Ab initio calculations of forbidden transition amplitudes and lifetimes of the low-lying states in V^{4+}

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We report electric quadrupole ($E2$) and magnetic dipole ($M1$) transition amplitudes of the first few low-lying states of quadruply ionized vanadium (V^{4+}), which are important in various experimental applications and astrophysics. To our knowledge, most of these presented results are determined for the first time in the literature. A relativistic multireference Fock-space coupled-cluster theory with single (S), double (D), and partial triple (T) excitations is employed to compute the forbidden transition probabilities and lifetimes of the low-lying states in V^{4+}. Estimations of different correlation effects arising through the above formalism have been highlighted by investigating core and valence electron excitations. A long lifetime is found for the first excited $3d\,^2D_{5/2}$ state, which suggests that V^{4+} may be one of the useful candidates for many important studies.

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I. INTRODUCTION

Electromagnetic forbidden transitions, especially for lighter neutral systems and their isoelectronic companions, are of immense importance in atomic experiments due to precise use of metastable states [1]. Forbidden transitions, which have relatively longer wavelengths compared to normal allowed transitions provide information about the thermal Doppler effects in many physical systems [2]. Different astronomical features have only been possible to observe due to these transitions in infrared and radio wavelengths. Optical forbidden transitions of these kinds of V^{4+} have dominant signatures in planetary nebulae and the aurora [3]. Similar transitions have been identified with the so-called coronal lines emitted by the sun [4]. Under certain circumstances, which prevail in astrophysics and low density laboratory Tokamak plasmas, electric quadrupole ($E2$) and magnetic dipole ($M1$) transition lines gain intensity. This phenomena can be used to infer information about plasma temperature and their dynamics [5]. The intensities of these transitions allow us to measure the concentration of impurity ions in Tokamak, which originate in the high temperature interior of the discharge [5]. From a many-body point of view, the importance of these results lies in the estimation of the accuracy of the electronic wave function throughout the radial extent of the atomic systems. This accuracy is estimated from the agreement between computed and experimental values of different atomic properties [6]. Also, the computed results are only the mean of estimations for many of these transitions wherever experimental measurements are difficult.

Here, we report calculated wavelengths and transition amplitudes of V^{4+} involving E2 and M1 radiative transitions. These transitions are also important in plasma research and can be used in many experiments in atomic and solid state physics [7–9]. The study of forbidden transitions between the fine structure states of the low-lying d states needs special attention. They play an important role in the doping of impurity in the Al_2O_3 crystal, which can be used to study high-frequency acoustic phonon in crystals [10]. It is also a good candidate to study electron spin resonance [11] and electron paramagnetic resonance [12] in quartz material. The detailed knowledge of the resonant core relaxation process of V^{4+} [13] needs accurate results of energy levels of this ion and transition amplitudes among them.

In this work, we employ the multireference (MR) Fock-space coupled-cluster (FSCC) method with single (S), double (D), and partial triple (T) excitations to compute forbidden transitions in V^{4+} using relativistic orbitals and/or spinors. The coupled-cluster (CC) theory is nonperturbative in nature and its relativistic extension has been successfully employed earlier in many sophisticated problems [14,15] to estimate various tiny effects precisely. In the present work, we investigate the core and valence electrons correlation contributions obtained from the MR-FSCCSD(T) method to the $M1$ and $E2$ transitions among the low-lying states in the considered system.

II. THEORY

A. Multireference Fock-space coupled-cluster (MR-FSCC) theory for one electron attachment process

A relativistic extension of multireference Fock-space coupled-cluster (MR-FSCC) theory is based on the no-virtual-pair approximation (NVPA) along with appropriate modification of orbital form and potential terms [16]. Relativistic CC theory begins with Dirac-Coulomb Hamiltonian (H) for an N electron atom, which is expressed as

$$H = \sum_{i=1}^{N} [c\vec{\alpha}_i \cdot \vec{p}_i + \beta mc^2 + V_{\mathrm{Nuc}}(r_i)] + \sum_{i<j}^{N} \frac{e^2}{r_{ij}}, \qquad (2.1)$$

with all the standard notations often used. The normal ordered form of the above Hamiltonian is given by

$$\mathcal{H} = H - \langle\Phi|H|\Phi\rangle = H - E_{\mathrm{DF}}$$
$$= \sum_{ij} \langle i|f|j\rangle\{a_i^\dagger a_j\} + \frac{1}{4}\sum_{i,j,k,l} \langle ij||kl\rangle\{a_i^\dagger a_j^\dagger a_l a_k\}, \quad (2.2)$$

where

$$\langle ij||kl\rangle = \langle ij|\frac{1}{r_{12}}|kl\rangle - \langle ij|\frac{1}{r_{12}}|lk\rangle. \quad (2.3)$$

Here E_{DF} is the Dirac-Fock energy, f is the one-electron Fock operator, a_i ($a_i^\dagger$) is the annihilation (creation) operator (with respect to the Dirac-Fock state as the vacuum) for the ith electron and $\{\cdots\}$ denotes the normal ordering of the creation and annihilation operators.

