Research Article

Calculation of the Rydberg Energy Levels for Francium Atom

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Based on the weakest bound electron potential model theory, the Rydberg energy levels and quantum defects of $ns^2S_{1/2}$ ($n = 8-50$), $nd^2D_{3/2}$ ($n = 6-50$), and $nd^2D_{5/2}$ ($n = 6-50$) spectrum series for francium atom are calculated. The calculated results are in excellent agreement with the 74 known experimentally measured levels (the absolute difference is less than 0.03 cm^{-1}) and 58 energy levels for highly excited states are predicted.

1. Introduction

Much work [1–19] has been carried out to investigate the energy structure in excited states of francium atom, the heaviest alkali metal atom. The experimental investigations of the francium spectrum were pioneered by Liberman et al. in 1978 [1]. Later on, the energy levels of $7p^2P_{1/2,3/2}^0$ and $8p^2P_{1/2,3/2}^0$ were investigated by Doppler-free laser spectroscopy techniques in 1986 and 1987 [2, 3]. The ns ($n = 23, 25-27, 29-31$) and nd ($n = 22-33$) Rydberg levels were observed by two-step laser excitation and detection techniques also in 1987 [4], the ns ($n = 10-22$) and nd ($n = 8-20$) series were determined by stepwise laser excitation in 1989 and 1990 [5, 6], and the $9s$ level was observed in 1996 [7]. Meanwhile, the ionization potential was determined in 1988 [8] and refined in 1989 [5]. More recently, an interferometric method was used to improve the accuracy of the $7S-7P$ transition frequency of francium by 1 order of magnitude in 2009 [9]. The theoretical investigation of the energy structure of francium could be outlined as follows. In 1995, many-body perturbation theory in screened Coulomb interaction was used to calculate energy levels, $E1$ transition amplitudes, and the parity-nonconserving $E1$ amplitude of the $7s-8s$ transition in francium by Dzuba et al. [10]. In 1998, Ritz formalism was utilized to predict the francium Rydberg ns , np , and nd levels up to $n = 30$ [12]. In 1999, removal energies of the $n = 7-10$ states and hyperfine constants of the $n = 7$ and 8 states

in francium were calculated by Safronova et al. [11], the calculations were based on the relativistic single-double approximation in which single and double excitations of Dirac-Hartree-Fock wave functions are included to all orders in perturbation theory. In 2004, pseudorelativistic Hartree-Fock method including core-polarization effects was used to investigate the radiative parameters for electric dipole transitions in the ions Ra II, Ac III, Th IV, and U VI along the francium isoelectronic sequence by Biémont et al. [13]. Also in 2004, relativistic Hartree-Fock method with several correlations was used to perform *ab initio* calculation of isotope shifts for isotopes of francium (from $A = 207$ to $A = 228$) by Dzuba et al. [14]. In 2005, radiative corrections to $E1$ matrix elements for $ns-np$ transitions in the alkali-metal atoms lithium through francium are evaluated by Sapirstein and Cheng [15]. In 2006, relativistic third-order and all-order methods were used to calculate the scalar and tensor polarizabilities for the $5f_{5/2}$ ground state in francium-like ion Th^{3+} by Safronova et al. [16]. In 2007, some $E1$ transitions in the francium isoelectronic sequence were computed in the “Dirac-Fock + core-polarization” approximation by Migdalek and Glowacz-Proszkiewicz [17], in which the core-valence electron correlation was treated in a semiclassical picture. Also in 2007, relativistic many-body perturbation theory was applied to study energies of the $7s$, $7p$, $6d$, and $5f$ states of francium-like ions with nuclear charges $Z = 87-100$, and also the transition rates, oscillator strengths, and lifetimes of francium-like ions with $Z = 87-92$

TABLE 1: Spectral coefficients of the four energy series for francium atom by fitting the experimental values.

	a_0	a_1	a_2	a_3
$ns^2S_{1/2}$	5.07085	0.323921	10.4546	96.28960
$nd^2D_{3/2}$	3.42366	0.101560	-0.18468	-1.68691
$nd^2D_{5/2}$	3.40262	0.133411	-0.117487	-0.89660

by Safronova et al. [18]. Most of the energy levels for neutral Francium have been compiled by Sansonetti in 2007 [19]

