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Energy and Oscillator Strength of V^{20+} Ion

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Abstract The ionization potentials and fine structure splittings of $1s^2nl$ ($l = s, p,$ and $d; n \leq 9$) states for lithium-like V^{20+} ion are calculated by using the full-core plus correlation (FCPC) method. The quantum defects of these three Rydberg series are determined according to the single-channel quantum defect theory (QDT). The energies of any highly excited states with $n \geq 10$ for these series can be reliably predicted using the quantum defects that are function of energy. The dipole oscillator strengths for the $1s^22s-1s^2np$ and $1s^22p-1s^2nd$ ($n \leq 9$) transitions of V^{20+} ion are calculated with the energies and FCPC wave functions obtained above. Combining the QDT with the discrete oscillator strengths, the discrete oscillator strengths for the transitions from the given initial state to highly excited states ($n \geq 10$) and the oscillator strength density corresponding to the bound-free transitions are obtained.

Keywords V^{20+} ion, ionization potential, quantum defect, oscillator strength

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1 Introduction

Research in the structure and properties of highly ionized atomic systems has recently aroused great interest because the results and data obtained play a dominant role in controlled thermonuclear reactions, where atomic radiation is

the primary energy loss mechanism, in astrophysical study for the knowledge of atomic abundance, and in plasma modeling. However, in the present, the available experimental data in the literature on these ions are far from satisfactory. Thus, reliable theoretical predictions for these important data are obviously of significance.

From a theoretical point of view, the key to solving the many-electron atomic system problems lies in the treatments of electron correlation and relativistic effects. The multiconfiguration Hartree-Fock (MCHF) and multiconfiguration Dirac-Fock (MCDF) methods have been used effectively for a long time. However, these traditional configuration interaction (CI) methods get tangled in the numerical convergence problems in many cases. An elegant and complete variation approach, namely, the full-core plus correlation (FCPC) method, has been developed by Chung [1]. This method has been successfully applied to the atomic systems with a $1s^2$ -core [2–5]. For example, the ionization potentials of the lithium-like ground states from $Z = 3-10$ are predicted to within 1 ppm of the experiment [2].

In this paper, we extend this method to the system with higher nuclear charge and in the higher energy region. The ionization potentials, fine structure splittings of $1s^2nl$ ($l = s, p,$ and $d; n \leq 9$) states, and the dipole oscillator strengths for $1s^22s-1s^2np$ and $1s^22p-1s^2nd$ ($n \leq 9$) transitions for lithium-like V^{20+} ion are calculated. The quantum defects of these three Rydberg series are determined as a function of energy. Combining the calculated results of discrete oscillator strengths with the single-channel quantum defect theory (QDT), the discrete oscillator strengths for the $1s^22s-1s^2np$ and $1s^22p-1s^2nd$ ($n \geq 10$) transitions and the oscillator strength densities corresponding to the bound-free transitions are predicted.

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2 Theoretical method

The details of the FCPC method used in this paper can be found in [1–4]. These presentations will not be repeated here. By using the square-integrated Slater-type basis sets,

the variational wave function of the $1s^2nl$ ($l = s, p,$ and d) state for lithium-like V^{20+} ion is given by

$$\Psi(1, 2, 3) = A \left[\Phi_{1s1s}(1, 2) \sum_i d_i r_3^i e^{-\beta r_3} Y_{l(i)}(3) X(3) + \sum_i C_i \Phi_{n(i),l(i)}(1, 2, 3) \right] \quad (1)$$

