Fine-structure in $3d^4$ States of Highly Charged Ti-like Ions

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A remarkable improvement of *ab initio* calculations was obtained for wavelengths of $(3d^4)$ $J = 3 \rightarrow 2$ forbidden transition. Present calculations reduced the long-standing discrepancy from measurements down to less than 0.2% for most high-Z titanium-like ions. In the present calculations, a large extent of configuration space was included so that most important many-body effects were taken into account. To this end, the *linearized* second-order Brillouin-Wigner perturbation theory was employed with optimized spin-orbitals. Transition probability and atomic g-factor were also calculated with the improved atomic wavefunctions.

INTRODUCTION

From a survey of atomic transitions using the multi-configuration Dirac-Fock (MCDF) method, Feldman, Indelicato and Sugar[1] reported that a forbidden transition between the lowest fine-structure levels of $(3d^4)$ $J = 2$ and $J = 3$ was to be observed in the optical region for most high-Z titanium-like ions. Besides its potential importance for high-temperature plasma diagnostics, the transition serves as a test-ground for many-body atomic structure theories, as will be seen shortly.

The first observation of the transition was made by Morgan et al.[2] for Xe^{32+} and Ba^{34+}. However, measured wavelengths were found to have an unexpectedly large discrepancy (≅ 5%) from state-of-the-art MCDF calculations.[3] Indelicato[4] tried to refine the MCDF calculations by including some valence-core correlations, but eventually found little improvement due to almost complete cancellation. A typical energy difference of this transition is of 10^{-5} relative to the individual energies. It suggests that a large extent of configuration space may participate in contributions to the wavelength. Beck[5] thoroughly investigated many sorts of the contributions by configuration interaction (CI) calculations, and reduced the discrepancy to ≅ 1%.

After the first measurement by Morgan et al.,[2] further wavelength measurements have been pursued by several groups.[6-11] Available measurements now cover a wide range of Z (= 51-83). It is noteworthy that, in Ref. 10, wavelengths for unmeasured elements in Z = 52-83 were evaluated by interpolating and extrapolating some available measurements; uncertainties in the evaluations were estimated to be within 0.1% that were much smaller than errors of the improved calculations by Beck.[5] The set of measurements thus serves as a benchmark for improvements of the many-body atomic structure theories.

In this paper, an efficient *ab initio* theoretical method is devised for further improvement of the calculations. With the devised method, calculations of the transition wavelength, the magnetic-dipole transition probability and the atomic g-factor are presented for the low-est fine-structure levels in the $3d^4$ state.

THEORETICAL METHOD

As already mentioned, a large extent of configuration space is involved in the transition, though the bulk of the configuration space has only marginal contributions to individual atomic states. In such a case, it is useless to perform all-order many-body calculations with the whole configuration space. A natural remedy to the useless computational burden is to adopt the perturbation theory to the marginal part of the configuration space.

The whole configuration space is divided into a principal part (P) and an orthogonal complementary part (Q). Interaction between P and Q is assumed to be the lowest-order perturbation. Total energy functional is partitioned into the

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zero-order part ($H^{(0)}$) and the re sid ual part (V). The Dirac-Fock en ergy func tional is cho sen as the zero-order part; the re sid ual part then rep re sents a cor re la tion en ergy func tional. The sec ond-order Brillouin-Wigner per tur ba tion the ory then leads to,

$$(E-H_{QQ}^{(0)})^{-1}V_{QP}\Psi_P = \Psi_Q,$$
$$[H_{PP}^{(0)}+V_{PP}+V_{PQ}(E-H_{QQ}^{(0)})^{-1}V_{QP}]\Psi_P = E\Psi_P. \quad (1)$$

The above equa tions de fine the first-order cor re la tion op er a-tor and the sec ond-order ef fec tive Hamiltonian op er a tor for the *P*-space, re spec tively. In the brack ets of the sec ond equa-tion, the first and second terms com pose the to tal en ergy func tional in the *P*-space, and the third term rep re sents the sec ond-order cor rec tion to the cor re la tion en ergy func tional in the *P*-space. The non-linear ef fec tive Hamiltonian equa-tion is writ ten in a linearized form,

$$\begin{pmatrix} H_{PP}^{(0)}+V_{PP} & V_{PQ} \\ V_{QP} & H_{QQ}^{(0)} \end{pmatrix}\begin{pmatrix}\Psi_P \\ \Psi_Q\end{pmatrix} = E\begin{pmatrix}\Psi_P \\ \Psi_Q\end{pmatrix}. \quad (2)$$

The re quire ment that the to tal en ergy func tional (E) is sta tion ary with re spect to vari a tions in spin-orbitals ($\{\phi\}$) un-der the nor mal iza tion and the orthogonality con di tions leads to a set of the Eu ler-Lagrange equa tions,

$$\frac{\delta E[\{\phi\}]}{\delta\phi_a} = \mu_a\phi_a + \sum_{b\neq a}\mu_{ab}\phi_b, \quad (3)$$

where $\{\mu\}$ are the Lagrange mul ti pli ers. The above equa tions are noth ing but re duced MCDF equa tions. That is to say, an ap par ent con nec tion be tween the sec ond-order Brillouin-Wigner per tur ba tion en ergy func tional and a set of the re-duced MCDF equa tions is pro vided.

