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RESEARCH ARTICLE

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Transition energy and dipole oscillator strength of $1s^2 3d\text{-}1s^2 nf$ transitions for Sc^{18+} ion

Abstract The transition energies of the $1s^2 3d\text{-}1s^2 nf$ ($4 \leqslant n \leqslant 9$) transitions and fine structure splittings of $1s^2 nf$ ($n \leqslant 9$) states for Sc^{18+} ion are calculated with the full-core plus correlation method. The quantum defect of $1s^2 nf$ series is determined by the single-channel quantum defect theory. The energies of any highly excited states with $n \geqslant 10$ for this series can be reliably predicted using the quantum defect as function of energy. Three alternative forms of the dipole oscillator strengths for the $1s^2 3d\text{-}1s^2 nf$ ($n \leqslant 9$) transitions of Sc^{18+} ion are calculated with the transition energies and wave functions obtained above. Combining the quantum defect theory with the discrete oscillator strengths, the discrete oscillator strengths for $1s^2 3d\text{-}1s^2 nf$ ($n > 9$) transitions and the oscillator strengths densities corresponding to the bound-free transitions are obtained.

Keywords Sc^{18+} ion, transition energy, quantum defect, dipole oscillator strength

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1 Introduction

Recently research on the structure and properties of highly ionized atomic systems has been an important subject because many fields in science and technology need the results and basic data obtained in this research [1, 2]. However, a limited number of experimental data on these ions can be found in the literature and the accuracy of these available data is far from satisfactory. In most cases one has to rely on reliable theoretical predictions for these basic data.

The full-core plus correlation (FCPC) method [3], as a new elegant variation approach, has been successfully applied to the calculations of atomic structure for the systems with a $1s^2$-core [3, 4]. Not long ago, this method was used to calculate the energy and oscillator strength of $1s^2 nl$ (l = s and p) states for Sc^{18+} ion [5]. In this paper, as a natural extension, we calculate the transition energies and dipole oscillator strengths of $1s^2 3d\text{-}1s^2 nf$ ($4 \leqslant n \leqslant 9$) transitions and the fine structure of $1s^2 nf$ ($4 \leqslant n \leqslant 9$) states for Sc^{18+} ion. In order to predict reliably the energy of any highly excited states ($n > 9$), the quantum defect of $1s^2 nf$ series, as function of energy, is determined. Combining the quantum defect theory (QDT) with the calculated results ($n \leqslant 9$) of discrete oscillator strengths, the discrete oscillator strengths for $1s^2 3d\text{-}1s^2 nf$ ($n > 9$) transitions and oscillator strengths densities corresponding to the bound-free transitions are obtained. Thus, the theoretical prediction on this important spectral property of Sc^{18+} ion is extended to the whole energy region.

2 Theoretical method

The detail of the FCPC can be found in [3, 4], and the presentations will not be repeated here. The wave function of the $1s^2 3d$ and $1s^2 nf$ states for lithium-like Sc^{18+} ion is given by using the square-integrated Slater-type basis sets as

$$\Psi(1,2,3) = A\left[\Phi_{\mathrm{lsls}}(1,2)\sum_i d_i r_3^i \mathrm{e}^{-\beta r_3} Y_{l(i)}(3)\chi(3) + \sum_i C_i \Phi_{n(i),l(i)}(1,2,3)\right] \quad (1)$$

where A is an antisymmetrization operator. The first term on the right–hand side of Eq. (1) is the product of a

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predetermined $1s^2$-core wave function $\Phi_{1s1s}(1,2)$ and a linear combination of Slater orbitals for the valence electron, and describes the electron correlation in $1s^2$-core and the effect of valence electron in three-electron system. The second term is similar to the expansion in terms of basis set in traditional configuration interaction (CI) method, and describes the relaxation of $1s^2$-core and the other possible correlations in the three-electron system [3,4]. The expressions of $\Phi_{1s1s}(1,2)$ and $\Phi_{n(i),\,l(i)}(1,2,3)$ in Eq. (1) can be found in [3, 4]. The non-relativistic energies E_0 of the $1s^2$-core, $1s^23d$ and $1s^2nf$ ($4 \leqslant n \leqslant 9$) states are calculated by minimizing the expectation value of their non-relativistic Hamiltonian operators, respectively, whose explicit expressions are given in [3, 4]. The FCPC wave functions Ψ of these states are simultaneously determined in this process. The corrections ΔE to energy of these states from relativistic effects, including the correction to kinetic energy, Darwin term, the electron-electron contact term and the orbit-orbit interaction, and mass-polarization effect are calculated by using the first–order perturbation theory. The explicit expressions of these operators are also given in [3, 4]. Thus, the total energy including the corrections is $E_{tot} = E_0 + \Delta E$. The ionization potential of $1s^2nl$ states is obtained by subtracting the total energy of three-electron system from the total energy of the core. The transition energy of $1s^23d$-$1s^2nf$ transitions is determined from the difference between the ionization potentials of $1s^23d$ and $1s^2nf$ states.