where A is an antisymmetrization operator. $\Phi_{1s1s}(1,2)$ is a predetermined $1s^2$ -core wave function, which is used as a single term in the total wave function of the three-electron system, and its expression can be found in [1]. The effect of the valence electron is accounted for by multiplying the core wave function with a linear combination of Slater orbitals for the valence electron. The second term on the right-hand side of Eq. (1) describes the relaxation of the $1s^2$ -core and the other possible correlations in the three-electron system. $\Phi_{n(i),l(i)}$ is the basis set of three-electron system [1–4]. The linear parameters in Eq. (1) are determined by solving the secular equation, and the nonlinear parameters are optimized by minimizing the energy of the system. The explicit expression of non-relativistic Hamiltonian is given in [1–4]. The nonrelativistic energies (upper bounds) E_0 of the $1s^2$ -core and the $1s^2nl$ ($l = s, p,$ and $d; n \leq 9$) states are obtained, and their corresponding FCPC wave functions Ψ are determined in this process. The relativistic effects, including the correction to kinetic energy, Darwin term, the electron–electron contact term, and the orbit–orbit interaction, and mass-polarization effect on the energies are calculated using the first-order perturbation theory. The total energy of the three-electron system is given by

$$E_{\text{tot}} = E_0 + \langle \Psi | H' | \Psi \rangle = E_0 + \Delta E \quad (2)$$

The explicit expressions of these operators are given in [1–4]; they will not be repeated here. To obtain a more accurate result for the larger Z system, the quantum-electrodynamics (QED) correction should be included. We assume that the QED effects of the core cancel out in the ionization potential (IP). Thus, this correction to energy can be evaluated for the valence electron by using a hydrogenic formula [6] with an effective nuclear charge. It can be shown [1–4] that this correction consists of two terms that cause a shift of the center of gravity for $1s^2nl$ configuration energy and a correction to the fine structure splitting of the 2L ($L = P$ or D) systems, respectively. Their explicit expressions can be found in [1–4,6].

The IPs for the $1s^2nl$ states of the V^{20+} ion are obtained from the difference between the energies of three-electron system and of the ion core:

$$IP(1s^2nl) = E_{\text{tot}}(1s^21S) - E_{\text{tot}}(1s^2nl^2L) - \Delta E_{\text{QED}}^g(nl) \quad (3)$$

The last term on the right-hand side of Eq. (3) is the correction to the center of gravity for the $1s^2nl$ configuration energy from the QED effect.

For the $1s^2nl$ ($l = p$ and d) states, the fine structure splittings mainly come from the spin–orbit and spin–other–orbit interactions. To calculate the splitting, the LSJ-coupling scheme is used, and the result is given by the summation of the expectation values of H_{SO} and H_{SOO} and the QED contribution to the splitting, namely,

$$\Delta E_{FS}^J = \langle LSJM_J | H_{\text{SO}} + H_{\text{SOO}} | LSJM_J \rangle + \Delta E_{\text{QED}}^J(nl) \quad (4)$$

where the expressions of operators H_{SO} and H_{SOO} can be found from [1–4].

According to the single channel QDT [7–9], the quantum defect μ_n of $1s^2nl$ state is defined by

$$E_n = -\frac{Z^2}{2(n - \mu_n)^2} \text{(in a.u.)} \quad (5)$$

where n is the principal quantum number and E_n is the term energy obtained above for $n \leq 9$. For highly excited states, quantum defect, μ_n , should be a smooth function of energy,

Table 1 The ionization potential of $1s^2ns$, $1s^2np$, and $1s^2nd$ states for V^{+20} ion

States	IP		Experimental (cm^{-1}) [11]
	a.u.	cm^{-1}	
$1s^22s$	57.657 856 93	12 654 301	12 660 000
$1s^23s$	25.243 174 47	5 540 177	5 545 600
$1s^24s$	14.095 191 73	3 093 504	
$1s^25s$	8.981 125 88	1 971 108	
$1s^26s$	6.218 460 75	1 364 780	
$1s^27s$	4.558 965 77	1 000 567	
$1s^28s$	3.484 870 24	764 832	
$1s^29s$	2.750 177 40	603 588	
$1s^22p$	55.877 256 04	12 263 509	12 269 163
$1s^23p$	24.745 084 21	5 430 860	5 435 333
$1s^24p$	13.888 454 47	3 048 130	3 057 000
$1s^25p$	8.876 940 99	1 948 242	1 967 000
$1s^26p$	6.158 502 64	1 351 620	1 352 000
$1s^27p$	4.521 353 53	992 312	1 000 000
$1s^28p$	3.459 752 19	759 320	
$1s^29p$	2.732 446 72	599 696	
$1s^23d$	24.529 217 66	5 383 483	5 386 940
$1s^24d$	13.799 517 47	3 028 612	3 030 520
$1s^25d$	8.831 108 59	1 938 183	1 939 000
$1s^26d$	6.132 090 45	1 345 824	1 345 000
$1s^27d$	4.504 754 37	988 669	985 000
$1s^28d$	3.448 643 27	756 882	754 000
$1s^29d$	2.724 647 44	597 985	