Since the MR-FSCC theory has been described elsewhere [17–20], we provide a brief review of this method. The MR-FSCC theory is based on the concept of the common vacuum for both the N and $N\pm m$ electron systems, which allows us to formulate a direct method for energy differences. In this method the holes and particles are defined with respect to the common vacuum for both the N and $N\pm m$ electron systems. The model space of a (m,n) Fock space contains determinants with m holes and n particles distributed within a set of what are termed as *active* orbitals. For example, in this present paper, we are dealing with a (0,1) Fock space, which is a complete model space (CMS) by construction and is given by

$$|\Psi_\mu^{(0,1)}\rangle = \sum_i C_{i\mu}|\Phi_i^{(0,1)}\rangle, \quad (2.4)$$

where $C_{i\mu}$'s are the coefficients of $\Psi_\mu^{(0,1)}$ and $\Phi_i^{(0,1)}$'s are the model space configurations. The dynamical electron correlation effects are introduced through the *valence-universal* wave-operator Ω [17,18],

$$\Omega = \{\exp(\tilde{S})\}, \quad (2.5)$$

where

$$\tilde{S} = \sum_{k=0}^{m}\sum_{l=0}^{n} S^{(k,l)} = S^{(0,0)} + S^{(0,1)} + S^{(1,0)} + \cdots. \quad (2.6)$$

At this juncture, it is convenient to single out the core-cluster amplitudes $S^{(0,0)}$ and call them T. The rest of the cluster amplitudes will henceforth be called S. Since Ω is in normal order, we can rewrite Eq. (2.5) as

$$\Omega = \exp(T)\{\exp(S)\} \equiv \Omega_c\Omega_v. \quad (2.7)$$

The "valence-universal" wave-operator Ω in Eq. (2.7) is parametrized in such a way that the states generated by its action on the reference space satisfy the Fock-space Bloch equation

$$H\Omega P^{(k,l)} = \Omega P^{(k,l)} H_{\mathrm{eff}} P^{(k,l)}, \quad (2.8)$$

where

$$H_{\mathrm{eff}} = P^{(k,l)} H\Omega P^{(k,l)}. \quad (2.9)$$

Equation (2.8) is valid for all (k,l) starting from $k=l=0$, the *core* problem to some desired *parent* model space, with $k=m$, $l=n$, say. In this present calculation, we truncate Eq. (2.6) at $m=0$ and $n=1$. The operator $P^{(k,l)}$ in Eqs. (2.8) and (2.9) is the model space projector for k-hole and l-particle model spaces, which satisfy

$$P^{(k,l)}\Omega P^{(k,l)} = P^{(k,l)}. \quad (2.10)$$

To formulate the theory for direct energy differences, we premultiply Eq. (2.8) by $\exp(-T)$ (i.e., Ω_c^{-1}) and get

$$\bar{H}\Omega_v P^{(k,l)} = \Omega_v P^{(k,l)} H_{\mathrm{eff}} P^{(k,l)} \quad \forall\ (k,l) \neq (0,0), \quad (2.11)$$

where $\bar{H} = e^{-T} H e^{T}$. Since $\bar{H}$ can be partitioned into a connected operator $\tilde{H}$ and $E_{\mathrm{ref/gr}}$ (N-electron closed-shell reference or ground state energy), we likewise define $\tilde{H}_{\mathrm{eff}}$ as

$$H_{\mathrm{eff}} = \tilde{H}_{\mathrm{eff}} + E_{\mathrm{ref/gr}}. \quad (2.12)$$

Substituting Eq. (2.12) in Eq. (2.11) we obtain the Fock-space Bloch equation for energy differences as follows:

$$\tilde{H}\Omega_v P^{(k,l)} = \Omega_v P^{(k,l)} \tilde{H}_{\mathrm{eff}} P^{(k,l)}. \quad (2.13)$$

Equations (2.8) and (2.13) are solved by Bloch projection method, involving the left projection of the equation with $P^{(k,l)}$ and its orthogonal complement $Q^{(k,l)}$ to obtain the effective Hamiltonian and the cluster amplitudes, respectively. At this juncture, we recall that the cluster amplitudes in MR-FSCC are generated hierarchically through the *subsystem embedding condition* (SEC) [19,21], which is equivalent to the *valence universality* condition used by Lindgren [17] in his formulation. For example, in the present application, we first solve the Fock-space CC for $k=l=0$ to obtain the core-cluster amplitudes T. The operator $\tilde{H}$ and $\tilde{H}_{\mathrm{eff}}$ are then constructed from this core-cluster amplitudes T to solve Eq.

TABLE I. Lifetimes of the low-lying states in V^{4+}.

States	Lifetimes (in seconds)
$3d_{5/2}$	3.84×10^{2}
$4s_{1/2}$	4.55×10^{-5}
$4p_{1/2}$	1.99×10^{-10}
$4p_{3/2}$	1.97×10^{-10}
$4d_{3/2}$	3.77×10^{-10}
$4d_{5/2}$	3.01×10^{-10}
$4f_{5/2}$	1.20×10^{-10}
$4f_{7/2}$	6.97×10^{-11}

TABLE II. Comparison between the DF [29] and our CC calculations of the $3d\rightarrow4s$ transition probabilities.

