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Finite-field calculation of electric quadrupole moments of $^2P_{3/2}$, $^2D_{3/2,5/2}$, and $^2F_{5/2,7/2}$ states for Yb^+ ion*

Xi-Tong Guo(郭希同)[1,2], Yan-Mei Yu(于艳梅)[2,†], Yong Liu(刘永)[1,‡], and Bing-Bing Suo(索兵兵)[3,§]

[1] *State Key Laboratory of Metastable Materials Science and Technology & Key Laboratory for Microstructural Material Physics of Hebei Province, School of Science, Yanshan University, Qinhuangdao* 066004, *China*

[2] *Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

[3] *Institute of Modern Physics, Northwest University, Xi'an* 710069, *China*

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Electric quadrupole moments of low-lying excited states of Yb^+ are calculated by relativistic coupled-cluster theory with perturbations from external fields. The field-dependent energy differentiation provides accurate values of the electric quadrupole moments of $^2P_{3/2}$, $^2D_{3/2,5/2}$, and $^2F_{5/2,7/2}$ states which agree well with experimental values. The important role of the electronic correlation to the electric quadrupole moments is investigated. Our calculations indicate the early dispute of the electric quadrupole moment of the $Yb^+(^2F_{7/2})$ state for which the measured and theoretical values have a large discrepancy. These electric quadrupole moment values can help us to determine the electric quadrupole shifts in start-of-the-art experiments of the Yb^+ ion.

Keywords: Yb^+, finite-field method, electric quadrupole moment, relativistic coupled-cluster

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1. introduction

The Yb^+ ion has been investigated by many national standards laboratories due to its potential application in optical clock with fractional uncertainties below 10^{-17}.[1–4] Two transitions of Yb^+, *e.g.*, E2: $^2S_{1/2} \leftarrow {}^2D_{3/2}$ and E3: $^2S_{1/2} \leftarrow {}^2F_{7/2}$, are accepted as secondary representations of the second transition, in which E2 is an electric quadrupole transition with the excitation wavelength of 436 nm, and E3 is an electric octupole transition with that of 467 nm. The E3 transition has an extremely long lifetime and has a natural linewidth on the order of nanohertz. The atomic clock based on the E3 transition has achieved a total systematical uncertainty of 3.2×10^{-18}.[5] The $^2S_{1/2} \rightarrow {}^2D_{3/2}$ transition is suggested as a suitable system to study the parity non-conservation (PNC).[6–8] Moreover, a comparison of two clock transitions of Yb^+ had set new constraints on the time variation of the proton-to-electron ratio and the fine structure constant.[4]

The $^2D_{3/2}$ and $^2F_{7/2}$ states have the electron configurations of $[Xe]4f^{14}5d$ and $[Xe]4f^{13}6s^2$, respectively. Both these two states have none-zero electric quadrupole moments (labeled as Θ). As one of the largest systematical energy shifts of the Yb^+ clock, the values of Θ are used to estimate electric quadrupole shifts due to the interaction of electric quadrupole moment with external electric field gradient. Besides, precise data of electric quadrupole moments are also useful for analyzing nuclear structures. A precise measurement of the electric quadrupole moment of Yb^+ has been implemented for two clock states, $^2D_{3/2}$ and $^2F_{7/2}$.[2,9] Comparisons of theoretical results with experimental measurements could serve as excellent tests to the relativistic atomic theories. However, calculation of the electric quadrupole moment of Yb^+ is a challenging task because Yb^+ is a heavy system which contains 69 electrons with 13–14 electrons occupied in the 4f orbital. Earlier theoretical studies on the Θ value of the Yb^+ $^2D_{3/2}$ state has given consistent results with measured values while theoretical values of the $^2F_{7/2}$ state show large discrepancies from the measured results, implying some effects of electronic correlation that occurs for the $^2F_{7/2}$ state other than the $^2D_{3/2}$ state. Furthermore, the electric quadrupole moment is found very sensitive to the configuration interaction. The quadrupole moment is expected to be small due to large cancellations of one-electron contributions. This makes the result obtained even for the biggest CI space inconclusive.[8] Therefore, further investigations to validate the disagreement and to understand the

