Transition frequency shifts with fine-structure constant variation for Yb II

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In this paper we report calculations of the relativistic corrections to transition frequencies (q factors) of Yb II for the transitions from the odd-parity states to the metastable state $^2F_{7/2}$. These transitions are of particular interest experimentally since they possess some of the largest $q$ factors calculated to date and the $^2F_{7/2}$ state can be prepared with high efficiency. This makes Yb II a very attractive candidate for the laboratory search for variation of the fine-structure constant $\alpha$.

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I. INTRODUCTION

A discovery of acceleration of the universe (see, e.g., [1]) is usually associated with the existence of the dark energy. The latter, according to the theories describing cosmological evolution, may be a reason of variations of the fundamental constants. There is an on-going discussion in the literature whether the fine-structure constant could change during evolution of the universe or not. The Australian group reported in [2] a nonzero result while other astrophysical groups do not confirm it [3, 4]. But as it was argued in [5], a more thorough analysis of the data used in [4] also leads to a nonzero result. New laboratory and astrophysical investigations are in progress.

Laboratory studies of hypothetical variation of the fine-structure constant are based on the fact that transition frequencies in atoms depend on $\alpha Z$, where $Z$ is the atomic number. Supposing that the modern value of $\alpha$ differs from its value in the earlier universe we can find relativistic transition frequencies shifts, determined by so-called $q$ factors, according to

$$\omega = \omega_{lab} + qx, \quad x \equiv \left(\alpha/\alpha_{lab}\right)^2 - 1. \quad (1)$$

Most advantageous for these studies are the atoms and ions for which $q$ factors of transitions between certain states significantly differ from each other.

In [6], it was proposed to use transitions whose $q$ factors are large and of opposite sign for laboratory measurements. In particular, it was shown that a good choice for an experiment would be Hg$^+$ because the $q$ factor of the transition from the ground state to the low-lying $^2D_{5/2}$ state is very large and negative. There are two main considerations for the choice of a second transition for a comparison: 1) it should be convenient for an experiment; 2) its $q$ factor should be small or positive because the measured quantity is proportional to the difference of $q/\omega$ of the transitions being compared.

At present the best laboratory constraint on the temporal variation of $\alpha$ of $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17}$/year was obtained by Rosenband et al. in Ref. [7] by comparing the frequencies of the $^1S_0 \to ^3P_0^o$ transition in $^{27}$Al$^+$ and the $^2S_{1/2} \to ^2D_{5/2}$ transition in $^{199}$Hg$^+$. In this paper we propose to use Yb II for future experiments because there are several transitions whose wavelengths can be synthesized with modern laser technologies and whose $q$ factors are very large and of opposite signs.

Yb II has two low-lying metastable states $4f^{14}5d^2^2D_{5/2}$ (24333 cm$^{-1}$) and $4f^{13}6s^2^2F_{7/2}$ (21419 cm$^{-1}$) decaying to the ground state $4f^{14}5s^2^2S_{1/2}$ through electric quadrupole and electric octupole transitions, correspondingly. The $q$ factors of the $^2D_{5/2}$ and $^2F_{7/2}$ states in respect to the ground state $^2S_{1/2}$ were calculated in [6, 8, 9]. For the former $q \approx 10000$ cm$^{-1}$ and for the latter $q \approx -60000$ cm$^{-1}$. In this work we carry out calculation of the $q$ factors for certain experimentally interesting odd-parity states with respect to the metastable state $4f^{13}6s^2^2F_{7/2}$. Combining the results obtained in this work with the results presented in [6, 8, 9], we can easily find $q$ factors ranging from $-60000$ cm$^{-1}$ to $+75000$ cm$^{-1}$ associated with experimentally accessible transitions. This observation can potentially increase the sensitivity of the measurements for Yb II to $\alpha$ variation by more than a factor of two compared to all previously considered comparisons and makes this ion a very good candidate to establish a record constraint on $\alpha$ variation in laboratory studies.

The paper is organized as follows. Sec. II is devoted to the method of calculation of the properties of Yb II. In Sec. III we discuss results and the experimental possibilities. Sec. IV contains concluding remarks. Atomic units ($\hbar = |e| = m_e = 1$) are used throughout the paper.
II. METHOD OF CALCULATION

To find $q$ factors we need to solve the atomic relativistic eigenvalue problem for different values of $\alpha$ or, respectively, for different values of $x$ from Eq. 11. The value of $x$ can be chosen somewhat arbitrarily, but two conditions should be satisfied. It should be sufficiently small to neglect nonlinear corrections and sufficiently large to make calculations numerically stable. Our experience shows that the choice of $|x| = 1/8$ allows us to meet both conditions.