In order to obtain a more accurate result for this ion with the larger nuclear charge Z, the quantum-electrodynamics (QED) effect on the energy should be included. It can be assumed that the QED effect of the core is canceled out in the ionization potential. We only need to consider the QED correction of the valence electron which can be evaluated by using the hydrogenic formula in [6] with an effective nuclear charge. This correction consists of two parts. One of them causes a shift of the centre-of-gravity of energy for $1s^2nl$ configuration, and another contributes to the fine structure splitting of the ^2L (L = D or F) systems [2-5]. Their explicit expressions are given in [3-5].

The fine structure splitting for $1s^2nf$ states of Sc^{18+} ion is obtained by the summation of the expectation values of H_{so} and H_{soo}, and the QED correction to the splittingt. H_{so} and H_{soo} are the operators representing the spin-orbit and spin-other-orbit interactions, respectively. Their explicit expressions can be found from [4].

According to single-channel QDT [7-9], the quantum defect μ_n of $1s^2nf$ state of Sc^{18+} ion is defined by

$$E_n = -\frac{Z^2}{2(n-\mu_n)^2} \quad \text{(in a.u.)} \tag{2}$$

where E_n is the term energy obtained above for $n \leqslant 9$, and n is principal quantum number. The quantum defect μ_n for highly excited states should be a smooth function of energy, and can be approximately expanded in terms of following form

$$\mu_n = \mu_0 + h_1 E + h_2 E^2 \tag{3}$$

where μ_0 is the quantum defect at the ionization threshold. The coefficients h_1 and h_2 can be determined by using an iteration method [2, 5]. The term energy of any highly excited states $1s^2nf$ ($n > 9$) for Sc^{18+} ion can be predicted from Eq. (2) and the μ_n value obtained above, as input.

It can be shown that the dipole oscillator strength is given by any of three alternative formulas which are called the length, velocity, and acceleration forms, respectively [7]. The explicit expressions of these three alternatives are given in [2, 5, 7]. All of them are equivalent theoretically when exact wave functions of the initial and final states are used. But they usually give rather different results when approximate wave functions are used, because the matrix elements in these three forms are weighted towards different regions of electron configuration space. Therefore, it is a rigorous evaluation for the quality of the wave functions used in calculation whether the f-values obtained from these three formulas are in agreement with each other. The dipole oscillator strength values of the length, velocity, and acceleration forms, f_L, f_V, and f_A, for $1s^23d$ -$1s^2nf$ ($4 \leqslant n \leqslant 9$) transitions of Sc^{18+} ion are calculated from the corresponding transition energies and the wave functions of initial and final states obtained above.

According to QDT [8, 9], a channel consists of an infinite number of discrete states and corresponding continuum states with the same angular momentum characters. The bound-bound transitions from a given initial state $1s^23d$ to any discrete final states in $1s^2nf$ channel for Sc^{18+} ion and the bound-continuum transitions from the same initial state to the continuum states in this channel can be treated in a unified form. There is the following relationship between them [7, 10]

$$\tau(E) = \frac{(n^*)^3}{Z^2} f_{ij} = \frac{\mathrm{d}f}{\mathrm{d}\varepsilon} = \left(\frac{E_i}{E_i - E_j}\right)^s \left.\frac{\mathrm{d}f}{\mathrm{d}\varepsilon}\right|_{\varepsilon=0} \tag{4}$$

where E_i and E_j are the energies of the initial and final states, respectively. $n^* = n - \mu_n$ is the effective quantum number of the final state. The oscillator strength at the threshold, $\mathrm{d}f/\mathrm{d}\varepsilon|_{\varepsilon=0}$, and s are determined from our predicted discrete oscillator strengths [2, 10]. Thus, the theoretical prediction on this important spectral property of Sc^{18+} ion can be extrapolated to the whole energy region including the continuum states.

