

## Introduction

Atomic structure and spectroscopic properties of the neutral and ionized vanadium is of great interest to several fields of applied and fundamental science

### Practical needs:

- astrophysics
- industrial devices
- plasma physics
- controlled thermonuclear fusion
- laser development

### Fundamental problems:

- term-dependence of orbitals
- electronic correlations
- orbital relaxation
- spectroscopic data for weak lines
- new theoretical models

## General information

### Vanadium:

transitional metal with open  $d$ -shell

$Z = 23$

$V_I: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2 4F$

$E_{ion} = 6.746 \text{ eV}$

$V_{II}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 5D$

$E'_{ion} = 14.634 \text{ eV}$

## Electronic structure

### Principal electronic configurations according to $LS$ approximation

In scope of  $LS$ -coupling scheme, most observed energy levels of excited states of singly ionized vanadium  $V_{II}$  can be classified as  $3d^3(^M L)nl$  and  $3d^2(^M L)4snl$  configurations with different ancestral terms ( $^M L$ ). Such complex electronic structure of vanadium atomic system leads to high number of  $LS$  terms.

Table 1. Number of terms for principal electronic configurations of  $V_{II}$  states

Configuration	Terms	Number of terms
$3d^4$	$1S^3P^1.3.5D^1.3FG^3H^1I$	11 (15)
$3d^3 4s$	$1.3.5P^1.3D^1.3.5F^1.3GH$	12 (16)
$3d^3 4p$	$1.3.5SPDFG^1.3HI^o$	19 (49)
$3d^2 4s^2$	$3P^1D^3F^1G$	4
$3d^2 4s 4p$	$1.3S^3.5P^1.3.5D^1.3.5G^3H^o$	13 (25)
...		

Note: number in parentheses indicates number of terms with same  $LS$  but different ancestral terms

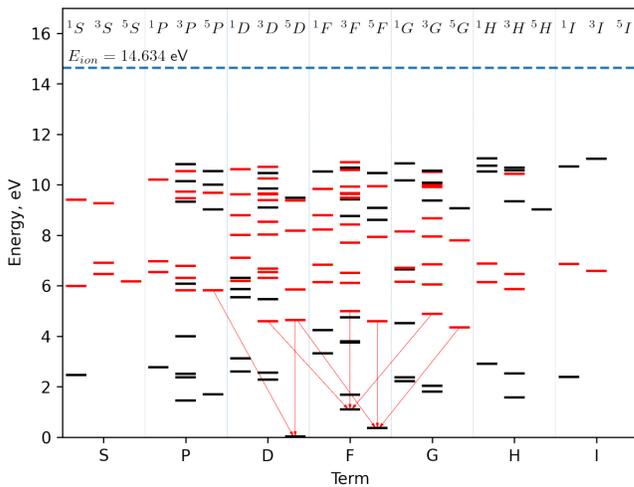


Figure 1. Energy levels and main transitions. Energy levels diagram of vanadium ion according to the NIST data [1]. The energies for multiplets are averaged over the fine structure levels. Black dashes correspond to even terms, red dashes – odd terms. Arrows indicate the main allowed transitions between the levels. The levels are grouped according to the total orbital angular momentum  $L$  and the multiplicity  $2S + 1$  of the terms in the  $LS$  coupling approximation.

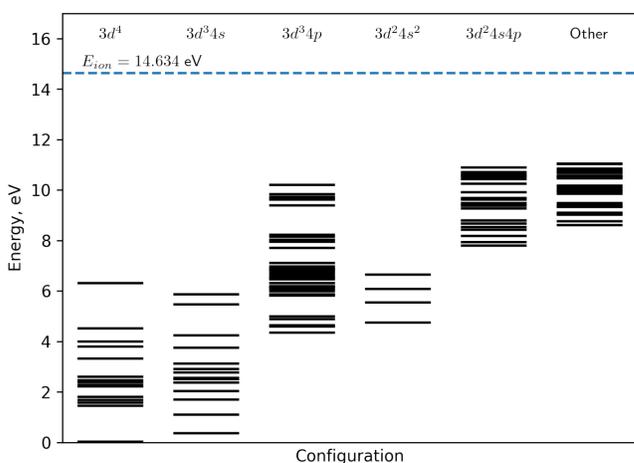


Figure 2. Energy levels diagram of vanadium ion according to the NIST data [1]. The energies for multiplets are averaged over the fine structure levels. The levels are grouped according to the electronic configuration of the atomic states in the  $LS$  coupling approximation.