In the Hamiltonian ma trix [Eq. 2], $H_{QQ}^{(00)}$ block is di ag o-nal. As a re sult, a com pu ta tion time and file sys tem size re-quired for cal cu la tions of the ma trix el e ments are re duced re-mark ably. The pres ent method thus has the po ten tial abil ity to take a very large ex tent of the con fig u ra tion space into ac-count, which is al most in ac ces si ble by full MCDF and CI meth ods, ac cu rately with rel a tively small com pu ta tional re-sources pro vided the *Q*-space con trib utes perturbatively to the *P*-space. Ad di tionally, the pres ent method is ex pected to be more ef fec tive than con ven tional per tur ba tion the o ries, since spin-orbitals are op ti mized au to mat i cally to a given per tur ba tion en ergy func tional so that a to tal en ergy is sta-tionary.

In the pres ent cal cu la tions, the *P*-space was spanned by $|0\rangle \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$, and in ter nal sin gle and dou ble ex ci-ta tions, i.e. in the sec ond quantization for mal ism, $a^\dagger_{3d}a_{3s}|0\rangle$, $a^\dagger_{3d}a^\dagger_{3d}a_{3s}a_{3s}|0\rangle$ and $a^\dagger_{3d}a^\dagger_{3d}a_{3p}a_{3p}|0\rangle$. The three-, four-, fold ex ci ta tions were omit ted. Rep re sen ta tive configurations in the *Q*-space were $a^\dagger_v a_{3l}|0\rangle$ (n = 4-7) and $a^\dagger_v a^\dagger_w a_{3d}a_{3d}|0\rangle$ (n = 4-6), so that the core po lar iza tion and the va lence cor re la tion ex cept for the va lence-core cor re la tion were in cluded. It is noted that, in the above, the non-relativistic no ta tion is used for sim plic ity. In Ta ble 1, num ber of the spin-orbital con fig u-ra tions and par ti tion of the whole con fig u ra tion space are sum ma rized. The low est-order quan tum elec tro dy nam ics cor rec tions: the sin gle trans verse-photon ex change in ter ac-tion and vac uum po lar iza tion, were in cluded ex cept for the self-energy cor rec tion. The nu clear charge dis tri bu tion was rep re sented by the spher i cal sym met ric Fermi-model. The pres ent cal cu la tions were im ple mented with the GRASP92 code.[12]

RESULTS AND DISCUSSION

In Ta ble 2, cal cu lated wave lengths for the $J = 3 \rightarrow 2$ for-bid den tran si tion are com pared with the avail able mea sure-ments and the CI cal cu la tions by Beck.[5] The pres ent agree-ment with the mea sure ments is ex cel lent; the dis crep ancy is less than 0.2% ex cept for Sb^{29+} (≅ 0.5% er ror) and Xe^{32+} (≅ 0.4% er ror). For Sm^{40+} and Eu^{41+}, Watanabe et al.[11] ob served

Table 1.

	State	J = 0	J = 1	J = 2	J = 3	J = 4
P-space	$\|0\rangle$	5	4	8	6	7
	$a^\dagger_{3d}a_{3s}\|0\rangle$	4	11	17	17	12
	$a^\dagger_{3d}a^\dagger_{3d}a_{3s}a_{3s}\|0\rangle$	5	4	8	6	7
	$a^\dagger_{3d}a^\dagger_{3d}a_{3p}a_{3p}\|0\rangle$	30	61	94	87	79
Q-space	$a^\dagger_v a_{3l}\|0\rangle$	885	2470	3585	4074	3959
	$a^\dagger_v a^\dagger_w a_{3d}a_{3d}\|0\rangle$	1004	2607	3944	4428	4454

Number of the spin-orbital configurations and partition of configuration space. A vacuum state is formed from occupied orbitals: $|0\rangle \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$. v and w represent virtual orbitals of n = 4-7 for the single excitation and of n = 4-6 for the double excitation.

Table 2.

