Using optical clock transitions in Cu II and Yb III for time-keeping and search for new physics

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We study the $^1S_0-^3D_2$ and $^1S_0-^3D_3$ transitions in Cu II and the $^1S_0-^3P_2$ transition in Yb III as possible candidates for the optical clock transitions. A recently developed version of the configuration (CI) method, designed for a large number of electrons above closed-shell core, is used to carry out the calculation. We calculate excitation energies, transition rates, lifetimes, scalar static polarizabilities of the ground and clock states, and blackbody radiation shift. We demonstrate that the considered transitions have all features of the clock transition leading to prospects of highly accurate measurements. Search for new physics, such as time variation of the fine structure constant, is also investigated.

I. INTRODUCTION

Extremely high accuracy of the frequency measurements for the optical clock transitions naturally lead to the use of the transitions not only for time keeping but also for the search of the manifestations of new physics beyond the standard model, such as local Lorentz invariance (LLI) violation and time variation of the fine structure constant ($\alpha = e^2/\hbar c$) (see, e.g. \cite{1–8}). Oscillating variation of the fine structure constant may be produced by interaction of low mass scalar dark matter field with photon field (see, e.g., Refs. \cite{9–13}). Therefore, the measurement of such variation provides an efficient method to search for dark matter using atomic clocks, which have already provided improvement of the constraints on the scalar - photon interaction constants up to 15 orders of magnitude \cite{9,12}.

The relative uncertainty of the frequency measurements for the best optical clocks is on the level of $10^{-18}$. For example, it is $9.4 \times 10^{-19}$ for Al\textsuperscript{3+} \cite{4}, $3.0 \times 10^{-18}$ for Yb\textsuperscript{2+} \cite{6}, and $1 \times 10^{-18}$ for Yb \cite{14}. Unfortunately, most of working optical clocks are not very sensitive to new physics. Among the examples listed above, only Yb\textsuperscript{2+} clock transition is highly sensitive to variation of the fine structure constant \cite{2,12,16} and to the LLI violation \cite{2,17}. Therefore, there is an ongoing search for new clock transitions which may combine high accuracy of the measurements with high sensitivity to new physics, e.g., to the time variation of the fine structure constant. One way of achieving this is to use highly charged ions \cite{15}. This is now a large area of research with very promising perspectives (see, e.g. \cite{19,21}).

Neutral or nearly neutral atoms are also considered. The important advantage of using them is that they are very well studied. In some cases, new promising transitions can be found in atoms that are already used for a high accuracy atomic clock. E.g., new transitions in Yb were recently suggested \cite{22,23} in addition to the currently used the $^1S_0-^3P_0$ clock transition. Clock transitions between metastable states in Yb II have been suggested in \cite{24}. A good guide for finding atomic clock transitions sensitive to variations of $\alpha$ is to look for metastable states which are connected to the ground state via transitions that can be approximately considered as $s-d$, $s-f$ or $p-f$ single-electron transitions \cite{25}. The $s-d$ transitions of this kind were considered in Cu, Ag and Au atoms in Ref. \cite{26}.

In the present paper, we consider the $^1S_0-^3D_2$ and $^1S_0-^3D_3$ transitions in Cu II and the $^1S_0-^3P_2$ transition in Yb III (see Figs. 1 and 2). Transitions in Cu II are the $s-d$ transitions, the transition in Yb III is the $s-f$ transition. In our early work \cite{15}, we suggested to use the $4f^{13}1s_0-4f^{13}5d_0$ transition in Yb III for the search of the variation of the fine structure constant. The prospect for precision measurement of the frequency of this transition was considered in a recent paper \cite{27}. However, this transition has an important drawback. There is a decay channel via magnetic dipole transition (M1) into lower-lying state $4f^{13}5d_0$. This may make the considered transition to be not sufficiently narrow to ensure high accuracy of the measurements. This problem was not discussed in \cite{15} or \cite{27}. In the present paper, we consider a different transition, a transition from the ground state to the first excited state $4f^{13}5d_0(\frac{7}{2}, \frac{3}{2})$. This is a very narrow transition with a similar sensitivity to the variation of the fine structure constant. We demonstrate that it has all features of the atomic clock transition.

Several studies have analyzed the energies and transition probabilities for both ions, Cu II \cite{28,31} and Yb III \cite{31,32} theoretically and experimentally (see also \cite{40} and references therein). This gives us an opportunity to compare results to have confidence in the accuracy of the analysis. None of the previous studies focused on transitions in Cu II and Yb III in sufficient details to study their suitability for time-keeping and searching for new physics.