## Theoretical methods

In most cases, the theoretical study of spectroscopic properties requires knowledge of wave functions. Multi-configuration Hartree-Fock (MCHF) method combined with configuration interaction (CI) methods are a method of choice for complex atoms where atomic state functions are expanded in a basis of configuration state functions [2].

Schrodinger equation:

$$H\Psi = E\Psi$$

Multi-configuration expansion:

$$\Psi(\gamma LS) = \sum_i c_i \Phi(\gamma_i LS), \quad \sum_i c_i^2 = 1$$

$\Psi$  – atomic state function (ASF),  $\Phi$  – configuration state function (CSF)

Configuration interaction method:

$$Hc = Ec$$

Hamiltonian matrix elements:

$$H_{ij} = \langle \Phi(\gamma_i LS) | H | \Phi(\gamma_j LS) \rangle$$

Hartree-Fock method:

$$\Phi(\gamma L S M_L M_S) = \sum_i c_i |u_1^i u_2^i \dots u_N^i\rangle$$

where  $|u_1 \dots u_N\rangle$  – Slater determinants

$$|u_1 \dots u_N\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \langle t_1 | u_1 \rangle & \dots & \langle t_1 | u_N \rangle \\ \vdots & \ddots & \vdots \\ \langle t_N | u_1 \rangle & \dots & \langle t_N | u_N \rangle \end{vmatrix}$$

$t = (\mathbf{r}, \sigma)$  – stands for position and spin of the individual electron, and  $u$  stands for the one-electron orbital  $|u\rangle = |nlm\mu\rangle$

## Computational details

To calculate the wave functions of the ground and lower excited states of vanadium ion  $V_{II}$  we employed multi-configuration Hartree-Fock method (MCHF) [3] together with configuration interaction (CI) approach with non-orthogonal orbitals and  $B$ -splines as basis functions [4, 5]. This approach allows to take into account the term-dependence of valence orbitals, the effects of correlation and relaxation.

Spectroscopic orbitals of deep core  $1s$ ,  $2s$ , and  $2p$  were calculated for the ground state of neutral vanadium  $3d^3 4s^2 4F$  using Hartree-Fock (HF) method.

Valence orbitals  $3s$ ,  $3p$ ,  $3d$ ,  $4s$  and  $4p$  were calculated separately for different configurations. They were obtained from term-average HF-calculations for each of the principal electronic configurations under consideration:  $3d^4$ ,  $3d^3 4s$ ,  $3d^3 4p$  and  $3d^2 4s^2$ .

After that, the spectroscopic orbitals mentioned above were supplemented by sets of correlation orbitals  $4l$  and  $5l$  ( $l = 0-4$ ). The correlation orbitals were obtained in separate MCHF calculations for one of the terms for each of the selected configurations. Subsequently, the obtained sets of the correlation orbitals were used in the calculations of all other terms with the same configuration. In the calculations of each of the sets of correlation orbitals, one- and two-electron excitations from the outer shells were included in the multi-configuration expansions.

$$\Psi(3d^2 n l n' l' LS) = \sum_i c_i \Phi(3d^2 \bar{n} \bar{l} \bar{n}' \bar{l}' LS)$$

where  $\bar{n} \bar{l} \bar{n}' \bar{l}'$  denotes all possible one- and two-electron promotions (for both spectroscopic and correlation orbitals)

The configurations with the mixing coefficients less than 0.001 were excluded from the final CI-expansions.