3 Results and discussion

In our calculations, 222 terms in seven l components are used for the $1s^2$-core. Eight d_i terms are used in the wave functions of three-electron system. The number of terms in $\Phi_{n(i),\,l(i)}$ of Eq. (1) ranges from about 400 to 600. Numerical calculations of energies converge very fast.

Our calculated results of the transition energies for $1s^23d$ -$1s^2nf$ ($4 \leqslant n \leqslant 9$) transitions of Sc^{18+} ion are listed in Table 1. There is only an experimental datum available in literature which is also given in this table. It is seen that the agreement between our result and experimental datum for the transition

energy of $1s^2 3d$-$1s^2 4f$ is quite good. The values of the fine structure splittings for $1s^2 nf$ states of Sc^{18+} ion are listed in Table 2 and shown in Fig.1. Our results follow a well-behaved variation regularity of spin-orbit interaction with n alone a Rydberg series [7], which is main physical reason leading to fine structure of the term energy. Up to now, however, no relative experimental data are available in literature. We hope that our theoretical results may stimulate some interest in making higher precision measurements.

Table 1 The transition energies of $1s^2 3d$-$1s^2 nf$ transitions for Sc^{18+} ion

Transitions	This work / cm^{-1}	Experimental [11] / cm^{-1}
$1s^2 3d$-$1s^2 4f$	1 929 669	1 929 600
$1s^2 3d$-$1s^2 5f$	2 821 130	
$1s^2 3d$-$1s^2 6f$	3 305 477	
$1s^2 3d$-$1s^2 7f$	3 597 551	
$1s^2 3d$-$1s^2 8f$	3 787 122	
$1s^2 3d$-$1s^2 9f$	3 917 098	

Table 2 Fine structure splittings of $1s^2 nf$ states for Sc^{18+} ion

States	Relativistic / cm^{-1}	QED corr. / cm^{-1}	Total / cm^{-1}
$1s^2 4f$	991.53	2.30	993.83
$1s^2 5f$	507.63	1.18	508.81
$1s^2 6f$	293.75	0.68	294.43
$1s^2 7f$	184.98	0.43	185.41
$1s^2 8f$	123.92	0.29	124.21
$1s^2 9f$	87.23	0.20	87.43

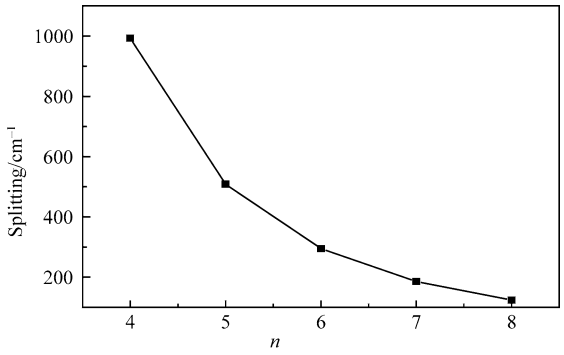

Fig. 1 The fine structure splitting for $1s^2 nf$ states of Sc^{18+} ion

Our obtained expansion coefficients [Eq. (3)] of the quantum defect μ_n for $1s^2 nf$ series of Sc^{18+} ion are given in Table 3. Thus the quantum defect μ_n of this series, as smoothly varying function of energy, is determined. With this μ_n value as input, the ionization potentials of $1s^2 nf$ states of Sc^{18+} ion are recalculated from Eq. (2) by using the iteration procedure mentioned in the previous section. The results are given in the third row marked by "Semiempirical" of Table 4. The comparison of these results with the corresponding results obtained from FCPC method, which is also listed in this table, indicates that the relative discrepancy between them is less than 10^{-4}, and the agreement is much better with the increasing of n. This shows that the quantum defect of $1s^2 nf$ series of Sc^{18+} ion determined above is reliable, and the energies of any highly excited states ($n > 9$) for this Rydberg series of Sc^{18+} ion can be accurately predicted.