In all these theoretical works; however, Rydberg energy levels for highly excited states ($n > 31$) of francium-like atoms have not been efficiently studied. The reason is that no matter what approximation method (including many-body perturbation theory, relativistic single-double approximation, pseudo-relativistic Hartree-Fock method, relativistic third-order and all-order methods, Dirac-Fock + core-polarization' approximation method, and so on) is used, it is hard to investigate the highly excited states for such a complicated system that the configuration of the ground state is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s$. A possible approach to solve this problem is to utilize model potential method. In a previous work [20], we have successfully calculated the Rydberg energy levels and the quantum defects of $1s^2 2s^2 2pns^3 P_{2,1,0}$ ($n = 3-50$) and $1s^2 2s^2 2pnd^3 F_{3,2}$ ($n = 3-50$) spectrum series for Carbon I atom by the weakest bound electron potential model theory (WBEPMT) [21–23]. In this paper, the WBEPMT is utilized to investigate the Rydberg energy levels and the quantum defects of $ns^2 S_{1/2}$ ($n = 8-50$), $nd^2 D_{3/2}$ ($n = 6-50$) and $nd^2 D_{5/2}$ ($n = 6-50$) spectrum series for francium atom. The calculated results are in excellent agreement with the 74 known experimentally measured levels [19] (the absolute difference is less than 0.03 cm^{-1}), and 58 energy levels for highly excited states are predicted, which might be significant for experiment guidance.

2. Theory of WBEPMT

In the weakest bound electron potential model theory (WBEPMT) [21–23], the term energy of an atom system is expressed as

$$T = T_{\text{limit}} + E, \quad (1)$$

where T_{limit} is the ionization limit corresponding to a given spectrum series, and E is the energy of the weakest bound electron (WBE), which is determined by the radial equation (in atom unit)

$$\frac{1}{2} \frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} + \left[E - V(r) - \frac{\ell(\ell+1)}{2r^2} \right] R = 0. \quad (2)$$

The potential that suffered by the WBE is modeled as [23]

$$V(r) = -\frac{Z'}{r} + \frac{k(k+1) + 2k\ell}{2r^2}, \quad (3)$$

in which Z' stands for the number of effective nuclear charge, and k an adjustable parameter and is not necessarily

an integer. The first term of (3) represents the Coulomb potential and the second term represents the dipole potential that originated from polarization.

Inserting (3) into (2), the radial equation becomes

$$\frac{1}{2} \frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} + \left[E + \frac{Z'}{r} - \frac{\ell'(\ell'+1)}{2r^2} \right] R = 0, \quad (4)$$

with

$$\ell' = \ell + k. \quad (5)$$

The solution to (4) is known as

$$R_{n\ell}(r) = A \exp\left(-\frac{Z'r}{n'}\right) r^{\ell'} L_{n-\ell'-1}^{2\ell'+1}\left(\frac{2Z'r}{n'}\right), \quad (6)$$

$$E = -R\left(\frac{Z'}{n'}\right)^2,$$

where $n' = n + k$, A is the normalization constant, and R the Rydberg constant. Let

$$\frac{Z'}{n'} = \frac{Z_{\text{net}}}{n - \delta_n}, \quad (7)$$

where Z_{net} is the net charge number of the atomic kernel and $Z_{\text{net}} = 1$ for atoms, δ_n is the quantum defect, the term energy described by (1) is turned into

$$T = T_{\text{limit}} + E = T_{\text{limit}} - R\left(\frac{Z_{\text{net}}}{n - \delta_n}\right)^2. \quad (8)$$

According to Martin's formula about quantum defect [24], δ_n can be expressed as

$$\delta_n = \sum_{i=0}^3 \frac{a_i}{(n - \delta_0)^{2i}}, \quad (9)$$

where δ_0 is the quantum defect of the lowest energy level in a given series, a_i ($i = 0, 1, 2, 3$) are parameters that can all be obtained through the least-square fitting of (8) with the first few experimental data in a given spectrum series.

3. Results and Discussion

By using the experimental data of the first four lowest energy levels of a given spectrum series, parameters a_i are fitted by least-square method, the results are listed in Table 1.