Transitions	A_{M1} (DF)	A_{M1} (CC)	A_{E2} (DF)	A_{E2} (CC)
$3d\,^2D_{3/2}\rightarrow4s\,^2S_{1/2}$	4.21(−06)	2.19(−02)	8.56(+03)	44.42(+03)
$3d\,^2D_{5/2}\rightarrow4s\,^2S_{1/2}$			1.27(+04)	6.60(+03)

(2.13) for $k=0$, $l=1$ to determine $S^{(0,1)}$ amplitudes. The effective Hamiltonian constructed from H, T, and $S^{(0,1)}$ is then diagonalized within the model space to obtain the desired eigenvalues and eigenvectors

$$\tilde{H}_{\text{eff}} C^{(0,1)} = C^{(0,1)} E, \tag{2.14}$$

where

$$\tilde{H}_{\text{eff}} = P^{(0,1)} [\tilde{H} + \widehat{\tilde{H} S^{(0,1)}}] P^{(0,1)}. \tag{2.15}$$

The expression $\widehat{AB}$ in Eq. (2.15) indicates that operators A and B are connected by common orbital(s).

B. Higher order excitations

It is now widely recognized that the effects of higher body clusters must be included in CC calculations to improve the accuracy of the predicted and computed quantities. Here by the term "higher body effects," we mean effects from triple, quadruple excitations, etc. In this study, we shall restrict ourselves only to triple excitations for the time being and will comment on other higher excitations later. The most straightforward approach is to include the full three-body excitation operators T_3 and $S_3^{(0,1)}$ in the CC ansatz via $T=T_1+T_2+T_3$ and $S^{(0,1)}=S_1^{(0,1)}+S_2^{(0,1)}+S_3^{(0,1)}$. This direct approach, known as CCSDT, is computationally very expensive.

In this paper, triple excitations are included in the open shell CC amplitude, which correspond to the correlation to the valence orbitals, by an approximation that is similar in spirit to CCSD(T) [22]. The approximate valence triple excitation amplitude is given by

$$S_{abk}^{(0,1)pqr} = \frac{\{\widehat{VT_2}\}_{abk}^{pqr} + \{\widehat{VS_2^{(0,1)}}\}_{abk}^{pqr}}{\varepsilon_a + \varepsilon_b + \varepsilon_k - \varepsilon_p - \varepsilon_q - \varepsilon_r}, \tag{2.16}$$

where $S_{abk}^{(0,1)pqr}$ are the amplitudes corresponding to the simultaneous excitation of orbitals a,b,k to p,q,r, respectively; $\widehat{VT_2}$ and $\widehat{VS_2^{(0,1)}}$ are the connected composites involving V and T, and V and $S^{(0,1)}$, respectively, where V is the two electron Coulomb integral and ε's are the orbital energies.

III. COMPUTATIONAL PROCEDURE

The transition matrix element due to any operator D is evaluated in the MR-FSCC method by expressing it as

$$D_{fi} = \frac{\langle \Psi_f | D | \Psi_i \rangle}{\sqrt{\langle \Psi_f | \Psi_f \rangle \langle \Psi_i | \Psi_i \rangle}} = \frac{\langle \Phi_f | \{1 + S_f^{(0,1)^\dagger}\} e^{T^\dagger} D e^T \{1 + S_i^{(0,1)}\} | \Phi_i \rangle}{\sqrt{\langle \Phi_f | \{1 + S_f^{(0,1)^\dagger}\} e^{T^\dagger} e^T \{1 + S_f^{(0,1)}\} | \Phi_f \rangle \langle \Phi_i | \{1 + S_i^{(0,1)^\dagger}\} e^{T^\dagger} e^T \{1 + S_i^{(0,1)}\} | \Phi_i \rangle}}. \tag{3.1}$$

For computational simplicity, we express $e^{T^\dagger} D e^T$ as effective terms using the generalized Wick's theorem [17] as

$$\bar{D} \equiv e^{T^\dagger} D e^T = \bar{D}_0 + \bar{D}_1 + \bar{D}_2 + \cdots, \tag{3.2}$$

where $\bar{D}_0, \bar{D}_1, \bar{D}_2$ are effective zero-body, one-body, and two-body terms, respectively. In this expansion of $\bar{D}$, the effective one-body and two-body terms are computed keeping terms of the form of

$$\bar{D} = D + \widehat{T^\dagger D} + \widehat{DT} + \widehat{T^\dagger DT}. \tag{3.3}$$

Other effective terms correspond to higher orders in the residual Coulomb interaction and hence they are neglected in the present calculation. Interesting correlation features of the transition operator D are found in the contraction of $\bar{D}$ with

TABLE III. Effects of unbound orbitals in V^{4+} on electric quadrupole transition amplitudes.

Terms	Transition amplitudes	
	(with bound orbitals)	(with all orbitals)
$4s_{1/2} \rightarrow 4d_{3/2}$	−5.8530	−5.7383
$\rightarrow 4d_{5/2}$	7.1673	7.0272
$4d_{3/2} \rightarrow 4d_{5/2}$	−6.1508	−5.9673
$6s_{1/2} \rightarrow 4d_{3/2}$	0.7921	0.7101
$\rightarrow 4d_{5/2}$	−0.9823	−0.8820
$4p_{1/2} \rightarrow 4p_{3/2}$	−6.2963	−6.1510
$\rightarrow 6p_{3/2}$	−0.1036	−0.2787
$4p_{3/2} \rightarrow 6p_{3/2}$	−0.0327	−0.1949
$\rightarrow 6p_{1/2}$	−0.0747	−0.2562
$6p_{1/2} \rightarrow 6p_{3/2}$	−0.5787	−4.6953

TABLE IV. Effects of unbound orbitals in V^{4+} on magnetic dipole transition amplitudes.