## References

- [1] Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2022). NIST Atomic Spectra Database (ver. 5.10). Available: <https://physics.nist.gov/asd>
- [2] C. Froese Fischer et al 2016 J. Phys. B. **49** 182004; doi:10.1088/0953-4075/49/18/182004
- [3] C. Froese Fischer et al 2007 Comput. Phys. Commun. **176** 8, 559-579; doi:10.1016/j.cpc.2007.01.006
- [4] O. Zatsarinny and C. Froese Fischer 2000 Phys. Commun. **124** 2-3, 247-289; doi:10.1016/S0010-4655(99)00441-5
- [5] O. Zatsarinny and C. Froese Fischer 2009 Comput. Phys. Commun. **180** 11, 2041-2065; doi:10.1016/j.cpc.2009.06.007

## Further improvement

- Additional research for states with  $3d^3 4s$  configuration
- Finetune energies using different cut-off parameters for CI-expansions
- Quasi-relativistic CI-calculations with Breit-Pauli Hamiltonian and  $J$ -dependent ASF

$$H_{BP} = H_{NR} + H_{RS} + H_{FS}$$

$$\Psi^{\beta J \pi} = \sum_{\alpha LS} C(\beta J \pi; \alpha LS \pi) \Phi^{\alpha LS \pi}$$

$\Phi^{\alpha LS \pi}$  – multiconfigurational expansions from the  $LS$  calculations

$C(\beta J \pi; \alpha LS \pi)$  – spin-orbit mixing of different  $LS$  terms

## Results

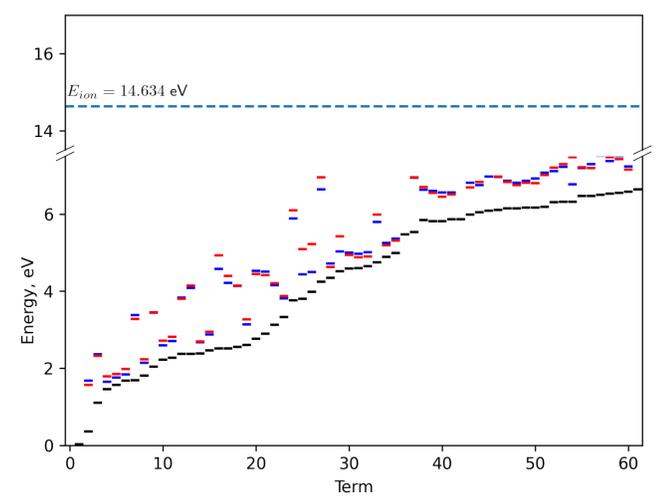


Figure 3. Comparison of excitation energies. Black dashes – experimental energies [1]; blue dashes – present calculations, full CI-expansion; red dashes – present calculations, CI-expansion with the mixing coefficients  $> 0.001$ .

Table 2. Excitation energies of the lower states of vanadium ion.

N	Config.	Term	$E_{ex}$ NIST, eV	$E_{ex}$ MCHF, eV	$\Delta E_{ex}$ , eV	$N_{conf}$
1	$3d^4$	$5D$	0.026	0		55 (94)
2	$3d^3(^4F)4s$	$3F$	0.363	1.676	1.313	51 (103)
3	$3d^3(^4F)4s$	$3F$	1.104	2.358	1.254	186 (356)
4	$3d^4$	$3P^2$	1.452	1.651	0.199	140 (239)
5	$3d^4$	$3H$	1.566	1.758	0.192	134 (252)
6	$3d^4$	$3F^2$	1.681	1.839	0.158	191 (356)
7	$3d^3(^4P)4s$	$3P$	1.692	3.381	1.689	40 (70)
8	$3d^4$	$3G$	1.807	2.138	0.331	139 (302)
9	$3d^3(^3G)4s$	$3G$	2.039	3.452	1.413	180 (302)
10	$3d^4$	$3G^2$	2.221	2.594	0.374	146 (239)
...						
60	$3d^3(^2H)4p$	$3P^o$	6.585	7.24	0.655	79 (174)
61	$3d^2 4s^2$	$3G$	6.646	7.656	1.01	130 (239)
62	$3d^3(^2D)4p$	$3D^o$	6.679	7.761	1.082	139 (322)

Table 3. Dependence of the deviation of the excitation energies on the number of configurations included in the CI-expansion.