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†Corresponding author. E-mail: ymyu@aphy.iphy.ac.cn

‡Corresponding author. E-mail: ycliu@ysu.edu.cn

§Corresponding author. E-mail: bsuo@nwu.edu.cn

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role of the electron correlation on the electric quadrupole moment of low-lying excited states of Yb^+ are strongly desired.

In this paper, we employ the relativistic coupled-cluster (RCC) method to treat the electron correlation in Yb^+. We adopt the finite-field (FF) approach to obtain the electric quadrupole moment by numerical differentiation of the FF-dependent energies. We calculate the electric quadrupole moments of the $^2P_{3/2}$, $^2D_{3/2,5/2}$, and $^2F_{5/2,7/2}$ states, and make comparisons with the experimented results and the early theoretical values. Our results for $^2D_{3/2,5/2}$ state show an excellent agreement with the measured and early theoretical values, while for the $^2F_{7/2}$ state, our result is in the line with the experimental measurement, but different with the early theoretical results obtained by the expectation-value method. Besides, we give a recommendation value of the electric quadrupole moment of the Yb^+ $^2P_{3/2}$ state which has not been reported before.

2. Computational method

The atomic properties are evaluated as the numerical differentiation of energy with respect to externally applied fields or field gradients in the FF method. For an atom or ion in a purely quadrupole electric field, the corresponding energy shift is written as[10–12]

$$E(|\gamma J\rangle)(F_{zz}) = -\Theta(|\gamma J\rangle)F_{zz}/2 - \cdots, \tag{1}$$

where $E(|\gamma J\rangle)$ is the energy of the state $|\gamma J\rangle$, and F_{zz} is the electric-field gradient in the z direction of an electric quadrupole field. The F_{zz}-dependent energies are fitted by a linear relationship, which yields the slope that equals $\Theta(|\gamma J\rangle)$. In the FF approach, the employed external electric field breaks degeneracy of the atomic energy levels and thus the fitted properties are obtained for each M_J component, where M_J is the projection of the angular moment J in the z direction. The electric quadrupole moment of the $|\gamma J\rangle$ state is therefore defined on its sublevel with $M_J = J$.

The field-dependent energies are calculated by using a two-step procedure. First, the four-component Dirac–Hartree–Fock (DHF) calculation is performed to generate the reference state and one-electron orbital for subsequent electron correlation calculations. Then, the Fock space coupled-cluster method (FSCC) is implemented by using single-electron orbitals from DHF.[13,14] For the $^2P_{3/2}$ and $^2D_{3/2,5/2}$ states, we carried out the DHF calculations for the closed-shell reference state of Yb^{2+}. Then, the electron attachment calculation is implemented by FSCC with the model space composed of the 6s, 6p, and 5d orbitals, which determines the electron affinity (EA) energies at the corresponding valence states. The $^2F_{7/2}$ state shows a multi-configurational manner and is troublesome. We first calculate the ^1S ground state of the Yb atom via DHF, then the electron detachment calculation is carried out by FSCC, in which one electron is removed from the model space $4f^{14}6s^2$ and then ionic potentials (IP) are obtained. The FSCC calculations are augmented by the extrapolated intermediate Hamiltonian approach to avoid the convergence difficulties in the coupled-cluster iterations.[13] All calculations are carried out by using the electronic structure code DIRAC.[15] The electron correlations of the core shells are restricted for appropriate sizes of the core to save computational costs.