Terms	Transition amplitude	
	(with bound orbitals)	(with all orbitals)
$4s_{1/2} \rightarrow 6s_{1/2}$	−0.0126	−0.0227
$4d_{3/2} \rightarrow 4d_{5/2}$	−1.5485	−1.5455
$4p_{1/2} \rightarrow 4p_{3/2}$	−1.1544	−1.1535
$\rightarrow 6p_{1/2}$	−0.0102	−0.0116
$\rightarrow 6p_{3/2}$	0.0071	0.0072
$4p_{3/2} \rightarrow 6p_{1/2}$	−0.0082	−0.0055
$\rightarrow 6p_{3/2}$	−0.0746	−0.0820
$6p_{1/2} \rightarrow 6p_{3/2}$	−1.5398	−1.5398

$S_1^{(0,1)}$ and $S_2^{(0,1)}$, which represent single excitation operators from valence orbital and double excitations from core-valence orbitals, respectively. Since the considered system is a single valence system, only one power of the $S^{(0,1)}$ operator will contribute in this MR-FSCCSD(T) calculation.

The reduced matrix element corresponding to $E1$, $E2$, and $M1$ transitions are given in our earlier papers [23,24]. The emission transition rate (in $s^{(-1)}$) for the $E2$ and $M1$ channels from states f to i are given by [25,26]

$$A_{f\to i}^{E2} = \frac{1.119\,95 \times 10^{18}}{\lambda^5 [j_f]} S^{E2}, \tag{3.4}$$

$$A_{f\to i}^{M1} = \frac{2.697\,35 \times 10^{13}}{\lambda^3 [j_f]} S^{M1}, \tag{3.5}$$

where $[j_f]=2j_f+1$ is the degeneracy of a f state, S is the square of the transition matrix elements of any of the corresponding transition operator D, and λ (in Å) are the corresponding transition wavelength.

The DF orbitals of V^{5+} are generated from the universal Gaussian-type orbital (GTO) basis functions [27] using $\alpha_0 = 0.008\,25$ and $\beta=2.91$. The number of DF orbitals for different symmetries used in the MR-FSCCSD(T) calculations are based on the convergent criteria of core correlation energy. There are 12, 10, 10, 9, and 8 active orbitals, which also include all core electrons, considered in the MR-FSCCSD(T) calculations for $l=0,1,2,3,4$ symmetries, respectively. Other higher energy orbitals that were present in the DF wave functions are considered as inactive.

IV. RESULTS AND DISCUSSIONS

The lifetime (in seconds) of a particular state is the reciprocal of total transition probabilities arising from all possible electromagnetic spontaneous transitions to the lower energy levels. In our previous work (hereafter referred to as paper I) on allowed transitions of the same system important for astrophysical applications [28], we have found excellent agreement with the experimental and MR-FSCCSD(T) computed ionization energies. The calculated lifetimes of many excited states are reported in Table I in this paper. These results are evaluated using both the allowed transition probabilities that are given in our earlier paper [28] and the forbidden transition probabilities in this paper. The forbidden transition probabilities are calculated from the transition amplitudes and wavelengths given in Table V. These results are determined for the first time to our knowledge, in the literature. These values show that the lifetime of the $3d\,^2D_{5/2}$ state is large, which seems to be useful in many atomic applications.

Ali and Kim [29] had calculated the $M1$ and $E2$ transition probabilities between the $3d$ and $4s$ states using the Dirac-Fock (DF) approximation. We have made a comparison with their results to ours in Table II. The difference between these results is due to the inclusion of electron correlation effects through the MR-FSCCSD(T) method. As shown in the table, the correlation effect is larger on $M1$ transitions than on $E2$ transitions. Also, another noticeable fact is to observe the opposite sign of the effect among $M1$ and $E2$ transitions. The

TABLE V. Transition wavelengths and transition amplitudes of V^{4+} for electric quadrupole and magnetic dipole transitions.