Thus, we have to calculate atomic frequencies $\omega_{\pm}$ for two values $x = \pm 1/8$ of the parameter $x$. The corresponding $q$ factor is given by

$$q = 4(\omega_+ - \omega_-).$$

(2)

The ground state configuration of Yb II is $(1s^2...4f^{14}6s^2)$. The configuration of the first excited state of Yb II is $(1s^2...4f^{14}6s^2)$. This is a metastable state because there is only weak (E3) transition from this state to the ground state. For experimental purposes this metastable state lives sufficiently long to be treated as a “ground” state. Since we are interested in calculation of $q$ factors with respect to the metastable state with the open $f$ shell, we have to treat Yb II as an ion with 15 electrons above closed shells. This makes calculations of Yb II rather complicated.

In this paper we have carried out pure ab initio calculations in the frame of the fifteen-electron CI method. The $(1s^2...5p^6)$ electrons are treated as core electrons while $4f$, $6s$, and $5d$ electrons are in the valence space.

We started by solving the Dirac-Hartree-Fock (DHF) equations. The self-consistency procedure was done for $(1s^2...4f^{14}6s^2)$ configuration. After that, the $5d_{3/2}$ and $5d_{5/2}$ orbitals were constructed as follows: all electrons were frozen and one electron from the $6s$ shell was moved to the $5d$ shell, thus constructing the valence orbitals $5d_{3/2}$ and $5d_{5/2}$ for the $4f^{13}5d6s$ configuration.

In the next stage, we constructed virtual orbitals using the method described in Eq. 11 and applied by us for calculating different properties of Fe I and Fe II. In this method, an upper component of virtual orbitals is formed from the previous orbital of the same symmetry by multiplication by some smooth function of radial variable $r$. The lower component is then formed using the kinetic balance condition.

Our basis sets included $s$, $p$, $d$, and $f$ orbitals with principle quantum number $n \leq N_{i,2}$ which we designate as $[N_1 sp N_2 df]$. We carried out the calculations of energy levels, $g$, and $r$ factors in a one-configurational (DHF) approximation and for two basis sets with $(N_1 = 7$ and $N_2 = 5$) and $(N_1 = 8$ and $N_2 = 6$). Configuration space was formed with single and double excitations from the configurations $4f^{13}6s^2$, $4f^{13}5d6s$, and $4f^{13}5d^2$. All results which we discuss below are obtained in the pure Coulomb approximation (i.e., the Breit interaction was not included).

III. RESULTS AND DISCUSSION

The results of the 15-electron CI calculations of the frequencies in respect to the metastable state $4f^{13}5d^2 F_{7/2}$ were obtained in the DHF approximation and for the basis sets $[7sp5df]$ and $[8sp6df]$. These results are given in Table I.

As is seen from the table, the values found for the $[7sp5df]$ basis set are in a good agreement with the experimental frequencies. For low-lying states this agreement is at the level of a few percent. For higher-lying levels the agreement is slightly worse but does not exceed 10%. The reason is that the configuration interaction is more significant for the high-lying states, as can be seen by comparison of the results obtained for the $[7sp5df]$ and $[8sp6df]$ basis sets. For the $[8sp6df]$ basis set an agreement between theoretical and experimental values for the high-lying states belonging to the configuration $4f^{13}5d^2$ becomes much better. Note that the configuration space constructed for the $[8sp6df]$ basis set included $\sim 200000$ determinants and the calculations of energies were rather lengthy and time-consuming for this basis so a further increase of the configuration space is impractical.