The Dyall's uncontracted correlation consistent double-, triple-, quadruple-ζ basis sets are used in calculations, which are referred to as $X\zeta$ with $X = 2,3$, and 4.[16] Arbitrary 4–8 field values are chosen in $F_{zz} = [0, 4.5 \times 10^{-5}]$ a.u. (a.u. is the atomic unit), where atomic unit of F_{zz} is 5.142250×10^{11} V/cm^2. The fitting is checked to remove the dependence of the studied properties on sampling. The energy convergence criterion is chosen as 10^{-10} Hartree (1 Hartree $= 4.3597 \times 10^{-27}$ J) in calculations. We adopt a composite scheme to get the convergent property. The energies and properties from FSCC/4ζ are corrected by three terms, Δ_{basis}, Δ_{core}, and Δ_{virt} to include contributions of the incomplete basis sets, truncations of the core, and virtual orbitals, respectively. We estimate Δ_{basis} by the differential values of the results obtained at $X = 3\zeta$ and $X = 4\zeta$. Moreover, Δ_{core} means the electron correlation contribution from the increasing of the core electrons, and Δ_{virt} estimates the contribution of the neglected virtual orbitals due to energy cutoff. The uncertainties in our final values are estimated by the dominant errors caused by the finite basis size and the neglected electronic correlations.

3. Results and discussion

In Table 1 we give the EA of Yb^+ at the ground $^2S_{1/2}$ state and the lowing excited states, $^2P_{3/2}$ and $^2D_{3/2,5/2}$. The FSCC labeled (core 40) SD $<$ 50 a.u. are performed first using the 2ζ, 3ζ, and 4ζ basis sets. Here, (core 40) SD $<$ 50 a.u. means the configuration interaction space composed of the single and double (SD) excitations from a core-orbital space with 40 electrons in 4s, 4p, 4d, 5s, 5p, and 4f orbitals to a truncated virtual orbital set with energies less than 50 a.u., *i.e.*, these calculations show the convergence of the results with increasing of the basis sets. Corrections due to the finite basis set are estimated in terms of the difference of the EA values obtained by the (core 40) SD $<$ 50 a.u. calculation at 3ζ and 4ζ basis sets, which are given in the row labeled by Δ_{basis}. Then, the FSCC calculations with an increasing number of correlated core–shell electrons, *i.e.*, (core 22) SD $<$ 50 a.u., (core 40) SD $<$ 50 a.u., and (core 68) SD $<$ 50 a.u., are conducted

at the 3ζ basis set. These calculations show that the dominant core-electron correlation contribution comes outer 40 electrons whereas the residual correlation arising from more core–shell electrons is negligible small. We use $\Delta_{\rm core}$ to denote the electron correlation contribution from the increasing of the core electrons from 40 to 68, which is determined by the variation of the EA values obtained by the (core 40) SD $<$ 50 a.u. and (core 68) SD $<$ 50 a.u. at the 3ζ basis set. The correction from the more correlated virtual orbitals is estimated through the difference of the EA values obtained by the (core 40) SD $<$ 50 a.u. and (core 40) SD $<$ 1000 a.u. calculations conducted at the 3ζ basis set, as listed in the row labeled by $\Delta_{\rm virt}$. We take the EA values obtained with the 4ζ basis sets, adding the corrections $\Delta_{\rm basis}$, $\Delta_{\rm core}$, and $\Delta_{\rm virt}$, as the final EA values of the $^2{\rm P}_{3/2}$ and $^2{\rm D}_{3/2,5/2}$ states with the uncertainty assigned by sum of various corrections. Our FSCC EA values show good agreement with the NIST[17] with errors less than 2%.

Table 1. Values of the electron affinity (EA) in a.u. at the Yb^+ $^2{\rm S}_{1/2}$, $^2{\rm P}_{3/2}$, and $^2{\rm D}_{3/2,5/2}$ states obtained by using the RCC method.