Z	Present calculation	Beck[5]	Measurements
51 (Sb^{29+})	472.905	-	470.24(3)[11]
53 (I^{31+})	430.705	-	430.33(8)[11]
54 (Xe^{32+})	415.644	407.93	413.88(7)[11], 413.94(20)[2]
55 (Cs^{33+})	402.846	-	402.14(12)[11]
56 (Ba^{34+})	393.649	386.63	393.08(18)[11], 393.24(20)[2], 93.239(8)[7]
60 (Nd^{38+})	375.382	367.93	375.3(2)[6]
62 (Sm^{40+})	372.386	-	372.52(2)[11]
63 (Eu^{41+})	371.743	-	371.75(3)[11]
64 (Gd^{42+})	371.202	367.53	371.3(2)[6]
70 (Yb^{48+})	367.670	-	367.64(15)[10]
72 (Hf^{50+})	365.434	-	365.54(4)[11]
73 (Ta^{51+})	364.077	-	364.18(5)[11]
74 (W^{52+})	362.568	360.15	362.67(2)[11], 362.713(10)[9], 362.6(2)[10]
75 (Re^{53+})	360.917	-	361.06(5)[11]
78 (Pt^{56+})	355.211	-	355.44(4)[11]
79 (Au^{57+})	353.097	-	353.2(2)[8]
83 (Bi^{61+})	343.870	344.16	344.29(15)[10]

Wavelengths (nm) of ($3d^4$) $J = 3 \rightarrow 2$ forbidden transition. Numbers in parentheses are experimental uncertainties, e.g. 393.08(18) represents 393.08 ± 0.18.

another forbidden transition of $J = 3 \rightarrow 4$ with wave lengths of 369.89(3) nm and 339.48(4) nm, respectively. Present calculations are 371.20 nm and 340.94 nm, respectively, within 0.4% error. The valence-core correlation was examined for Nd^{38+}, since it was omitted in the present calculations. It turned out to be significant in the individual energies as the core polarization and the valence correlation. Nevertheless, it has little contribution to the wave length due to almost complete cancellation in the energy difference.

The present calculations and the measurements are plotted in Fig. 1. An intriguing feature seen is a plateau of wave length change in Z = 60-70. Such a fine-structure has been explored theoretically in other cases,[4] and the transitions with wave lengths almost independent on Z were found in the near infrared region for highly charged zirconium-like ($4d^4$) and neodymium-like ($4f^6$) ions too. Wave lengths for this sort of transition are expected to scale as Z^{-4}, provided the transitions are in a single LS-term. In Ref. 13, however, it was pointed out that the LS-coupling scheme already failed in the Z range where the plateau took place. It suggests that intermediate coupling in the $3d^4$ state plays a crucial role in a mechanism by which the plateau takes place. To see this, wavelengths obtained from calculations with ($3d^4$) ^{5}D term only and those with $3d^3_{3/2}3d_{5/2}$ term only are plotted in the figure. As expected, the wave length for the ($3d^4$) ^{5}D term falls rapidly into the shorter wave length region as Z increases. On the contrary, it turns out that the wave length for the $3d^3_{3/2}3d_{5/2}$ term decreases with so a gentle slope that the wave length is found still in the optical region up to $Z \cong 90$. The realistic wavelength decreases rapidly along the former wavelength-curve in low-Z region, and finds its way eventually to the latter wave length-curve in high-Z region. In the course, the plateau takes place in dicating the intermediate coupling switches from the LS-coupling to the jj-coupling in a rather narrow Z range.

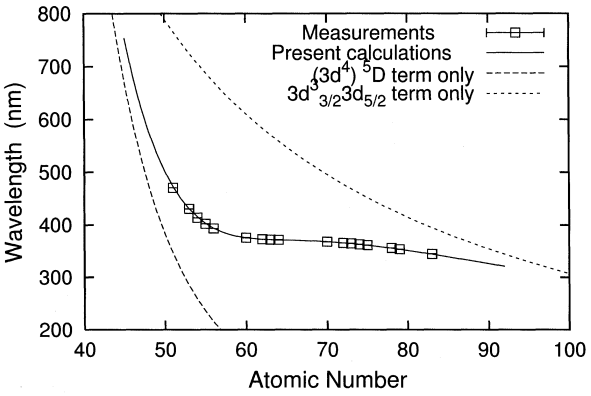

Fig. 1. Plateau in the wavelength change. Solid curve is plot of the present calculations, long-dash curve plot of calculations with ($3d^4$) ^{5}D term only, short-dash curve plot of calculations with $3d^3_{3/2}3d_{5/2}$ term only, and open-squares measurements.