Transitions	λ_{NIST} (Å)	λ_{CC} (Å)	$E2$	$M1$
$3d_{3/2} \to 3d_{5/2}$			−0.7475	−1.5398
$\to 4d_{3/2}$	340.24	340.22	1.0870	0.0684
$\to 4d_{5/2}$	340.08	341.71	0.7290	0.0022
$\to 5d_{3/2}$	257.74	258.63	−0.3948	−0.0362
$\to 5d_{5/2}$	257.70	258.53	−0.2659	−0.0006
$\to 6d_{3/2}$	230.25	230.95	−0.1950	−0.0219
$\to 6d_{5/2}$	230.23	230.93	−0.1321	−0.0001
$\to 4s_{1/2}$	675.02	684.25	−1.4876	
$\to 5s_{1/2}$	304.67	306.30	0.0683	
$\to 6s_{1/2}$	247.61	248.25	0.0269	
$\to 5g_{7/2}$	240.17	240.98	−0.8463	
$\to 6g_{7/2}$	222.21	222.19	−0.6366	
$3d_{5/2} \to 4d_{3/2}$	340.97	341.04	−0.7357	−0.0062
$\to 4d_{5/2}$	340.80	340.86	1.4290	0.1860
$\to 5d_{3/2}$	258.16	258.05	0.2682	0.0027
$\to 5d_{5/2}$	258.11	258.00	−0.5192	−0.0984
$\to 6d_{3/2}$	230.58	230.45	0.1337	0.0013
$\to 6d_{5/2}$	230.56	230.44	−0.2574	−0.0598
$\to 4s_{1/2}$	677.88	680.17	−1.8310	
$\to 5s_{1/2}$	305.25	305.44	0.0829	
$\to 6s_{1/2}$	247.99	247.68	0.0329	
$\to 5g_{7/2}$	240.53	241.39	0.2839	
$\to 5g_{9/2}$	240.53	241.39	−1.0037	
$\to 6g_{7/2}$	222.51	222.54	0.2133	
$\to 6g_{9/2}$	222.51	222.55	−0.7539	
$4d_{3/2} \to 4d_{5/2}$			−5.9673	−1.5455
$\to 5d_{3/2}$	1062.99	1060.41	−5.5444	−0.1248
$\to 5d_{5/2}$	1062.23	1059.60	−3.8912	−0.0015
$\to 6d_{3/2}$	712.24	710.74	−1.8378	−0.0540
$\to 6d_{5/2}$	712.05	710.59	−1.3032	0.0008
$\to 4s_{1/2}$	686.06	684.00	5.7383	
$\to 5s_{1/2}$	2914.22	2925.88	9.4581	
$\to 6s_{1/2}$	909.48	904.77	−0.7101	
$\to 5g_{7/2}$	816.61	826.14	16.3355	
$\to 6g_{7/2}$	640.52	640.52	6.1353	
$4d_{5/2} \to 5d_{3/2}$	1064.62	1062.18	3.9140	0.0050
$\to 5d_{5/2}$	1063.86	1061.36	−7.2728	−0.3485
$\to 6d_{3/2}$	712.97	711.53	1.3062	0.0006
$\to 6d_{5/2}$	712.79	711.38	−2.4142	−0.1508
$\to 4s_{1/2}$	685.38	683.27	7.0272	
$\to 5s_{1/2}$	2926.53	2939.35	11.6086	
$\to 6s_{1/2}$	910.68	906.06	−0.8820	
$\to 5g_{7/2}$	817.57	827.21	−5.4566	
$\to 5g_{9/2}$	817.56	827.25	19.2923	
$\to 6g_{7/2}$	641.11	641.16	−2.0469	
$\to 6g_{9/2}$	641.12	641.18	7.2372	
$5d_{3/2} \to 5d_{5/2}$			−19.0483	−1.5436
$\to 6d_{3/2}$	2158.58	2155.39	15.9663	0.1210

TABLE V. (*Continued.*)