Table 2 Fine structure splittings of $1s^2nl$ ($l = p, d$) states for V^{+20} ion

States	This work/cm ⁻¹	Experiment [11]/cm ⁻¹
1s ² 2p	74 338	75 550
1s ² 3p	21 964	22 000
1s ² 4p	9 258	
1s ² 5p	4 732	
1s ² 6p	2 737	
1s ² 7p	1 722	
1s ² 8p	1 537	
1s ² 9p	810	
1s ² 3d	7 022	6 600
1s ² 4d	2 960	3 800
1s ² 5d	1 515	
1s ² 6d	877	
1s ² 7d	552	
1s ² 8d	370	
1s ² 9d	260	

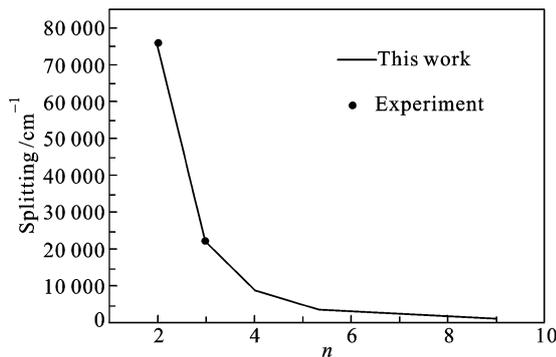
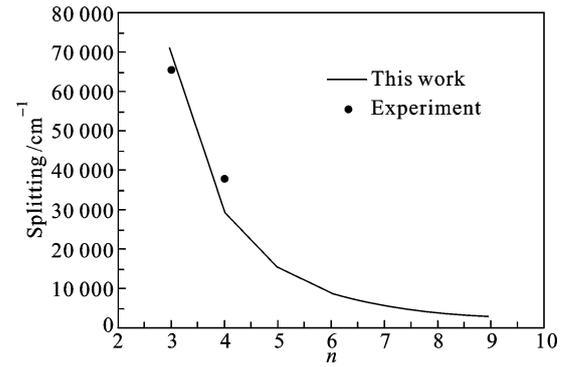
and hence, it can be approximated in terms of a weakly varying function of energy in following form

$$\mu_n = \mu_0 + h_1 E + h_2 E^2 \quad (6)$$

The coefficients μ_0 , h_1 , and h_2 for each Rydberg series are determined by using the μ_n values obtained from Eq. (5). Treating Eqs. (5) and (6) as a set of equations for E_n and μ_n , the quantum defect, μ_n , and term energy, E_n , for highly excited states ($n \geq 10$) are determined by an iteration method. Firstly, we set $\mu_n \approx \mu_0$ and put it into Eq. (5). Then, E_n and μ_n can be refined by iteration procedure. Finally, the quantum defect, μ_n , and the term energy, E_n , are obtained.

It can be shown that the dipole oscillator strength is given by any of the following three forms [7]:

$$\begin{aligned} f_L &= \frac{2}{3} (E_j - E_i) |\langle \Psi_i | \mathbf{r} | \Psi_j \rangle|^2 \\ f_V &= \frac{2}{3} (E_j - E_i)^{-1} |\langle \Psi_i | \nabla | \Psi_j \rangle|^2 \\ f_A &= \frac{2}{3} (E_j - E_i)^{-3} |\langle \Psi_i | \frac{\mathbf{r}}{r^3} | \Psi_j \rangle|^2 \end{aligned} \quad (7)$$

**Fig. 1** Fine structure of $1s^2np$ states for V^{+20} ion. Experiment data are taken from [11]**Fig. 2** Fine structure of $1s^2nd$ states for V^{+20} ion. Experiment data are taken from [11]

Here, $(E_j - E_i)$ is the transition energy. Ψ_i and Ψ_j are the wave functions of the initial and final states, respectively. These three alternatives are called the length, velocity, and acceleration forms, respectively. They should be calculated by summing over the final states and averaging over the initial states.

