namely $\tau_{\rm cal}$, $\tau_{\rm exp}$ and $\tau_{\rm DHF}$ are also listed in Tables 3 − 5. The experimental values of radiative lifetime are from Refs. [14,15]. The values for calculating $T_{\rm cal}$ are 109737.02 cm^{-1} for R and 49265.91 cm^{-1} for $T_{\rm lim}$[16].

Table 2. Coefficients of the Five Series for Tl I by Fitting the Experimental Values in Eq. (11)

Series	τ_0	α
$6s^2ns^2S_{1/2}$ $(n=7-20)$	0.907402	2.77179
$6s^2nd^2D_{3/2}$ $(n=6-20)$	0.503762	2.70988
$6s^2nd^2D_{5/2}$ $(n=6-20)$	0.183427	3.44603
$6s^2np^2P^0_{1/2}$ $(n=7-20)$	3.35620	3.01344
$6s^2np^2P^0_{3/2}$ $(n=7-20)$	2.21675	3.03623

Table 3. Theoretical and Experimental Energy (cm^{-1}) and Lifetime (ns) Values of $6s^2ns^2S_{1/2}$

n	$T_{\rm exp}$[14]	$T_{\rm cal}$	Difference	$\tau_{\rm exp}$[14]	$\tau_{\rm cal}$	$\tau_{\rm DHF}$[14]
7	26477.5	26477.5	0	7.3 ± 0.4	7.46	6.79
8	38745.9	38745.6	−0.3	25 ± 2	21.75	21.59
9	43166.2	43166.8	0.6	54 ± 4	46.33	57.03
10	45296.8	45295.8	−1.0	50 ± 4	83.66	53.32
11	46456.9	46456.5	−0.4	145 ± 10	135.67	120.3
12	47178.9	47179.1	0.2	225 ± 20	204.49	210.4
13	47654.7	47654.2	−0.5	310 ± 30	292.23	329.4
14	47983.2	47984.4	1.2	410 ± 50	400.91	481.1
15		48222.3			532.48	
16		48399.6			688.86	
17		48535.2			871.91	
18		48641.3			1083.42	
19		48725.9			1325.20	
20		48794.4			1598.98	

Table 4. Theoretical and Experimental Energy (cm^{-1}) and Lifetime (ns) Values of $6s^2nd^2D_{3/2,5/2}$

n	$6s^2nd^2D_{3/2}$						$6s^2nd^2D_{5/2}$					
	T_{exp}[14]	T_{cal}	Difference	τ_{exp}[14]	τ_{cal}	τ_{DHF}[14]	T_{exp}[14]	T_{cal}	Difference	τ_{exp}[14]	τ_{cal}	τ_{DHF}[14]
6	36117.9	36117.9	0	8.5 ± 0.5	8.93	5.9	36199.9	36199.9	0	7.2 ± 0.6	7.18	11.09
7	42011.4	42012.1	0.7	20.5 ± 1.5	19.99	16.48	42049.0	42048.1	−0.9	19.8 ± 1.5	19.95	27.25
8	44672.6	44672.0	−0.6	45 ± 5	37.12	37.12	44692.7	44693.5	0.8	44.0 ± 4	43.81	57.93
9	46098.5	46097.5	−1.0	56 ± 6	61.40	71.79	46110.3	46111.7	1.4		83.06	108.5
10	46949.9	46950.6	0.7	81 ± 9	93.92	125.0	46958.0	46954.5	−3.5		141.93	185.3
11	47499.8	47500.5	0.7	130 ± 20	135.62	202.2	47504.1	47502.0	−2.1		226.12	296.0
12	47876.0	47875.5	−0.5	210 ± 30	187.43	311.1	47876.0	47875.9	−0.1		340.88	452.3
13		48142.6			250.24			48142.5			491.97	
14		48339.5			324.91			48339.2			685.46	
15		48488.8			412.29			48488.5			927.70	
16		48604.8			513.20			48604.4			1225.30	
17		48696.6			628.44			48696.2			1585.12	
18		48770.5			758.78			48770.2			2014.28	
19		48830.9			904.99			48830.6			2520.12	
20		48880.9			1067.82			48880.7			3110.49	

Table 5. Theoretical and Experimental Energy (cm^{-1}) and Lifetime (ns) Values of $6s^2np^2P^0_{1/2,3/2}$

n	$6s^2np^2P^0_{1/2}$						$6s^2np^2P^0_{3/2}$					
	T_{exp}[14]	T_{cal}	Difference	τ_{exp}[15]	τ_{cal}	τ_{DHF}[14]	T_{exp}[14]	T_{cal}	Difference	τ_{exp}[15]	τ_{cal}	τ_{DHF}[14]
7	34159.9	34159.9	0	63.1 ± 1.7	66.60	59.36	35161.1	35161.1	0	48.6 ± 1.3	49.93	41.11
8	41368.1	41368.1	0	184.1 ± 4.4	176.93	157.4	41470.8	41470.8	0	127.7 ± 4.9	125.84	125.3
9	44380.9	44380.9	0	391.1 ± 21.8	364.89	323.1	44562.5	44562.5	0	273.6 ± 13.5	264.49	277.2
10	45939.3	45939.3	0	656.8 ± 14.5	651.0	570.6	46043.6	46043.6	0	480.8 ± 31.6	469.63	509.4
11	46853.8	46853.8	0	991.1 ± 50.8	1056.63	929.6	46917.1	46917.1	0	725.5 ± 28.8	758.96	854.2
12		47436.7			1602.98			47474.5			1145.03	
13		47831.1			2311.32			47854.4			1644.19	
14		48110.5			3202.92			48125.3			2272.23	
15		48315.5			4299.06			48325.3			3044.83	
16		48470.4			5621.07			48477.1			3977.63	
17		48590.4			7190.24			48595.0			5086.26	
18		48685.1			9027.97			48688.5			6386.33	
19		48761.2			11155.6			48763.7			7893.50	
20		48823.3			13594.5			48825.1			9623.47	

Tables $3-5$ show that our calculating energy levels are very close to the experimental data, with an absolute deviation generally no more than 3.5 cm^{-1} and a relative deviation generally no more than $7.45 \times 10^{-3}\%$. Furthermore, our accuracy is better than Biémont's[14]. 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. Moreover, our calculating radiative lifetimes, whose accuracy is better than Ref. [14], also agree well with the experimental values except for the $6s^210s^2S_{1/2}$ level ($\tau_{exp} = 40 \pm 10$ ns[14]). Its main reason is that the perturbation coming from $6s6p^2\ ^4P_{1/2}$ (45220 cm^{-1}) is very strong.

In conclusion, WBEPM theory is an effective and suitable method for studying the spectral series of the many-valence electron Tl 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.

This work was supported by the Basic Research Foundation of Xi'an University of Architecture and Technology (No. JC0724) and the Foundation for Talents of Xi'an University of Architecture and Technology (No. RC0604).
C. Zhou's e-mail address is zc0921@sina.com.

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