Transitions	λ_{NIST} (Å)	λ_{CC} (Å)	$E2$	$M1$
$\rightarrow 6d_{5/2}$	2156.85	2153.97	11.2383	0.0012
$\rightarrow 4s_{1/2}$	416.95	415.80	0.1076	
$\rightarrow 5s_{1/2}$	1673.36	1663.21	18.2095	
$\rightarrow 6s_{1/2}$	6298.00	6164.49	-29.2917	
$\rightarrow 5g_{7/2}$	3523.20	3739.47	44.8003	
$\rightarrow 6g_{7/2}$	1611.66	1617.59	−27.9356	
$5d_{5/2} \rightarrow 6d_{3/2}$	2161.69	2158.76	−11.3019	−0.0044
$\rightarrow 6d_{5/2}$	2159.95	2157.34	20.9536	−0.0039
$\rightarrow 4s_{1/2}$	416.83	415.67	0.1240	
$\rightarrow 5s_{1/2}$	1671.50	1661.21	22.2903	
$\rightarrow 6s_{1/2}$	6324.53	6192.12	−35.9371	
$\rightarrow 5g_{7/2}$	3531.49	3749.62	−14.9385	
$\rightarrow 5g_{9/2}$	3531.31	3770.43	52.8170	
$\rightarrow 6g_{7/2}$	1613.40	1619.49	9.3478	
$\rightarrow 6g_{9/2}$	1613.38	1619.60	−33.0483	
$6d_{3/2} \rightarrow 6d_{5/2}$			−49.7139	−1.5453
$\rightarrow 4s_{1/2}$	349.45	348.55	0.1295	
$\rightarrow 5s_{1/2}$	942.62	938.79	0.5210	
$\rightarrow 6s_{1/2}$	3284.21	3314.19	47.8467	
$\rightarrow 5g_{7/2}$	5573.05	5088.16	−29.2475	
$\rightarrow 6g_{7/2}$	6361.01	6483.01	128.4251	
$6d_{5/2} \rightarrow 4s_{1/2}$	349.40	348.52	0.1553	
$\rightarrow 5s_{1/2}$	942.29	938.52	0.6557	
$\rightarrow 6s_{1/2}$	3280.21	3310.84	58.5607	
$\rightarrow 5g_{7/2}$	5561.54	5080.26	9.7363	
$\rightarrow 5g_{9/2}$	5562.00	5078.78	−34.4251	
$\rightarrow 6g_{7/2}$	6376.81	6495.88	−42.8137	
$\rightarrow 6g_{9/2}$	6375.81	6497.70	151.3704	
$5g_{7/2} \rightarrow 5g_{9/2}$		−14.0132		
$\rightarrow 6g_{7/2}$	2970.51	2850.75	25.5408	
$\rightarrow 6g_{9/2}$	2970.45	2851.10	7.7503	
$5g_{9/2} \rightarrow 6g_{7/2}$	2970.64	2850.29	−7.7543	
$\rightarrow 6g_{9/2}$	2970.58	2850.64	28.8149	
$6g_{7/2} \rightarrow 6g_{9/2}$			−44.2007	
$4p_{1/2} \rightarrow 4p_{3/2}$	78971.47	77464.73	−6.1510	−1.1535
$\rightarrow 5p_{1/2}$	689.14	688.02		−0.0207
$\rightarrow 5p_{3/2}$	686.69	685.73	−3.5604	0.0053
$\rightarrow 6p_{1/2}$	478.40	478.18		−0.0116
$\rightarrow 6p_{3/2}$	477.82	478.23	−0.2787	0.0072
$\rightarrow 4f_{5/2}$	697.92	709.04	8.4251	
$5p_{1/2} \rightarrow 4p_{3/2}$	695.21	694.18	−3.6670	
$\rightarrow 5p_{3/2}$			−21.5598	−1.1530
$\rightarrow 6p_{1/2}$	1564.46	1567.89		0.0179
$\rightarrow 6p_{3/2}$	1558.23	1568.41	2.9529	−0.0077
$\rightarrow 4f_{5/2}$	54796.32	23207.88	13.7048	
$6p_{1/2} \rightarrow 4p_{3/2}$	481.32	481.15	−0.2562	
$\rightarrow 5p_{3/2}$	1577.24	1579.91	3.0066	
$\rightarrow 6p_{3/2}$			−4.6953	−1.4409
$\rightarrow 4f_{5/2}$	1521.03	1468.67	−0.7073	
$4p_{3/2} \rightarrow 5p_{1/2}$	695.21	694.18		0.0072
$\rightarrow 5p_{3/2}$	692.72	691.85	−3.4660	−0.1305
$\rightarrow 6p_{1/2}$	481.32	481.15		−0.0055
$\rightarrow 6p_{3/2}$	480.73	481.20	−0.1949	−0.0820
$\rightarrow 4f_{5/2}$	704.14	715.59	−4.5351	
$\rightarrow 4f_{7/2}$	706.25	715.71	−11.0889	
$5p_{3/2} \rightarrow 6p_{1/2}$	1577.24	1579.91		0.0061
$\rightarrow 6p_{3/2}$	1570.91	1580.45	2.6031	0.1222
$\rightarrow 4f_{5/2}$	37839.08	20858.40	−7.3110	
$\rightarrow 4f_{7/2}$	32616.42	20755.93	−17.8582	
$6p_{3/2} \rightarrow 4f_{5/2}$	1515.14	1469.13	0.3491	
$\rightarrow 4f_{7/2}$	1505.49	1468.62	0.8998	
$4f_{5/2} \rightarrow 4f_{7/2}$			5.5868	1.8435
$5g_{7/2} \rightarrow 5g_{9/2}$				−2.1081
$\rightarrow 6g_{7/2}$	2970.51	2850.75		0.0379
$\rightarrow 6g_{9/2}$	2970.45	2851.10		−0.0001
$5g_{9/2} \rightarrow 6g_{7/2}$	2970.64	2850.29		0.0000
$\rightarrow 6g_{9/2}$	2970.58	2850.64		0.0663
$6g_{7/2} \rightarrow 6g_{9/2}$				−2.1080
$4s_{1/2} \rightarrow 5s_{1/2}$	555.32	554.40		−0.5404
$\rightarrow 6s_{1/2}$	391.06	389.52		−0.0227
$5s_{1/2} \rightarrow 6s_{1/2}$	1322.08	1309.81		0.0496

detailed correlation effects on these transitions are explained in the last part of this section.

The effect of the unbound orbitals in the correlation calculation of the $E2$ and $M1$ transition amplitudes in the framework of the MR-FSCCSD(T) approach is studied quantitatively in Tables III and IV, respectively. Here, we have considered transitions involving few close and far away excited states from the ground state. As expected, these effects are large on the higher excited states compared to the low-lying excited states. It has to be noticed that the $E2$ transition amplitudes are generally large in all these transitions. This can be explained by considering the dependence of these transition amplitudes in the diffused region of wave functions.

Table V presents the magnetic dipole and electric quadrupole transition wavelengths and amplitudes, respectively, for most of the low-lying states. They are all relevant to astrophysical studies. The calculated wavelengths have good agreement for most of the cases with the result obtained from the website of National Institute of Standard and Technology (NIST) [30]. From a physics point of view, the important transitions among these are the forbidden transitions among the fine structures of the $3d$ and $4p$ states. The former one falls in the infrared region, which has many applications in the plasma research and infrared laser spectroscopy [31]. The latter one falls in the optical region and has an immense prospect in different atomic physics experiments. We have not reported wavelengths for most of the other fine structure

TABLE VI. Explicit contributions from the MR-FSCCSD(T) calculations to the absolute magnitude of reduced $E2$ transitions matrix elements in a.u.