As is known, the oscillator strength densities corresponding to the final states in the continuum are associated with the discrete oscillator strengths corresponding to the bound-bound transitions. We can define the oscillator strength densities of the bound-bound transition as

$$\tau(E) = \frac{(n^*)^3}{Z^2} f_{ij} \text{ (in a.u.)} \quad (8)$$

where Z is the charge of the ion core, E is the energy of the final state, and f_{ij} is the discrete oscillator strength. The effective principal quantum number of the final state, n^* , which is given by

$$n^* = n - \mu_n \quad (9)$$

According to QDT, 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 the given initial state to any discrete states in the channel and the bound-continuum from the same initial state to the continuum states in the channel can be treated in unified form. In the limit $E \rightarrow I$ (from below), where I is the ionization potential of the system, $\tau(E)$, as a

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

States	μ_0	h_1	h_2
1s ² ns	0.045 507 02	-0.000 062 64	0.000 000 89
1s ² np	0.016 286 42	-0.000 061 79	0.000 000 22
1s ² nd	0.004 197 75	-0.000 130 17	0.000 001 31

Table 4 The comparison of ionization potentials for $1s^2nl$ states obtained from the FCPC method and semiempirical method for V^{+20} ion^a

Number	$1s^2ns$		$1s^2np$		$1s^2nd$	
	FCPC	Semiempirical	FCPC	Semiempirical	FCPC	Semiempirical
6	6.218 461	6.218 236	6.158 503	6.157 621	6.132 090	6.132 047
7	4.558 966	4.558 734	4.521 353	4.520 657	4.504 754	4.504 681
8	3.484 870	3.484 664	3.459 752	3.459 200	3.448 643	3.448 557
9	2.750 177	2.749 860	2.732 447	2.732 000	2.724 647	2.724 555

^aIn a.u.

function of E , will match the oscillator strength densities, $df/d\varepsilon$ of continuum states, namely

$$\tau(E) = \frac{(n^*)^3}{Z^2} f_{ij} = \frac{df}{d\varepsilon} \quad (10)$$

For the $1s^22s-1s^2np$ and $1s^22p-1s^2nd$ transitions of V^{20+} ion under consideration, neither the Cooper minimum nor the following maximum is found in the near-threshold energy region. Hence, Eq. (10) can be used to extrapolate the discrete oscillator strength, f_{ij} , below the threshold to the discrete oscillator strength densities, $df/d\varepsilon$, above the threshold. In the near-threshold region ($|E| \leq I/2$), the oscillator strength and the oscillator strength densities can be accurately approximated by [10]

$$\tau(E) = \frac{(n^*)^3}{Z^2} f_{ij} = \frac{df}{d\varepsilon} = \left(\frac{E_i}{E_i - E_j} \right)^s \frac{df}{d\varepsilon} \Big|_{\varepsilon=0} \quad (11)$$

where E_i and E_j are the energies of the initial state and final state, respectively; s is a coefficient to be determined; and $df/d\varepsilon|_{\varepsilon=0}$ is the oscillator strength density at the threshold. Equations (8) and (11) make it possible to determine the oscillator strengths easily for transition from a certain initial state to all possible final states, including the discrete and continuum states, of the Rydberg series.