II. METHOD OF CALCULATION

As can be seen from the spectra of the Cu II and Yb III ions, the excited states of the Cu II ion have an open 3d shell and the excited states of the Yb III ion have
The eigenvalues \( E \) and eigenstates \( \psi \) can be found by solving the CI equations with the effective \( H^{CI} \) matrix

\[
(H^{CI} - EI) \psi = 0, \tag{1}
\]

where \( I \) is the unit matrix. Matrix elements of the effective CI matrix contain PT-type corrections from the high-energy states

\[
\langle a|H^{CI}|b \rangle \rightarrow \langle a|H^{CI}|b \rangle + \sum_h \frac{\langle a|H^{CI}|h \rangle \langle h|H^{CI}|b \rangle}{E_h - E}, \tag{2}
\]

Here \( a \) and \( b \) are low-energy states, and \( E_h \) is the diagonal matrix element between high-energy states, \( (E_h = \langle h|H^{CI}|h \rangle \delta_h) \). To produce a set of complete single-electron basis states for both ions, we start the calculations with the Dirac-Hartree-Fock (DHF) method in the

\[V^N\] approximation with all atomic electrons included. It seems to be natural to start from the \([\text{Ar}]3d^{10}\) configuration for Cu II and the \([\text{Xe}]4f^{14}\) configuration for Yb III. However, such a choice of initial approximation is good for calculating the ground states of the ions. Since we need to calculate excited states as well, which have excitations from the 3d or 4f subshell, the choice of initial approximation is not obvious, and it is dictated by the accuracy of the final results. It turns out that the best results are obtained if we start from the \([\text{Ar}]3d^9\) configuration for Cu II and the \([\text{Xe}]4f^{13}\) configuration for Yb III.

The single-electron basis states are then constructed using B-splines \([31,32]\) with forty B-splines states of the order \( k=9 \) in a box of the radius \( R_{\text{max}} = 40a_B \) with orbital angular momentum \( 0 \leq l < 4 \).

To carry out the calculations of the transition amplitudes and hyperfine structure (hfs), we use the time-dependent Hartree-Fock (TDHF) method \([30]\), which is equivalent to the random-phase approximation (RPA). The RPA equations can be written as

\[
(H^{RHF} - \epsilon_c)\delta \psi_c = -(\hat{d} + \delta V^N)\psi_c. \tag{3}
\]

Here \( \hat{d} \) refers to the operator of an external field, which can be any field, which is sufficiently weak to be considered in linear approximation. \( \epsilon_c \) is the energy of electron state \( c, \psi_c \) is the state wave function, and \( \delta V^N \) denotes the correction to the self-consistent potential caused by
the effect of an external field. Equations (3) are solved self-consistently for all states $c$ in the core. Then matrix elements for valence states are calculated using the expression

$$A_{b\rightarrow a} = \langle \psi_a | \hat{d} + \delta V^N | \psi_b \rangle.$$  (4)

The electric dipole (E1), magnetic dipole (M1), electric quadrupole (E2), magnetic quadrupole (M2), and electric octupole (E3) transition probabilities (in atomic units) from upper state $b$ to lower state $a$ can be written as

$$T_{E1,M1} = \frac{4}{3} (\alpha \omega)^3 \frac{A_{E1,M1}^2}{2J_b + 1},$$  (5)

$$T_{E2,M2} = \frac{1}{15} (\alpha \omega)^5 \frac{A_{E2,M2}^2}{2J_b + 1},$$  (6)

$$T_{E3} = 0.00169 (\alpha \omega)^7 \frac{A_{E3}^2}{2J_b + 1}.$$  (7)

Here $\alpha$ is the fine structure constant, $\omega$ is the energy difference between the lower and upper states, $A$ is the transition amplitude (3), $J_b$ is the total angular momentum of the upper state $b$. Note that magnetic amplitudes $A_{M1,M2}$ contain the Bohr magneton $\mu_B$ ($\mu_B = \alpha/2 \approx 3.65 \times 10^{-3}$ in atomic units). For some strongly forbidden transitions leading contribution comes from electromagnetic transitions mediated by the hyperfine interaction. Clock transitions in $^{63,65}$Cu II and $^{171,173}$Yb III are good examples of such transitions. The transition amplitude is

$$A_{\text{hfs--E1,E2}}(b \rightarrow a) = \sum_n \left( \frac{\langle a | A_{\text{hfs}} | n \rangle \langle n | A_{E1,E2} | b \rangle}{\Delta E} \right) + \left( \frac{\langle b | A_{\text{hfs}} | n \rangle \langle n | A_{E1,E2} | a \rangle}{\Delta E} \right).$$  (8)

Here $A_{\text{hfs}}$ is the operator of the magnetic dipole or electric quadrupole hfs interaction, and $A_{E1,E2}$ are the operators of the E1 and E2 transitions. Summation in (8) goes over a complete set of intermediate states $| n \rangle$ (for more details, see, e.g., 29, 37, 38). In practice, it is usually sufficient to include few close states into the summation over $n$. For example, the leading contribution to the transition amplitude of the $^{1}S_0$ -- $^{3}D_3$ clock transition in Cu II comes from the electric quadrupole transition mediated by the magnetic dipole hfs interaction. It is sufficient to include three intermediate states into the summation, the $3d^94s$ $^{3}D_2$, $^{1}D_2$, and $^{3}D_1$ states. Then Eq. (8) becomes

$$A_{\text{hfs--E2}}(3d^94s ~^{3}D_3 \rightarrow 3d^{10} ~^{1}S_0) =$$

$$\frac{(^{3}D_3 | \hat{H}_{\text{hfs}} | ^{3}D_2) (^{3}D_2 | \hat{E}_2 | ^{1}S_0)}{\Delta E} +$$

$$\frac{(^{3}D_3 | \hat{H}_{\text{hfs}} | ^{1}D_2) (^{1}D_2 | \hat{E}_2 | ^{1}S_0)}{\Delta E} +$$

$$\frac{(^{3}D_1 | \hat{E}_2 | ^{3}D_1) (^{3}D_1 | \hat{H}_{\text{hfs}} | ^{1}S_0)}{\Delta E}.$$  (9)