Table 3 The coefficients in the expansions of quantum defect for $1s^2 nf$ states

States	μ_0	h_1	h_2
$1s^2 nf$	0.002 478 45	–0.000 257 31	0.000 008 44

Table 4 The comparison of ionization potentials for $1s^2 nf$ states of Sc^{18+} ion obtained from FCPC method and semiempirical method

n	6	7	8	9
FCPC / a.u.	5.016 195	3.685 380	2.821 631	2.229 411
Semiempirical /a.u.	5.016 230	3.685 405	2.821 596	2.229 359

The results of the dipole oscillator strengths for $1s^2 3d$ -$1s^2 nf$ ($4 \leqslant n \leqslant 9$) transitions of Sc^{18+} ion are listed in Table 5. So far as we know, there are no relative experimental data available for the comparison. Even so, we have reason to believe that our results are reliable. As can seen from Table 5, the agreement among our f-values obtained from the length, velocity, and acceleration formulae is up to four digits in most cases. This situation shows that our FCPC wave functions have a reasonable behavior over the whole configuration space for Sc^{18+} ion.

Table 5 The dipole oscillator strengths of $1s^2 3d$-$1s^2 nf$ transitions for Sc^{18+} ion

Transitions	f_L	f_V	f_A
3d-4f	1.065 09	1.064 85	1.075 59
3d-5f	0.164 16	0.164 16	0.164 66
3d-6f	0.057 35	0.057 36	0.057 49
3d-7f	0.027 23	0.027 25	0.027 35
3d-8f	0.027 23	0.015 34	0.015 35
3d-9f	0.009 05	0.009 05	0.009 03

Figure 2 depicts Eq. (4) for the $1s^2 3d$-$1s^2 nf$ dipole transition of Sc^{18+} ion. This figure indicates that the discrete

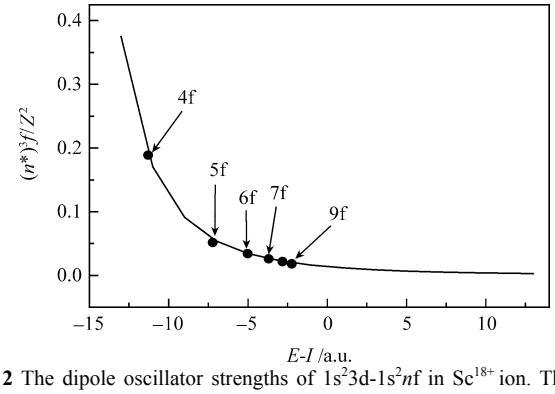

Fig. 2 The dipole oscillator strengths of $1s^2 3d$-$1s^2 nf$ in Sc^{18+} ion. The *full curve* is obtained from Eq. (4), and the *dots* represent the f-values computed from the FCPC method multiplied by factor $(n^*)^3/Z^2$. In Eq. (4), $\mathrm{d}f/\mathrm{d}s|_{s=0} = 0.03872$, and $s = 3.1615$

oscillator strengths calculated from the transition energies and FCPC wave functions in this work follow closely along the curve represented by Eq. (4), and they and the oscillator strength densities corresponding to the bound-free transitions join smoothly across the ionization threshold $E = I$.

4 Summary

In this paper, we have calculated the transition energies and oscillator strengths of $1s^2 3d$-$1s^2 nf$ ($4 \leqslant n \leqslant 9$) transitions for Sc^{18+} ion. The *f*-values of three alternative forms agree well with each other. Our evaluated fine structure splittings of $1s^2 nf$ ($4 \leqslant n \leqslant 9$) states for Sc^{18+} ion follow a well-behaved regularity. The quantum defect of $1s^2 nf$ series for Sc^{18+} ion, as function of energy, has been determined. It has provided a reliable physical basis for predicting the energies of any highly excited states ($n > 9$) below the ionization limit for this Rydberg series of Sc^{18+} ion. By combining our obtained *f*-values with QDT, a reliable theoretical prediction of the dipole oscillator strength from a given initial state $1s^2 3d$ to the $1s^2 nf$ states for Sc^{18+} ion has been extrapolated to the whole energy region including the continuum states. We hope that the results in this paper will provide a reference for the experimental measurements in the future.

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