Config.		MCHF			MCHF 0.001			MCHF 0.01		
		$\Delta E_{ex}$ , eV	$\frac{\Delta E_{ex}}{E_{ex}}$ , %	$N_{conf}$	$\Delta E_{ex}$ , eV	$\frac{\Delta E_{ex}}{E_{ex}}$ , %	$N_{conf}$	$\Delta E_{ex}$ , eV	$\frac{\Delta E_{ex}}{E_{ex}}$ , %	$N_{conf}$
$3d^4$	min	0.155	7	78	0.158	7	55	0.279	13	15
	max	0.539	21	356	0.634	21	191	1.289	34	38
	median	0.409	14	239	0.413	14	140	0.490	21	30
$3d^3 4s$	min	1.029	33	70	1.029	33	40	1.082	35	10
	max	2.570	362	356	2.606	362	199	2.782	332	44
	median	1.655	63	240	1.695	63	183	1.638	63	33
$3d^3 4p$	min	0.357	7	34	0.359	7	30	0.253	5	14
	max	0.960	15	348	1.082	16	143	1.126	17	34
	median	0.740	12	220	0.747	12	110	0.706	11	28
$3d^2 4s^2$	min	0.463	10	239	0.891	15	130	1.101	17	29
	max	1.395	25	356	1.405	25	175	1.461	26	41
	median	0.807	13	240	1.032	19	164	1.330	25	35
Total	min	0.155	7	34	0.158	7	30	0.253	5	10
	max	2.570	362	356	2.606	362	199	2.782	332	44
	median	0.751	14	239	0.785	14	138	0.863	18	30

Table 4. Correlation configurations and their mixing coefficients for the primary configurations of vanadium ion.

Primary config.	Correlation config.	Mixing coeff.	Primary config.	Correlation config.	Mixing coeff.
$3d^4$	$3d^2 4d^2$	0.073	$3d^2 4s^2$	$3d^3 4s$	0.433
	$3d^2 4d^2$	0.051		$3d^4$	0.423
	$3d^2 4d^2$	0.049		$3d^3 4d$	0.151
	$3d^2 4d$	0.040		$3d^3 4d$	0.089
	$3d^2 4d^2$	0.036		$3d^3 4d$	0.085
	$3d^2 4f^2$	0.035		$3d^2 4s 4d$	0.081
	$3d^2 4f^2$	0.032		$3d^3 4d$	0.073
	$3d^2 4f^2$	0.030		$3d^3 4d$	0.068
	$3d^2 4p^2$	0.023		$3d^3 4d$	0.068
	$3d^2 4p^2$	0.022		$3d^2 4s 4d$	0.066
$3d^3 4s$	$3d^2 4p 4f$	0.041	$3d^3 4s$	0.059	
	$3d^3 5s$	0.035	$3d^2 4s 4d$	0.051	
	$3d^2 4d 5s$	0.033	$3d^4$	0.047	
	$3d^2 4p 4f$	0.032	$3d^2 4p^2$	0.037	
	$3d^2 4s 4d$	0.021	$3d^2 4s 4d$	0.032	
	$3d^3 5s$	0.021	$3d^3 5s$	0.032	
$3d^3 4p$	$3d^3 5p$	0.060	$3d^2 4p^2$	0.032	
	$3d^2 4d 5p$	0.038	$3d^2 5d$	0.027	
	$3d^2 4s 4f$	0.033	$3d^3 4d$	0.023	
	$3d^2 4d 4f$	0.028	$3d^2 4s 4d$	0.023	
	$3d^2 4d 5p$	0.024	$3d^2 4p 4f$	0.023	
	$3d^2 4s 4p$	0.021			
$3d^2 4s 4f$	0.021				

## Conclusions

- The wave functions of the ground and 61 excited states of the singly ionized vanadium were calculated in scope of non-relativistic  $LS$  approximation using the MCHF method and CI approach
- The calculated values of the excitation energies are in satisfactory agreement with the available experimental data
- For the multi-configuration expansions for each of four types of electronic configurations under considerations ( $3d^4$ ,  $3d^3 4s$ ,  $3d^3 4p$ , and  $3d^2 4s^2$ ) the main correlation contributions were investigated
- Obtained sets of the wave functions can be used in further calculations of
  - radiative parameters of  $V_{II}$ -lines
  - low-energy electron scattering by vanadium ion
  - wave functions of  $V_I$  using BSR method
  - photoionization processes