The Rydberg energy levels of the spectrum series of $ns^2 S_{1/2}$ ($n = 8-50$), $nd^2 D_{3/2}$ ($n = 6-50$), and $nd^2 D_{5/2}$ ($n = 6-50$) for francium atom are calculated by (9). The calculated energy levels, quantum defects, and the differences between calculated and measured energy levels [19] are shown in Table 2 to Table 4, respectively. The unit of energy levels is expressed in cm^{-1} .

From Tables 2, 3, and 4, it can be seen that the calculated results are in excellent agreement with the known experimental data since the absolute difference is less than 0.03 cm^{-1} .

Therefore, by using the experimental data of the first four lowest energy levels for a given spectrum series, the Rydberg

TABLE 2: Comparison of the calculated and measured values of $ns^2S_{1/2}$ ($n = 8-50$) energy levels series for francium atoms.

n	T_{cal}	T_{exp}	Diff.	δ_{cal}	n	T_{cal}	T_{exp}	Diff.	δ_{cal}
8	19739.98	19739.98	0.00	5.10670	30	32672.29	32672.29	0.00	5.07131
9	25671.00	25671.00	0.00	5.08998	31	32685.64			5.07128
10	28310.617	28310.617	0.00	5.08263	32	32697.54			5.07125
11	29718.909	29718.909	0.000	5.07883	33	32708.19			5.07122
12	30559.490	30559.504	0.014	5.07662	34	32717.74			5.07120
13	31101.518	31101.539	0.022	5.07523	35	32726.36			5.07117
14	31471.443	31471.465	0.024	5.07429	36	32734.16			5.07115
15	31735.158	31735.182	0.021	5.07363	37	32741.23			5.07114
16	31929.768	31929.789	0.014	5.07315	38	32747.67			5.07112
17	32077.478	32077.492	0.016	5.07279	39	32753.55			5.07110
18	32192.235	32192.251	0.018	5.07250	40	32758.93			5.07109
19	32283.162	32283.180	0.016	5.07228	41	32763.86			5.07108
20	32356.428	32356.444	0.011	5.07210	42	32768.40			5.07107
21	32416.329	32416.340	0.008	5.07195	43	32772.59			5.07106
22	32465.929	32465.937	0.010	5.07183	44	32776.46			5.07104
23	32507.46	32507.47	0.00	5.07173	45	32780.04			5.07104
24	32542.59	32542.59	0.00	5.07164	46	32783.36			5.07103
25	32572.55	32572.56	0.01	5.07156	47	32786.45			5.07102
26	32598.33	32598.34	0.01	5.07150	48	32789.33			5.07101
27	32620.66	32620.67	0.01	5.07144	49	32792.01			5.07100
28	32640.14	32640.14	0.00	5.07139	50	32794.51			5.07100
29	32657.22	32657.22	0.00	5.07135					

TABLE 3: Comparison of the calculated and measured values of $nd^2D_{3/2}$ ($n = 6-50$) energy levels series for francium atoms.

n	T_{cal}	T_{exp}	Diff.	δ_{cal}	n	T_{cal}	T_{exp}	Diff.	δ_{cal}
6	16229.87	16229.87	0.00	3.43035	29	32681.11	32681.11	0.00	3.42381
7	24244.03	24244.03	0.00	3.42887	30	32693.50	32693.50	0.00	3.42379
8	27600.657	27600.657	0.000	3.42731	31	32704.57			3.42378
9	29316.497	29316.497	0.000	3.42630	32	32714.49			3.42378
10	30309.964	30309.962	0.002	3.42564	33	32723.42			3.42377
11	30936.330	30936.325	0.005	3.42519	34	32731.49			3.42376
12	31356.512	31356.506	0.006	3.42488	35	32738.81			3.42375
13	31652.007	31652.000	0.007	3.42465	36	32745.46			3.42375
14	31867.687	31867.682	0.005	3.42448	37	32751.53			3.42374
15	32029.910	32029.909	0.001	3.42435	38	32757.08			3.42374
16	32154.989	32154.979	0.010	3.42425	39	32762.17			3.42373
17	32253.455	32253.449	0.006	3.42417	40	32766.85			3.42373
18	32332.356	32332.354	0.002	3.42410	41	32771.15			3.42373
19	32396.553	32396.552	0.001	3.42405	42	32775.13			3.42372
20	32449.484	32449.483	0.001	3.42400	43	32778.81			3.42372
21	32493.64	32493.64	0.00	3.42397	44	32782.22			3.42372
22	32530.86	32530.86	0.00	3.42394	45	32785.39			3.42371
23	32562.52	32562.52	0.00	3.42391	46	32788.34			3.42371
24	32589.68	32589.68	0.00	3.42388	47	32791.08			3.42371
25	32613.15	32613.15	0.00	3.42386	48	32793.65			3.42371
26	32633.57	32633.57	0.00	3.42385	49	32796.04			3.42370
27	32651.44	32651.44	0.00	3.42383	50	32798.29			3.42370
28	32667.18	32667.18	0.00	3.42382					