Table 5 The oscillator strengths of dipole transitions $1s^22s-1s^2np$ ($n \leq 9$) and $1s^22p-1s^2nd$ ($n \leq 9$) for V^{+20} ion

Transitions	f_L	f_V	f_A	Experimental [12]
2s-2p	0.059 43	0.059 43	0.068 30	0.062
2s-3p	0.379 25	0.379 21	0.379 60	0.372
2s-4p	0.094 36	0.094 35	0.094 34	0.099
2s-5p	0.039 14	0.039 15	0.039 12	0.040
2s-6p	0.020 35	0.020 35	0.020 34	0.021 2
2s-7p	0.012 04	0.012 04	0.012 03	0.012 4
2s-8p	0.007 75	0.007 75	0.007 75	
2s-9p	0.005 30	0.005 30	0.005 29	
2p-3d	0.680 94	0.680 73	0.682 18	0.68
2p-4d	0.122 09	0.122 09	0.121 84	0.12
2p-5d	0.044 83	0.044 84	0.044 80	0.045 0
2p-6d	0.021 94	0.021 94	0.021 97	0.022 0
2p-7d	0.012 53	0.012 54	0.012 52	0.012 6
2p-8d	0.007 89	0.007 90	0.007 89	
2p-9d	0.005 32	0.005 32	0.005 31	

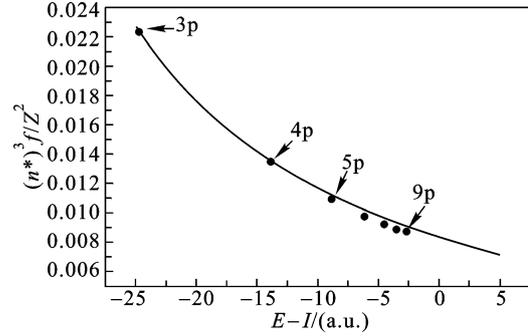


Fig. 3 The oscillator strengths of $1s^22s-1s^2np$ in V^{+20} ion. The full curve is obtained from Eqs. (8) and (11), and the dots represent the values computed from Eq. (8). The discrete oscillator strengths are multiplied by a respective factor $(n^*)^3/Z^2$. The continuous oscillator strength density above the threshold is $df/d\varepsilon$

3 Results and discussion

For the $1s^2$ -core wave function, we used 222 terms in seven l components. To calculate the $1s^2nl$ energy, we used eight d_i terms. The number of terms in $\Phi_{n(i),l(i)}$ ranges from about 900 to 1000 terms. Numerical calculations of energies converge rather fast.

Our calculated results of the IPs for the $1s^2nl$ ($l = s, p, d$; $n \leq 9$) states of the V^{20+} ion and the experimental data available in the literature [11] are listed in Table 1. It is noted that the uncertainties quoted in these experiments are about $10^3-10^4 \text{ cm}^{-1}$ in most cases. To sum up the comparison between our predicted IPs for these states for the V^{20+} ion and the available experimental data, we found that our results agree well with the experimental data. We hope

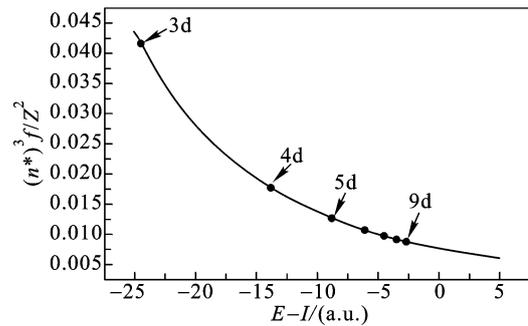


Fig. 4 The oscillator strength density of $1s^22s-1s^2nd$ in V^{+20} ion. The full curve is obtained from Eqs. (8) and (11), and the dots represent the values computed from Eq. (8). The discrete oscillator strengths are multiplied by a respective factor $(n^*)^3/Z^2$. The continuous oscillator strength density above the threshold is $df/d\varepsilon$

that our theoretical results will stimulate some interest in making higher precision experimental measurements.

According to Eq. (4), our obtained fine structure splittings for the $1s^2np$ and $1s^2nd$ ($n \leq 9$) states of V^{20+} ion are listed in Table 2. Their variations with principal quantum number n are shown in Figs. 1 and 2. It evident from Table 2 that the error bar in the experimental data available in the literature [11] is quite large, and even in many cases, we are not aware of any experimental results for comparison with theory. Figures 1 and 2 show that, with the increase in n , our results of the splittings for the $1s^2np$ and $1s^2nd$ ($n \leq 9$) states of the V^{20+} ion follow a well-behaved variation regularity of spin-orbit interaction with n , which is main physical reason leading to fine structure splitting, along a Rydberg series [7].