At the same time, as it follows from Tables II and...
TABLE II: The fifteen-electron CI calculations of g factors for different basis sets. The Dirac-Coulomb Hamiltonian in the frozen-core approximation is used. The experimental data presented in the last row are taken from [14].

| Config. | Term | J | DHF [7sp5df] | [8sp6df] | Exp. |
|---------|------|---|--------------|----------|------|
| $4f^{13}(2p^6)6s^2$ | $^2P^o$ | 7/2 | 1.143 | 1.143 | 1.145 |
| $4f^{13}(2p^6)6s^3$ | $^4P^o$ | 9/2 | 0.934 | 0.933 | 0.933 | 0.935 |
| $4f^{13}(2p^6)5d^6s$ | $^3[11/2]^o$ | 11/2 | 1.122 | 1.121 | 1.121 | 1.112 |
| $4f^{13}(2p^6)5d^6s$ | $^3[11/2]^o$ | 11/2 | 1.122 | 1.121 | 1.121 | 1.112 |
| $4f^{13}(2p^6)5d^6s$ | $3[7/2]^o$ | 7/2 | 1.377 | 1.375 | 1.371 | 1.331 |
| $4f^{13}(2p^6)5d^6s$ | $3[9/2]^o$ | 7/2 | 1.296 | 1.286 | 1.278 | 1.264 |
| $4f^{13}(2p^6)5d^6s$ | $1[11/2]^o$ | 11/2 | 1.093 | 1.195 | 1.131 | 1.119 |
| $4f^{13}(2p^6)5d^6s$ | $3[9/2]^o$ | 9/2 | 1.132 | 1.140 | 1.147 | 1.158 |
| $4f^{13}(2p^6)5d^6s$ | $3[7/2]^o$ | 7/2 | 1.048 | 1.066 | 1.084 | 1.124 |
| $4f^{13}(2p^6)5d^6s$ | $3[9/2]^o$ | 11/2 | 1.244 | 1.143 | 1.206 | 1.214 |
| $4f^{13}(2p^6)5d^6s$ | $3[7/2]^o$ | 7/2 | 1.130 | 1.120 | 1.121 | 1.119 |
| $4f^{13}(2p^6)5d^6s$ | $3[5/2]^o$ | 7/2 | 0.720 | 0.720 | 0.718 | 0.720 |
| $4f^{13}(2p^6)5d^6s$ | $3[9/2]^o$ | 9/2 | 0.984 | 0.983 | 0.982 | 0.967 |
| $4f^{13}(2p^6)5d^6s$ | $3[9/2]^o$ | 11/2 | 1.127 | 1.128 | 1.129 | 1.115 |
| $4f^{13}(2p^6)5d^6s$ | $3[5/2]^o$ | 7/2 | 1.002 | 1.020 | 1.045 | 1.10 |
| $4f^{13}5d^2$ | $^o$ | 7/2 | 1.295 | 1.297 | 1.277 | 1.18 |
| $4f^{13}(2p^6)5d^6s$ | $1[9/2]^o$ | 9/2 | 0.945 | 0.993 | 1.000 | 1.01 |
| $4f^{13}(2p^6)5d^6s$ | $3[7/2]^o$ | 7/2 | 1.168 | 1.158 | 1.144 | 1.150 |
| $4f^{13}(2p^6)5d^6s$ | $3[7/2]^o$ | 9/2 | 1.147 | 1.092 | 1.086 | 1.10 |
| $4f^{13}(2p^6)5d^6s$ | $3[7/2]^o$ | 9/2 | 1.311 | 1.310 | 1.309 | 1.29 |
| $4f^{13}(2p^6)5d^6s$ | $3[13/2]^o$ | 11/2 | 0.957 | 0.955 | 0.955 | 0.97 |

III where the results for g and q factors are presented, both these quantities are rather insensitive to the size of the configuration space. Using the experimental g factors and comparing them with the calculated ones, we are able to identify properly the calculated energy levels. For the majority of the calculated levels there is a very satisfactory agreement between theoretical and experimental g factors. This means that the configuration interaction is represented in a proper way for these states and also means that the q factors obtained for them are correct.

Comparing the values of g and q factors obtained for the [7sp5df] and [8sp6df] basis sets, we see that almost all of them agree to each other at the level of few per cent. An exception is the levels with J = 11/2 belonging to the terms $^3J[11/2]^o$ and $^3J[9/2]^o$. These two states are closer in the [7sp5df] basis set approximation than in real experimental data so as to result in an artificial mixing of these levels and, consequently, to a change in their g and q factors.

As is seen from Table III the levels belonging to the $4f^{13}5d^2$ configuration have the largest q factors. This is not surprising because this configuration differs by two electrons from the configuration of the metastable state $4f^{13}6s^2$. When the fine structure constant $\alpha$ tends to its nonrelativistic limit, one-electron energies of the 6s and 5d levels change in different directions, which leads to an increase of the q factors. Note in this respect that the high-lying levels which nominally belong to the $4f^{13}6s5d$ configuration have (in reality) a rather large admixture of the $4f^{13}5d^2$ configuration. As a consequence their q factors are also large.