Level of excitation	$^2{\rm S}_{1/2}$	$^2{\rm P}_{3/2}$	$^2{\rm D}_{3/2}$	$^2{\rm D}_{5/2}$
Basis: 2ξ (24s, 19p, 13d, 8f, 2g)				
(core 40) SD $<$ 50 a.u.	−97126	−66219	−73172	−71903
Basis: 3ξ (30s,24p,16d,11f,3g,2h)				
(core 22) SD $<$ 50 a.u.	−97634	−66496	−73785	−72537
(core 40) SD $<$ 50 a.u.	−97625	−66420	−73506	−72270
(core 68) SD $<$ 50 a.u.	−97621	−66407	−73474	−72242
(core 40) SD $<$ 1000 a.u.	−97642	−66429	−73542	−72303
Basis: 4ξ (35s, 30p, 19d, 13f, 5g, 4h, 2i)				
(core 40) SD $<$ 50 a.u.	−97799	−66515	−73851	−72576
$\Delta_{\rm core}$	4	13	32	28
$\Delta_{\rm virt}$	−17	−9	−36	−33
$\Delta_{\rm basis}$	−174	−95	−345	−306
EA (final)	−97986	−66606	−74200	−72887
Uncertainty	−187	−91	−349	−311
NIST[17]	−98232	−67840*	−75272*	−73910*

* derived by EA of $^2{\rm S}_{1/2}$ state adding excited energies.

Table 2 lists the obtained $\Theta(|\gamma J\rangle)$ values by calculations at various levels of hierarchy of the electron correlation. Using the same composite scheme as that for EA, we give the recommended values of $\Theta(|\gamma J\rangle) = 4.980\ (-13)$, $2.050\ (-33)$, and $3.064\ (-44)$ for the $^2{\rm P}_{3/2}$ and $^2{\rm D}_{3/2,5/2}$ states with the uncertainty estimated by sum of the $\Delta_{\rm basis}$, $\Delta_{\rm core}$, and $\Delta_{\rm virt}$ corrections. In contrast to EA, the $\Theta(|\gamma J\rangle)$ value is insensitive to the hierarchy of the electron correlation. The increasing size of the basis sets and the increasing number of the correlated core electrons and virtual orbitals bring very small contribution to the final value of $\Theta(|\gamma J\rangle)$. The $\Theta(|\gamma J\rangle)$ value for the $^2{\rm D}_{3/2}$ state has been measured in considering its application as a clock state.[9] There are several early studies that gave the expectation value of the $\Theta(|\gamma J\rangle)$ for the $^2{\rm D}_{3/2}$ and $^2{\rm D}_{5/2}$ states by using the multi-configuration Dirac–Hartree–Fock (MCDHF) method and the relativistic coupled-cluster (RCC) method.[18–21] Our results for the $^2{\rm D}_{3/2}$ and $^2{\rm D}_{5/2}$ states agree with the measured values and the early theoretical values obtained by the expectation-value method. Besides, we give a recommendation value of $\Theta(|\gamma J\rangle)$ for the $^2{\rm P}_{3/2}$ state which has no reported value available before. The excellent results for the $^2{\rm D}_{3/2}$ and $^2{\rm D}_{5/2}$ states verify the reliability of the finite-field approach adopted for $\Theta(|\gamma J\rangle)$.

Table 2. Values of $\Theta(|\gamma J\rangle)$, in units of a.u., of the $^2{\rm P}_{3/2}$ and $^2{\rm D}_{3/2,5/2}$ states of the Yb^+ ion obtained by using the RCC method.

