Calculation of Rydberg energy levels for the francium atom*

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Based on the weakest bound electron potential model theory, the Rydberg energy levels and quantum defects of the $np^2P^\circ_{1/2}$ (n=7–50) and $np^2P^\circ_{3/2}$ (n=7–50) spectrum series for the francium atom are calculated. The calculated results are in excellent agreement with the 48 measured levels, and 40 energy levels for highly excited states are predicted.

Keywords: weakest bound electron potential model theory, francium atom, Rydberg energy level

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1. Introduction

Much work[1−9] has been carried out to investigate the energy structure in excited states of the francium atom, the heaviest alkali metal atom. In 1995, many-body perturbation theory in screened Coulomb interaction was used by Dzuba to calculate energy levels, E1 transition amplitudes and the parity-nonconserving E1 amplitude of the 7s–8s transition in the francium atom.[1] In 1999, energies of the n=7–10 states and hyperfine constants of the n = 7 and 8 states in francium were calculated by Safronova;[2] 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, the pseudo-relativistic 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 Bíemont.[3] Also in 2004, the relativistic Hartree–Fock method with several correlations was used by Dzuba to perform an *ab initio* calculation of isotope shifts for isotopes of francium (from A = 207 to A = 228).[4] In 2005, radiative corrections to E1 matrix elements for ns–np transitions in the alkali-metal atom lithium through francium were made by Sapirstein.[5] In 2006, relativistic third-order and all-order methods were used by Safronova to calculate the scalar and the tensor polarizabilities for the $5f_{5/2}$ ground state in francium-like ion Th^{3+}.[6] In 2007, some E1 transitions in the francium isoelectronic sequence were computed in the 'Dirac–Fock + core-polarization' approximation by Migdalek,[7] in which the core–valence electron correlation was treated in a semiclassical picture. Also in 2007, relativistic many-body perturbation theory was used by Safronova 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, the oscillator strengths, and the lifetimes of francium-like ions with Z=87–92.[8]

In all the work above, however, Rydberg energy levels for highly excited states of francium-like atoms were not efficiently studied. In our previous work,[9] we successfully calculated the Rydberg energy levels and the quantum defects of the $1s^22s^22pns^3P^\circ_{2,1,0}$ (n=3–50) and $1s^22s^22pnd^3F^\circ_{3,2}$ (n=3–50) spectrum series for the carbon I atom by the weakest bound electron potential model theory (WBEPMT).[10−13] In the present paper, the WBEPMT is utilized to investigate the Rydberg energy levels and the quantum defects of the $np^2P^\circ_{1/2}$ (n=7–50) and $np^2P^\circ_{3/2}$ (n=7–50) spectrum series for the francium atom. The calculated results are in excellent agreement with the 48 measured levels, and 40 energy levels for highly excited states are predicted, which might be significant for experimental guidance.

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2. Theory of WBEPM

In the WBEPMT,[10−13] the energy term of an atom is expressed as

$$T = T_{\rm limit} + E, \tag{1}$$

where $T_{\rm limit}$ 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 atomic units)

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

The potential that is suffered by the WBE is modelled as[13]

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

in which Z' denotes the number of effective nuclear charge, and k an adjustable parameter. The first term on the right-hand side of Eq. (3) represents the Coulomb potential and the second term refers to the dipole potential originating from polarization.

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

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

with

$$\ell' = \ell + k. \tag{5}$$

The solution to Eq. (4) is known as[14,15]

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

$$E = -R\left(\frac{Z'}{n'}\right)^2, \tag{6b}$$

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

$$\frac{Z'}{n'} = \frac{Z_{\rm net}}{n-\delta_n}, \tag{7}$$

where $Z_{\rm net}$ is the net charge number of the atomic kernel and $Z_{\rm net} = 1$ for atoms, δ_n is the quantum defect, then the term energy described by Eq. (1) will turn into

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

According to Martin's formula for the quantum defect,[16], δ_n can be expressed as

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

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 Eq. (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 the least-square method; the results are listed in Table 1.

Table 1. Spectral coefficients of the two energy series for the francium atom by fitting experimental values.

	a_0	a_1	a_2	a_3
$n{\rm p}^2{\rm P}^{\circ}_{1/2}$	4.59985	0.472906	12.8064	53.93290
$n{\rm p}^2{\rm P}^{\circ}_{3/2}$	4.50198	0.457929	14.1583	24.08807

The Rydberg energy levels of the spectrum series of $n{\rm p}^2{\rm P}^{\circ}_{1/2}$ (n=7–50) and $n{\rm p}^2{\rm P}^{\circ}_{3/2}$ (n=7–50) for the francium atom are calculated from Eq. (8). The calculated energy levels and quantum defects and the difference between calculated and measured energy levels[17] are listed in Tables 2 and 3, respectively. The unit of energy level is expressed in ${\rm cm}^{-1}$.