TABLE 4: Comparison of the calculated and measured values of $nd^2D_{5/2}$ ($n = 6-50$) energy levels series for francium atoms.

n	T_{cal}	T_{exp}	Diff.	δ_{cal}	n	T_{cal}	T_{exp}	Diff.	δ_{cal}
6	16429.64	16429.64	0.00	3.41476	29	32681.39	32681.39	0.00	3.4028
7	24332.93	24332.93	0.00	3.41028	30	32693.75	32693.75	0.00	3.40280
8	27645.373	27645.373	0.000	3.40771	31	32704.79			3.40279
9	29341.817	29341.817	0.000	3.40621	32	32714.69			3.40278
10	30325.611	30325.605	0.006	3.40528	33	32723.60			3.40277
11	30946.651	30946.643	0.008	3.40467	34	32731.66			3.40276
12	31363.667	31363.655	0.012	3.40425	35	32738.96			3.40275
13	31657.168	31657.155	0.013	3.40394	36	32745.60			3.40274
14	31871.529	31871.514	0.015	3.40371	37	32751.65			3.40273
15	32032.847	32032.821	0.026	3.40354	38	32757.19			3.40273
16	32157.283	32157.274	0.009	3.40340	39	32762.27			3.40272
17	32255.281	32255.275	0.006	3.40330	40	32766.94			3.40272
18	32333.834	32333.827	0.007	3.40321	41	32771.24			3.40271
19	32397.765	32397.761	0.004	3.40314	42	32775.21			3.40271
20	32450.490	32450.488	0.002	3.40308	43	32778.88			3.40270
21	32494.48	32494.48	0.00	3.40303	44	32782.29			3.40270
22	32531.57	32531.57	0.00	3.40299	45	32785.45			3.40269
23	32563.13	32563.13	0.00	3.40295	46	32788.40			3.40269
24	32590.20	32590.20	0.00	3.40292	47	32791.14			3.40269
25	32613.60	32613.60	0.00	3.40289	48	32793.70			3.40268
26	32633.97	32633.97	0.00	3.40287	49	32796.09			3.40268
27	32651.80	32651.79	0.01	3.40285	50	32798.33			3.40268
28	32667.49	32667.49	0.00	3.40283					

energy levels and the quantum defects of $ns^2S_{1/2}$ ($n = 8-50$), $nd^2D_{3/2}$ ($n = 6-50$), and $nd^2D_{5/2}$ ($n = 6-50$) spectrum series for francium atom have been calculated by virtue of the WBEPMT, the calculated results are in excellent agreement with the 74 known experimentally measured levels, one exception ($22d^2D_{5/2}$) is noticed, and 58 energy levels for highly excited states are predicted, which might be significant for experiment guidance.

This implies that the WBEPMT is not only reliable to investigate the Rydberg energy levels of FrI, but also dependable to probe the Rydberg energy levels of FrI. Compared with many-body perturbation theory, relativistic single-double approximation, pseudo-relativistic Hartree-Fock method, relativistic third-order and all-order methods, and Dirac-Fock + core-polarization' approximation method, the advantage of WBEPMT is that the program code, which can be easily written by the Mathematica language, is simpler and the running time is much shorter. The disadvantage of WBEPMT; however, is that the wave functions of the Rydberg states cannot be obtained, which might be settled by combining the WBEPMT with other theories.

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