Level of excitation	$^2{\rm P}_{3/2}$	$^2{\rm D}_{3/2}$	$^2{\rm D}_{5/2}$
Basis: 2ξ (24s, 19p, 13d, 8f, 2g)			
(core 40) SD $<$ 50 a.u.	5.104	2.060	3.048
Basis: 3ξ (30s, 24p, 16d, 11f, 3g, 2h)			
(core 22) SD $<$ 50 a.u.	4.996	2.100	3.129
(core 40) SD $<$ 50 a.u.	5.007	2.116	3.152
(core 68) SD $<$ 50 a.u.	5.009	2.118	3.155
(core 40) SD $<$ 1000 a.u.	5.006	2.114	3.149
Basis: 4ξ (35s, 30p, 19d, 13f, 5g, 4h, 2i)			
	4.993	2.083	3.108
$\Delta_{\rm core}$	0.002	0.002	0.003
Δ_{virt}	−0.001	−0.002	−0.003
$\Delta_{\rm basis}$	−0.014	−0.033	−0.044
$\Theta(\|\gamma J\rangle)$ (final)	4.980	2.050	3.064
Uncertainty	−0.013	−0.033	−0.044
Exp.[9]		2.08	
MCDHF[18]		2.174	3.244
RCC[19]		2.157	
RCC[20]		2.068	3.116
RCC[21]		2.079	

In Table 3 we summarizes the results of ionic potentials (IP) of the 6s $^2{\rm S}_{1/2}$ and 4f $^2{\rm F}_{5/2,7/2}$ electrons of Yb. In calculations labeled by (core 24) SD $<$ 50 a.u., the outer core–shell electrons of the 5s, 5p, 4f, and 6s orbitals and the virtual orbitals with energies below 50 a.u. are correlated. We find that the convergence of the obtained IP values in such calculations is slow when the basis sets increase with $X = 2$, 3, and 4. We estimate the $\Delta_{\rm basis}$ correction by the difference of the obtained IP values of the (core 24) SD $<$ 50 a.u. calculations at $X = 3$ and 4 basis sets, and the $\Delta_{\rm virt}$ correction by the differential IP values between the (core 24) SD $<$ 50 a.u. and (core 24) SD $<$ 1000 a.u. calculations with $X = 3$ basis set. We can find that the largest correction to the IP value arises from the finite size of the basis set. The FSCC calculation of IP of heavy systems usually has a problem of intruder states, which may prevent convergence for one or more sectors. The latter issue can be alleviated but not completely avoided by the use of the intermediate Hamiltonian formalism. When we are trying to include the core–shell electrons more than 24 electrons for

the Yb^+ $^2F_{5/2,7/2}$ states, we found that such an FSCC implementation causes significant underestimation of the IP energy for the current version of dyall's basis set. Therefore, in the present work we cannot identify the role of the electron correlation coming from the larger core–shells. In Table 3 the final IP values for the Yb^+ $^2F_{5/2,7/2}$ states are given in terms of the results obtained by the (core 24) SD < 50 a.u. calculation at the $X = 4$ basis set plus the Δ_{basis} and Δ_{virt} corrections but with the Δ_{basis} correction absent. Such results underestimate the IP values 2%, as compared with the experimental values,[17] which may be attributed to the finite basis size of our adopted basis set.

Table 3. Values of the ionic potentials (IP), in units of a.u., of the $^2S_{1/2}$ and $^2F_{5/2,7/2}$ electrons obtained by using the RCC method.

Level of excitation	$^2S_{1/2}$	$^2F_{7/2}$	$^2F_{5/2}$
Basis: 2ξ (24s, 19p, 13d, 8f, 2g)			
(core 24) SD < 50 a.u.	50292	66390	76913
Basis: 3ξ (30s, 24p, 16d, 11f, 3g, 2h)			
(core 24) SD < 50 a.u.	50534	67722	78281
(core 24) SD < 1000 a.u.	50538	67752	78314
Basis: 4ξ (35s, 30p, 19d, 13f, 5g, 4h, 2i)			
(core 24) SD < 50 a.u.	50657	69190	79691
Δ_{virt}	4	29	33
Δ_{basis}	123	1467	1410
IP (final)	50783	70687	81134
Uncertainty	126	1497	1443
NIST[17]	50443	71861*	82011*

* derived by IP of $^2S_{1/2}$ state adding excited energies.