Table 2. Comparison between calculated and measured values of the $n{\rm p}^2{\rm P}^{\circ}_{1/2}$ (n=7–50) energy level series for the francium atom.

n	$T_{\rm cal}$	$T_{\rm exp}$	Diff.	$\delta_{\rm cal}$	n	$T_{\rm cal}$	$T_{\rm exp}$	Diff.	$\delta_{\rm cal}$
7	12237.409	12237.409	0.00	4.69260	29	32664.54	32664.57	0.03	4.60058
8	23112.960	23112.960	0.00	4.64271	30	32678.77	32678.80	0.03	4.60052
9	27118.21	27118.21	0.00	4.62402	31	32691.41			4.60048
10	29064.18	29064.18	0.00	4.61523	32	32702.70			4.60043
11	30160.86	30161.07	0.21	4.61057	33	32712.81			4.60039
12	30840.70	30840.98	0.28	4.60774	34	32721.91			4.60036
13	31291.45	31291.72	0.27	4.60592	35	32730.13			4.60033

Table 2. (*Continued*).

n	$T_{\rm cal}$	$T_{\rm exp}$	Diff.	$\delta_{\rm cal}$	n	$T_{\rm cal}$	$T_{\rm exp}$	Diff.	$\delta_{\rm cal}$
14	31605.70	31605.95	0.25	4.60467	36	32737.57			4.60030
15	31833.55	31833.76	0.21	4.60377	37	32744.33			4.60027
16	32004.02	32004.20	0.18	4.60311	38	32750.50			4.60025
17	32134.88	32135.03	0.15	4.60261	39	32756.14			4.60022
18	32237.52	32237.65	0.13	4.60221	40	32761.30			4.60020
19	32319.52	32319.63	0.11	4.60190	41	32766.05			4.60019
20	32386.06	32386.15	0.09	4.60164	42	32770.42			4.60017
21	32440.79	32440.87	0.08	4.60144	43	32774.45			4.60015
22	32486.36	32486.43	0.07	4.60126	44	32778.18			4.60014
23	32524.70	32524.76	0.06	4.60112	45	32781.64			4.60012
24	32557.27	32557.32	0.05	4.60099	46	32784.85			4.60011
25	32585.16	32585.20	0.04	4.60088	47	32787.83			4.60010
26	32609.23	32609.27	0.04	4.60079	48	32790.61			4.60009
27	32630.15	32630.19	0.04	4.60071	49	32793.21			4.60008
28	32648.45	32648.48	0.03	4.60064	50	32795.63			4.60007

Table 3. Comparison between calculated and measured values of the $n{\rm p}^2{\rm P}^{\circ}_{3/2}$ (n=7–50) energy levels series for the francium atom.

n	$T_{\rm cal}$	$T_{\rm exp}$	Diff.	$\delta_{\rm cal}$	n	$T_{\rm cal}$	$T_{\rm exp}$	Diff.	$\delta_{\rm cal}$
7	13923.998	13923.998	0.00	4.59198	29	32666.01	32666.04	0.03	4.50268
8	23658.306	23658.306	0.00	4.54454	30	32680.08	32680.10	0.02	4.50263
9	27366.20	27366.20	0.00	4.52615	31	32692.58			4.50258
10	29198.09	29198.09	0.00	4.51743	32	32703.74			4.50254
11	30241.37	30241.60	0.23	4.51268	33	32713.75			4.50250
12	30892.86	30893.16	0.30	4.50983	34	32722.75			4.50247
13	31327.15	31327.46	0.31	4.50800	35	32730.89			4.50244
14	31631.22	31631.49	0.27	4.50674	36	32738.26			4.50241
15	31852.41	31852.65	0.24	4.50585	37	32744.96			4.50238
16	32018.35	32018.55	0.20	4.50519	38	32751.07			4.50236
17	32146.03	32146.20	0.17	4.50468	39	32756.66			4.50234
18	32246.36	32246.51	0.15	4.50429	40	32761.78			4.50232
19	32326.65	32326.77	0.12	4.50398	41	32766.49			4.50230
20	32391.89	32391.99	0.10	4.50373	42	32770.83			4.50228
21	32445.62	32445.71	0.09	4.50352	43	32774.83			4.50227
22	32490.41	32490.48	0.07	4.50335	44	32778.53			4.50225
23	32528.13	32528.19	0.06	4.50321	45	32781.96			4.50224
24	32560.19	32560.25	0.06	4.50309	46	32785.15			4.50223
25	32587.67	32587.72	0.05	4.50298	47	32788.11			4.50222
26	32611.41	32611.45	0.04	4.50289	48	32790.87			4.50221
27	32632.05	32632.09	0.04	4.50281	49	32793.45			4.50220
28	32650.12	32650.15	0.03	4.50274	50	32795.86			4.50219

From Tables 2 and 3, it can be seen that the calculated results are in excellent agreement with the experimental data since the absolute difference is less than 0.31 $\rm cm^{-1}$.

Therefore, by using the experimental data of the first four lowest energy levels for a given spectrum series, the Rydberg energy levels and the quantum defects of the $n{\rm p}^2{\rm P}^{\circ}_{1/2}$ (n=7–50) and $n{\rm p}^2{\rm P}^{\circ}_{3/2}$ (n=7–50) spectrum series for the francium atom are calculated by virtue of the WBEPMT; the calculated results are in excellent agreement with the 48 measured levels, and 40 energy levels for highly excited states are predicted, which might be significant for experimental guidance. This implies that the WBEPMT is not only reliable for investigating

the Rydberg energy levels of CI but also dependable for probing the Rydberg energy levels of FrI, the heaviest alkali metal atom. Compared with the 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 WBEPMT is obviously advantageous in that the program code, which can be easily written in 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; this might be settled by combining the WBEPMT with other theories.

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