CC terms	$3d_{3/2}\rightarrow 3d_{5/2}$	$3d_{3/2}\rightarrow 4d_{3/2}$	$3d_{3/2}\rightarrow 4s_{1/2}$	$3d_{3/2}\rightarrow 5s_{1/2}$	$3d_{3/2}\rightarrow 5g_{7/2}$	$3d_{5/2}\rightarrow 4d_{3/2}$	$3d_{5/2}\rightarrow 4s_{1/2}$	$3d_{5/2}\rightarrow 5s_{1/2}$	$3d_{5/2}\rightarrow 5g_{7/2}$
Dirac-Fock D	−0.8554	1.1077	−1.5552	0.0624	−0.9137	−0.7289	−1.9121	0.0748	0.3061
$\bar{D}$	−0.8466	1.1079	−1.5505	0.0604	−0.9125	−0.7287	−1.9060	0.0722	0.3057
$\bar{D}S_{1i}^{(0,1)}$	0.0180	−0.0896	0.0882	0.0284	0.0774	0.0585	0.1078	0.0348	−0.0257
$S_{1f}^{(0,1)^\dagger}\bar{D}$	0.0178	0.0252	−0.0019	−0.0351	−0.0096	−0.0355	−0.0023	−0.0432	0.0032
$\bar{D}S_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}D$	0.0625	0.0501	−0.0244	0.0092	−0.0036	−0.0337	−0.0318	0.0124	0.0014
$S_{1f}^{(0,1)^\dagger}\bar{D}S_{1i}^{(0,1)}$	0.0000	−0.0012	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{1f}^{(0,1)^\dagger}\bar{D}S_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}\bar{D}S_{1i}^{(0,1)}$	0.0001	0.0010	−0.0013	0.0006	−0.0004	−0.0006	−0.0016	0.0007	0.0001
$S_{2f}^{(0,1)^\dagger}\bar{D}S_{2i}^{(0,1)}$	−0.0078	0.0039	−0.0104	0.0048	−0.0021	−0.0026	−0.0127	0.0053	0.0006
Important effective two-body terms of $\bar{D}$									
$S_{2f}^{(0,1)^\dagger}DT_1$	0.0003	0.0002	0.0002	−0.0001	0.0000	−0.0002	0.0002	−0.0001	0.0000
$T_1^\dagger DS_{2i}^{(0,1)}$	0.0003	0.0000	0.0001	0.0000	0.0000	0.0000	0.0002	−0.0001	0.0000
$T_2^\dagger DS_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}DT_2$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	−0.0026	0.0015	0.0000
Normal	0.0075	−0.0107	0.0143	−0.0004	0.0044	0.0072	0.0175	−0.0005	−0.0014
Total	−0.7475	1.0870	−1.4876	0.0683	−0.8463	−0.7357	−1.8310	0.0829	0.2839

transitions that fall far beyond the infrared region. The relatively large differences in the wavelengths between some of the transitions from $4f(^2F)$ states call for further experimental and theoretical investigations on these states.

Quantitative contributions from different correlation terms for a few $E2$ transitions among low-lying states are presented in Tables VI and VII. These tables show comparative estimations of core-polarization, core-correlation, and pair-

TABLE VII. Explicit contributions from the MR-FSCCSD(T) calculations to the absolute magnitude of reduced $E2$ transitions matrix elements in a.u.

CC terms	$3d_{5/2}\rightarrow 5g_{9/2}$	$4d_{3/2}\rightarrow 4s_{1/2}$	$4d_{3/2}\rightarrow 5s_{1/2}$	$4d_{3/2}\rightarrow 5g_{7/2}$	$4p_{1/2}\rightarrow 4p_{3/2}$	$4p_{1/2}\rightarrow 4f_{5/2}$	$4p_{3/2}\rightarrow 4f_{5/2}$	$4p_{3/2}\rightarrow 4f_{7/2}$	$4f_{5/2}\rightarrow 5f_{7/2}$
Dirac-Fock D	−1.0825	5.9612	10.0120	17.4676	−6.4365	9.1096	−4.9059	−12.0170	6.5586
$\bar{D}$	−1.0810	5.9612	10.0120	17.4678	−6.4367	9.1094	−4.9061	−12.0174	6.5585
$\bar{D}S_{1i}^{(0,1)}$	0.0912	0.0177	−0.6124	−1.0685	0.1011	−0.2782	0.1485	0.3639	−0.2998
$S^{(0,1)^\dagger}{}_{1f}\bar{D}$	−0.0110	−0.1701	0.1189	0.0334	0.0982	−0.0815	0.0463	0.1145	−0.3017
$\bar{D}S_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}D$	−0.0047	−0.0430	0.0060	−0.0264	0.0654	−0.0557	0.0302	0.0733	−0.0195
$S_{1f}^{(0,1)^\dagger}\bar{D}S_{1i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{1f}^{(0,1)^\dagger}\bar{D}S_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}\bar{D}S_{1i}^{(0,1)}$	-0.0005	-0.0010	0.0010	0.0001	0.0007	−0.0002	0.0001	0.0003	−0.0011
$S_{2f}^{(0,1)^\dagger}\bar{D}S_{2i}^{(0,11)}$	−0.0026	0.0277	−0.0013	0.0113	−0.0316	0.0479	−0.0245	−0.0614	0.0389
Important effective two-body terms of $\bar{D}$									
$S_{2f}^{(0,1)^\dagger}DT_1$	0.0000	−0.0002	0.0001	0.0000	0.0003	−0.0001	0.0000	0.0001	0.0000
$T_1^\dagger DS_{2i}^{(0,1)}$	0.0000	−0.0001	0.0001	0.0000	0.0000	−0.0003	0.0001	0.0003	0.0000
$T_2^\dagger DS_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0055	0.0029	−0.0017	−0.0040	0.0000
$S_{2f}^{(0,1)^\dagger}DT_2$	0.0000	0.0003	−0.0002	0.0000	−0.0025	0.0000	0.0000	0.0000	0.0000
Normal	0.0051	−0.0543	−0.0657	−0.0822	0.0557	−0.3186	0.1714	0.4418	−0.3881
Total	−1.0037	5.7383	9.4581	16.3355	−6.1510	8.4251	−4.5351	−11.0889	5.5868