Table 4. Values of $\Theta(|\gamma J\rangle)$, in units of a.u., of the $^2F_{5/2,7/2}$ states of the Yb^+ ion obtained by using the RCC method.

Level of excitation	$^2F_{7/2}$	$^2F_{5/2}$
Basis: 2ξ (24s, 19p, 13d, 8f, 2g)		
(core 24) SD < 50 a.u.	−0.059	−0.057
Basis: 3ξ (30s, 24p, 16d, 11f ,3g, 2h)		
(core 24) SD < 50 a.u.	−0.059	−0.057
(core 24) SD < 1000 a.u.	−0.059	−0.057
Basis: 4ξ (35s, 30p, 19d, 13f, 5g, 4h, 2i)		
(core 24) SD < 50 a.u.	−0.059	−0.058
Δ_{virt}	< 0.001	< 0.001
Δ_{basis}	< 0.001	−0.001
$\Theta(|\gamma J\rangle)$ (Final)	−0.059	−0.059
Uncertainty	< 0.001	−0.001
Exp.[2]	−0.041	
Rough values based on CI + MBPT[8]	−0.1	
RCC[20]	−0.216	−0.177
RCC[21]	−0.224	

Table 4 summarizes the results of $\Theta(|\gamma J\rangle)$ for the Yb^+ $^2F_{5/2,7/2}$ states. The (core 24) SD < 50 a.u. calculations are conducted with the $X = 2$, 3, and 4 basis sets. Upon the increasing sizes of the basis sets, the $\Theta(|\gamma J\rangle)$ value for both F-states show excellent convergence. The changes of the $\Theta(|\gamma J\rangle)$ values for the Yb^+ $^2F_{5/2,7/2}$ states with more correlated virtual orbitals are negligibly small. Finally, the $\Theta(|\gamma J\rangle)$ values for the Yb^+ $^2F_{5/2,7/2}$ states are determined to be −0.059 (1). Our results are in the line with the measured values −0.041,[2] but still having about 20% deviation. Our results are also close to the Porsev, *et al.*'s guess value −0.1, based on their configuration interaction plus many-body perturbation theory (CI + MBPT) method,[8] however it is significant different from the early theoretical data, −0.216 and −0.224, calculated by using the RCC expectation value method.[20,21]

4. Conclusion

In conclusion, we have performed the FF method on the FSCC level of theory to calculate the $\Theta(|\gamma J\rangle)$ values of the low-lying $^2P_{3/2}$, $^2D_{3/2,5/2}$, $^2F_{5/2,7/2}$ states of the Yb^+ ion. The standard Dyall's basis sets of varying size are adopted. In order to study the effects of the electron correlation on $\Theta(|\gamma J\rangle)$, we have investigated the sensitivity of $\Theta(|\gamma J\rangle)$ to various computational parameters, *i.e.*, the size of the basis sets, the number of correlated electrons, and the chosen virtual energy cutoff, allowing us to estimate the uncertainty of our results. The $\Theta(|\gamma J\rangle)$ values of the $^2D_{3/2}$ and $^2F_{7/2}$ states have been measured for their application in the E2 and E3 clock transitions, and there are also early theoretical studies by using the expectation-value method. For the $^2D_{3/2}$ state, the expectation-value method gives the consistent results with the experimental measurements, while for the $^2F_{7/2}$ states, there is large discrepancy between the measured and the expectation-value theoretical values. The insufficient electron correlation effect and lack of the response of wavefunction to the external field were supposed to be the reason for such a dispute. By combining FSCC with the FF approach, we obtained the values of the electric quadrupole moments of the D and F states that both show excellent agreement with the measured results. The theoretical $\Theta(|\gamma J\rangle)$ values of the $^2P_{3/2}$, $^2D_{3/2,5/2}$, and $^2F_{5/2,7/2}$ states can be used to estimate the related electric quadruple shift in the Yb^+ experiments.

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