We can estimate the accuracy of the calculated q factors as a difference between the largest and smallest values (in each line) listed in Table III for three basis sets. Such a conservative estimate shows that the accuracy of our calculations is not worse than 10%. In Table IV we present the recommended values of the q factors found in this work. For future reference, we also list in the table the q factors of the lowest-lying even-parity $4f^{14}5d^2D_{3/2,5/2}$ states and the $4f^{13}6s^2\ 2F_{7/2}$ state found in Refs. [8, 9]. These values were obtained with respect to the ground state. Using the q factors found in this work with respect to the metastable state and $q(2F_{7/2})$ obtained in [8, 9] with respect to the ground state, it is easy to recalculate the q factors presented in Table III with respect to the ground state. It can be done just by subtracting $q(2F_{7/2})$ from these q factors because for positive $\omega = \omega_1 - \omega_2$ the value of q is equal to $(q_1 - q_2)$.

Experimentally one can search for a variation of $\alpha$ by comparing two frequencies of atomic transitions over a long period of time. Following the Ref. [8] we can repre-
sent a measured quantity $\Delta(t)$ as

$$\Delta(t) = \frac{d}{dt} \left( \ln \frac{\omega_1}{\omega_2} \right) = \frac{\omega_1}{\omega_1} - \frac{\omega_2}{\omega_2},$$

(3)

where $\dot{\omega} = d\omega/dt$. Taking into account Eq. (1) we can rewrite Eq. (3) as follows

$$\Delta(t) \approx \left( \frac{2q_1}{\omega_1} - \frac{2q_2}{\omega_2} \right) \left( \frac{\dot{\alpha}}{\alpha_{\text{lab}}} \right).$$

(4)

Of particular interest experimentally are narrow transitions with large $q$ values. Many of these exist from the $^2F^o_{7/2}$ metastable state to higher-lying states with wavelengths which can be synthesized with modern laser technologies. As is seen in Table IV a very large $\Delta(t)$ can be expected if the frequencies of the $4f^{14}5d^2D_{3/2}$ (22961 cm$^{-1}$) – $4f^{13}6s^2^2F^o_{7/2}$ (21419 cm$^{-1}$) and $4f^{14}6s^2^2S_{1/2}$ (the ground state) – $4f^{13}6s^2^2F^o_{7/2}$ (21419 cm$^{-1}$) transitions are compared. The $q$ factor of the former ($q_1$) is positive ($q_1 \approx 71000$ cm$^{-1}$) and the $q$ factor of the latter ($q_2$) is negative ($q_2 \approx -60000$ cm$^{-1}$). The transition $4f^{13}6s^2^2F^o_{7/2}$ – $4f^{14}5d^2D_{5/2}$ has nearly the same $q$ value as the $4f^{13}6s^2^2F^o_{7/2}$ – $4f^{14}5d^2D_{3/2}$ transition and the necessary wavelength at 3.4 $\mu$m is somewhat easier to synthesize than the 6.5 $\mu$m to the $^2D_{3/2}$ state. Another consideration is that the transition to $^2D_{3/2}$ at 6.5 $\mu$m is forbidden for even isotopes, but is weakly allowed through the hyperfine interaction within odd isotopes. In either case, transitions from $m_F = 0 \rightarrow m'_F = 0$ in odd isotopes are preferred due to the smaller (and quadratic) Zeeman shift to the transitions relative to the linear shift within the even isotopes.

Substituting the $q$ values into Eq. (4) for the two most sensitive transitions described above, and using the estimate $|\dot{\alpha}/\alpha_{\text{lab}}| < 10^{-16}$ yr$^{-1}$ [2] we find

$$\Delta(t) < 10^{-14} \text{ yr}^{-1}.$$

(5)

It is worth noting that a presence of transitions for which the $q$ factors are very large and have opposite sign is favorable. First, it leads to increasing $\Delta(t)$ (as it follows from Eq. (3)) and, second, allows better control of some systematic errors that are not correlated with signs and magnitudes of the frequency shifts.