TABLE VIII. Explicit contributions from the MR-FSCCSD(T) calculations to the absolute magnitude of reduced $M1$ transition matrix elements in a.u.

CC terms	$3d_{3/2}\rightarrow 3d_{5/2}$	$3d_{3/2}\rightarrow 4d_{3/2}$	$4s_{1/2}\rightarrow 5s_{1/2}$	$4p_{1/2}\rightarrow 4p_{3/2}$	$4f_{5/2}\rightarrow 4f_{7/2}$	$5g_{7/2}\rightarrow 5g_{9/2}$
Dirac-Fock D	−1.5489	−0.0004	0.0004	−1.1545	1.8515	−2.1081
$\bar{D}$	−1.5291	−0.0020	0.0015	−1.1538	1.8515	−2.1081
$\bar{D}S_{1i}^{(0,1)}$	0.0001	0.0511	−0.0440	0.0002	0.0000	0.0000
$S_{1f}^{(0,1)^\dagger}\bar{D}$	0.0000	0.0000	0.0000	−0.0002	0.0000	0.0000
$\bar{D}S_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}\bar{D}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{1f}^{(0,1)^\dagger}\bar{D}S_{1i}^{(0,1)}$	0.0000	0.0017	−0.0006	0.0000	0.0000	0.0000
$S_{1f}^{(0,1)^\dagger}\bar{D}S_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}\bar{D}S_{1i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}\bar{D}S_{2i}^{(0,1)}$	−0.0187	0.0199	−0.0118	−0.0106	0.1203	−0.0008
Important effective two-body terms of $\bar{D}$						
$S_{2f}^{(0,1)^\dagger}DT_1$	0.0011	−0.0009	0.0002	0.0001	0.0000	0.0000
$T_1^\dagger DS_{2i}^{(0,1)}$	0.0011	−0.0006	0.0001	0.0001	0.0000	0.0000
$T_2^\dagger DS_{2i}^{(0,1)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_{2f}^{(0,1)^\dagger}DT_2$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Normal	0.0154	−0.0006	0.0003	0.0104	−0.1280	0.0008
Total	−1.5398	0.0684	−0.5404	−1.1535	1.8435	−2.1081

correlation effects in these transitions. The diagrams involving these contributions are discussed in our earlier papers [32]. We found from these tables that all the order core-polarization effects ($\bar{D}S_{2i}^{(0,1)}$) coming from the initial state for all the transitions are small. But we cannot neglect these $S_2^{(0,1)}$ operators totally due to significant contributions of ($S_{2f}^{(0,1)^\dagger}\bar{D}$), especially in the $E2$ transition amplitudes. The correlation contributions to these transitions coming from $S_2^{(0,1)}$ cluster operators vary to a large extent. Among D states the effect is large: 4–8 %. Moderate contributions come in the D to S states: around 1–3 %, whereas, for D to G states they are significantly small.

Though almost similar correlation trends have been observed in Table VIII for the $M1$ transitions case, here core-polarization contributions are almost zero. The noticeable features are the transitions between the same symmetries, but different principle quantum numbers. In these cases, the DF contributions are very small (almost 1%) compared to the all order pair-correlation effects arising from the initial state. They are the prime correlation contributors. Other strong contributions come from $S_{2f}^{(0,1)}\bar{D}S_{2i}^{(0,1)}$ in all the transitions presented in the same table apart from transitions among G states.

V. CONCLUSION

Lifetimes of the low-lying bound states of V^{4+} have been calculated using the MR-FSCC approach with the Dirac-Coulomb Hamiltonian. Long lifetime has been observed for the first excited D state and it can be used as a potential metastable state for experiments in physics. Magnetic dipole and electric quadrupole transition amplitudes among the bound states of the system are important for astronomical observations and plasma researches. Here, we have reported these results for the first time. Especially, forbidden transitions between the fine structure $4p$ states may be considered for different atomic experiments of fundamental physics due to its optical transition line. We have also highlighted different correlation effects arising through the MR-FSCCSD(T) method.

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