In accordance to the procedure of determining quantum defect, given in the previous section, our obtained expansion coefficients in Eq. (6) are given in Table 3. Thus, the quantum defects, μ_n , of these three series, $1s^2ns$, $1s^2np$, and $1s^2nd$, of the V^{20+} ion, as smoothly varying functions of energy, are determined. With these μ_n values as input, the IPs of the $1s^2nl$ ($l = s, p, d; n \leq 9$) states for V^{20+} ion are calculated by using the iteration method described in the previous section. The results are given in the columns marked by ‘‘Semiempirical’’ in Table 4. Corresponding results obtained from the FCPC method are also listed in this table for comparison. It is seen that the agreement between them is quite good, and relative discrepancy is less than 10^{-4} . We have reason to believe that the quantum defects of these three series for the V^{20+} ion determined in this work are reliable, and the energies of any discrete states ($n \geq 10$) of these series for the V^{20+} ion below the ionization limit can be accurately predicted using their quantum defects, μ_n , as input.

The three forms of the dipole oscillator strength given in Eq. (7) are equivalent when exact wave functions 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, whether the f values obtained from the three formulae are in agreement with each other is a rigorous evaluation of the quality of the wave functions for the initial and final states used in the calculation.

The calculated results of the oscillator strengths for the $1s^22s-1s^2np$ ($2 \leq n \leq 9$) and $1s^22p-1s^2nd$ ($3 \leq n \leq 9$) transitions of V^{20+} ion are given in Table 5. The experimental data [12] available in the literature are also listed in the table. As can be seen from this table, the agreement between our f values obtained from the length, velocity, and acceleration formulae is up to four digits in most cases, and the agreement of our calculated results with experimental data is also fairly satisfactory. The results for the oscillator strengths in this work show that our FCPC wave functions have a reasonable behavior over the whole configuration space of V^{20+} ion.

The oscillator strengths for transitions from a certain initial state to all states for the Rydberg series are determined using Eqs. (8) and (11). Figures 3 and 4 depict

Eq. (11) corresponding to the $1s^22s-1s^2np$ and $1s^22p-1s^2nd$ transitions of V^{20+} ion, respectively. For $1s^22s-1s^2np$ ($2 \leq n \leq 9$) transitions, $df/d\varepsilon|_{\varepsilon=0} = 0.00828$, and $s = 1.77$. For $1s^22p-1s^2nd$ ($3 \leq n \leq 9$) transitions, $df/d\varepsilon|_{\varepsilon=0} = 0.00775$ and $s = 2.91$. It is shown that the discrete oscillator strengths calculated from the transition energies and FCPC wave functions obtained above lie rather well along the curves expressed by Eq. (11), and these discrete oscillator strengths and the oscillator strength densities corresponding to the bound-free transitions join smoothly across the ionization threshold $E = I$. Thus, reliable theoretical predictions of dipole oscillator strengths for V^{20+} ion have been extrapolated to the whole energy region.

4 Conclusion

In this paper, we have calculated the structure and spectral property in the whole energy region, from discrete states to continuum states, for the V^{20+} ion by combining the FCPC method with QDT. The comparisons of the IPs of the $1s^2nl$ ($n \leq 9$) states for V^{20+} ion that we obtained and the experimental data available in the literature indicate that our results should be reliable. Our evaluated fine structure splittings of $1s^2np$ and $1s^2nd$ ($n \leq 9$) states for V^{20+} ion follow a well-behaved regularity. By using our determined quantum defects, as function of energy, the energies of any highly excited states ($n \geq 10$) of these series for V^{20+} ion below the ionization limit can be accurately predicted. The agreement between the values of oscillator strength obtained from the length, velocity, and acceleration formulae shows that our FCPC wave functions should be accurate in the whole configuration space and that the predicted f values should also be accurate. Combining the f values with QDT, we have obtained reliable and accurate oscillator strengths for dipole transitions from the given initial states to all possible states, including the oscillator strength densities corresponding to bound-free transitions. The results of this paper will provide valuable reference for other research in the future.

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