In Fig. 2, the magnetic-dipole probabilities of the $J = 3 \rightarrow 2$ and the $J = 3 \rightarrow 4$ ($J = 4 \rightarrow 3$ for $Z < 52$) transitions are presented. Variation of the probabilities are not monotonic. A

vanishing probability of the $J = 3 \rightarrow 4$ transition near $Z = 52$ is due to a level crossing between $J = 3,4$. The early MCDF calculations by Feldman et al.[1] are also plotted in the figure. The present calculations have smaller probabilities for both the transitions which is attributed probably to smaller energy differences of the present calculations; improvement always reduces the energy differences in the present case. The discrepancy disappears apparently in high-Z region for the $J = 3 \rightarrow 2$ transition. One and only one available measurement for Xe^{32+} by Serpa et al.[14] is also plotted in the figure. The discrepancy from the measurement attains about 10%. It is noted that the electric-quadrupole contribution to this transition was calculated to be six orders of magnitude smaller than the magnetic-dipole. For the transition probabilities, there is no reason to cancel the individual contributions. The large discrepancy might be attributed to omission of the valence-core correlation in the present calculations.

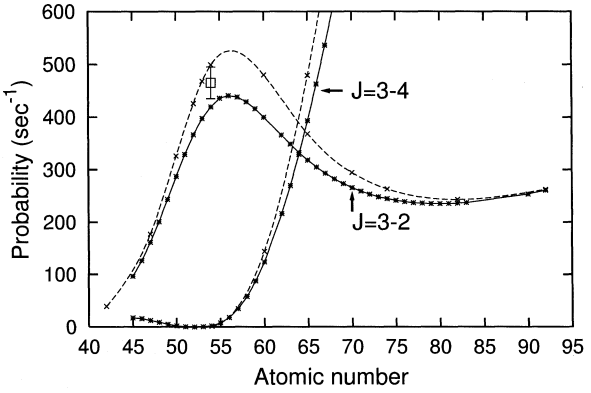

Fig. 2. Magnetic-dipole probabilities (sec^{-1}) of $J = 3 \rightarrow 2$ and $J = 3 \rightarrow 4$ ($J = 4 \rightarrow 3$ for $Z < 52$) transitions. Solid curves are plot of the present calculations, dash curves plot of the MCDF calculations by Feldman et al.,[1] and a open-square the measurement by Serpa et al.[14] for Xe^{32+}.

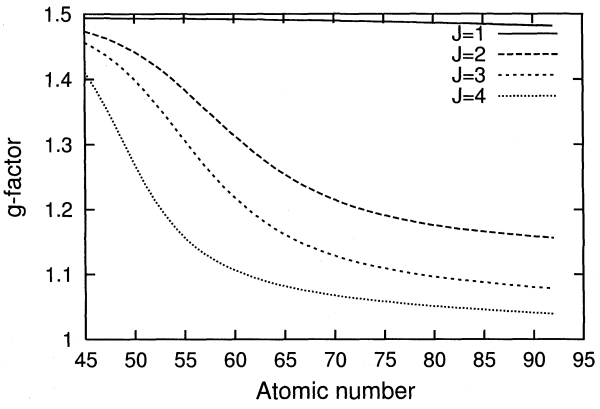

Fig. 3. Atomic g-factor for $(3d^4)$ $J = 1$-4.

In Fig. 3, calculations of the atomic g-factor are shown for the lowest levels of $(3d^4)$ $J = 1$-4. They decrease from the Landé's value (1.5 for ^{5}D term) as Z increases. The g-factors of $J = 2$-4 change by ~ 20% in $Z = 45$-92, while the g-factor of $J = 1$ changes little in the Z range. With the present g-factors, splitting in the Zeeman-induced triplet structure (π- and $\sigma^{+,-}$-components) of the $J = 3 \rightarrow 2$ line was estimated to be $\cong 1.9 \times 10^{-4}$ eV for U^{70+} at magnetic-field strength of 3 T, while to be $\cong 2.6 \times 10^{-4}$ eV with the Landé's value. It indicates that such a high resolving power as $>10^4$ is necessary to observe the triplet structure. Finer splitting within each component (the Zeeman shift) is even smaller: $\cong 1.4 \times 10^{-5}$ eV for U^{70+}. A preliminary Fabry-Perot interferometry study[15] has been made for Ba^{34+}, but could not resolve the triplet structure due to the Doppler-broadening of the line.

In concluding remarks, an effective second-order perturbation theory was devised. The theory treats the principal configuration space up to all-order, while contribution of the complementary space is treated as the second-order perturbation. It reduces the computational time and the file system size remarkably, since the off-diagonal part of effective Hamiltonian matrix elements in the large complementary space can be omitted in the second-order calculations. An advantage over the conventional perturbation theory is that the spin-orbitals are optimized automatically to the perturbation energy functional by solving reduced MCDF type equations. The present calculations of the wavelength for transition between the lowest levels of $(3d^4)$ $J = 2$ and $J = 3$ reduced the error in other theories down to less than 0.2% for most high-Z elements. However, it might be too optimistic to be confident with the present calculations, since a choice of the principal configuration space is still somewhat an art. Convergence must be examined with respect to partitioning of the principal space as well as the size of the whole configuration space.

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Key Words

Ab initio many-body atomic structure theory; Highly charged ions; Optical and forbidden transition.

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