It is also important to see that transitions from the $4f^{13}6s^2^2F^o_{7/2}$ state to higher-lying states with $J > 7/2$ possess more easily synthesized wavelengths. States with $J > 7/2$ with energies less than 48000 cm$^{-1}$ are most likely all metastable since there are no even-parity states with $J > 5/2$ below this energy. The $q$-factors are somewhat lower, but this consideration may be outweighed by practical considerations such as available sources of narrowband laser light. The value of $\Delta(t)$ for a comparison between $4f^{14}6s^2^2S_{1/2} - 4f^{13}6s^2^2F^o_{7/2}$ and one of these transitions is still significantly greater than any other comparison considered to date.

Preparation of the metastable state $4f^{13}6s^2^2F^o_{7/2}$ has already been performed in the laboratory by several groups including one of us (JRT). One of the simplest schemes to populate this state is from the $^2D_{3/2}$ state at 22961 cm$^{-1}$ which is populated by spontaneous decay from $^2P^o_{1/2}$ at 27062 cm$^{-1}$; the upper state of the most accessible laser cooling transition. Transitions from $^2D_{3/2}$ at 861 nm, 1062 nm and 1163 nm can all be used with varying efficiencies. For example, we have used a simple external cavity diode laser at 861 nm to prove the technique. For any of these wavelengths, state preparation is limited by the 5 ms lifetime of the $^2D_{5/2}$ state at 24333 cm$^{-1}$.

IV. CONCLUSION

We have calculated relativistic frequency shifts ($q$ factors) for a number of transitions from excited states of Yb II to the metastable state $4f^{13}6s^2^2F^o_{7/2}$ state. We found that all these $q$ factors are large (10$^4$ cm$^{-1}$) and positive. The $q$ factor for the transition $^2S_{1/2} - ^2F^o_{7/2}$ is very large and negative. Because the $^2F^o_{7/2}$ state is convenient for an experiment and can be prepared with high efficiency, we conclude that Yb II is a very good candidate for the laboratory search for possible variation of the fine-structure constant $\alpha$.

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TABLE IV: The recommended values of the $q$-factors (in cm$^{-1}$) found in this work with respect to the $4f^{13}6s^2\,2F_7/2$ state and the $q$ factors found in Refs. [6, 8, 9] with respect to the ground state $4f^{14}6s \,2S_{1/2}$.

| Config. | Term | $J$ | This work | Ref. [9] | Ref. [8] | Ref. [6] |
|---------|------|-----|-----------|---------|---------|---------|
| $4f^{14}5d$ | $^2D$ | 3/2 | 10118 | 12582 |
| | $^2D$ | 5/2 | 10397 | 11438 |
| $4f^{13}(2F^o)6s^2$ | $^2F^o$ | 7/2 | -63752 | -56737 |
| $4f^{13}(2F^o)5d6s$ | $^3[11/2]^o$ | 9/2 | 14100 |
| | $^3[11/2]^o$ | 11/2 | 14500 |
| | $^3[11/2]^o$ | 13/2 | 15400 |
| | $^3[5/2]^o$ | 7/2 | 14200 |
| | $^3[7/2]^o$ | 9/2 | 14400 |
| | $^3[9/2]^o$ | 7/2 | 14500 |
| | $^1[11/2]^o$ | 11/2 | 16600 |
| | $^3[9/2]^o$ | 9/2 | 15300 |
| | $^3[7/2]^o$ | 7/2 | 15400 |
| | $^3[9/2]^o$ | 11/2 | 16000 |
| | $^1[7/2]^o$ | 7/2 | 17700 |
| $4f^{13}(2F^o)5d6s$ | $^3[9/2]^o$ | 9/2 | 17600 |
| $4f^{13}(2F^o)5d6s$ | $^3[9/2]^o$ | 7/2 | 23100 |
| | $^3[9/2]^o$ | 9/2 | 23700 |
| | $^3[9/2]^o$ | 11/2 | 24800 |
| $4f^{13}(2F^o)5d6s$ | $^3[5/2]^o$ | 7/2 | 24400 |
| $4f^{13}5d^2$ | $^3[9/2]^o$ | 9/2 | 25900 |
| $4f^{13}(2F^o)5d6s$ | $^3[7/2]^o$ | 7/2 | 24000 |
| $4f^{13}(2F^o)5d6s$ | $^3[7/2]^o$ | 9/2 | 25500 |
| $4f^{13}(2F^o)5d^2$ | $^3[7/2]^o$ | 9/2 | 27600 |
| $4f^{13}(2F^o)5d^2$ | $^3[13/2]^o$ | 11/2 | 26600 |

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