For the 2-1 clock transition in the Yb III ion, the hyperfine-induced E1 transition amplitude is expressed as

$$A_{\text{hfs--E1}}(4f^{13}5d ~^{3}P_0^0 \rightarrow 4f^{14} ~^{1}S_0) =$$

$$\frac{(^{3}P_0^0 | \hat{H}_{\text{hfs}} | ^{3}P_0^0) (^{3}P_0^0 | \hat{E}_1 | ^{1}S_0)}{\Delta E}.$$  (10)

To find corresponding transition rates, we use Eq. (5, 6), replacing $A_{E1}$ by $A_{\text{hfs--E1}}$ in Eq. (5), and $A_{E2}$ by $A_{\text{hfs--E2}}$ in Eq. (6).

Radiative lifetimes $\tau_b$ of each excited state $b$ can be obtained as

$$\tau_b = 1/ \sum_a T_{ab}.$$  (11)

where summation goes over all possible transitions to lower states $a$.

III. RESULTS

A. Energy levels, transition probabilities, and lifetimes.

Table I presents calculated energy levels and lifetimes of the low-energy states of Cu II and Yb III ions compared with experimental data and other calculations. The lifetimes were calculated using transition probabilities presented in Table II. The results for the energies are in sufficiently good agreement with experimental data from NIST. The average difference between the NIST and calculated data for Cu II is $\sim 100$ cm$^{-1}$, while for Yb III, the difference is $\sim 4000$ cm$^{-1}$. Note that different sources present different state labeling for Yb III (see, e.g., 27, 40). Therefore, for the sake of easy comparison, we present in the table state labeling based on both commonly used schemes, the $J$ -- $J$ and $L$ -- $S$ schemes.

Table I presents calculated transition amplitudes and transition rates and compares them to the experimental data and other theoretical values. Lifetimes of the states calculated using transition rates from Table I are presented in Table II. As can be seen from the tables, the present results for the Cu II ion are in good agreement with the experimental data and other calculations. For the transition between the first excited state $3d^{9}4s$ $^{3}D_3$ and the ground state, the dominating contribution comes from the hfs-induced electric quadrupole transition (see Eq. (3)). This transition was studied before in Ref. 29 using the same strategy. However, the authors calculated the transition rates separately for different hfs components of the states. Their results for transition rates for $^{63,65}$Cu II for different values of the total angular momentum $F$ ($F = J + I$, where $I$ is unclear spin) range between $(3.10 \times 10^{-12} - 4.29 \times 10^{-9}$ s$^{-1}$) and $(3.19 \times 10^{-12} - 1.06 \times 10^{-8}$ s$^{-1}$), respectively, indicating good agreement with our calculations.
The present results are compared three times (see Table I). The significant contribution into the transition rate, and this core polarisation (CP) effect.

For the transition rates of Yb III ion, we compared our results with the theoretical values of Safronova et al. They carried out theoretical calculations using the second-order relativistic many-body perturbation theory (RMBPT). The results are in reasonably good agreement with our calculations. The most noticeable disagreement is about two times difference in the 2 transition rate between the clock and ground states.

TABLE I. Excitation energies (E, cm$^{-1}$) and lifetimes ($\tau$) for some low states of Cu II and Yb III ions.

| N   | Conf.   | Term     | Present | NIST 40 | Cal. | Present | Exp. | Other | Cal. |
|-----|---------|----------|---------|--------|------|---------|------|-------|------|
| 1   | $3d^{10}$ | $^1S_0$   | 0       | 0      | 0$^a$ | $\infty$ | 2.5-10$^{+8}$ s | 7.8 s |
| 2   | $3d^94s$  | $^3D_1$   | 21932   | 21929  | 22469$^a$ |         |         |
| 3   |          | $^3D_2$   | 22733   | 22847  | 23381$^a$ |         |         |
| 4   |          | $^3D_4$   | 23705   | 23998  | 24495$^a$ |         |         |
| 5   | $3d^94s$  | $^1D_2$   | 25833   | 26265  | 26840$^a$ |         |         |
| 6   | $3d^94p$  | $^3P_2^o$ | 66623   | 66419  | 66984$^a$ |         |         |
| 7   | $3d^94p$  | $^3P_1^o$ | 67922   | 67917  | 68703$^a$ |         |         |
|     |          |          | 2.2 ns  | 2.36±0.05 ns$^c$ | 2.39 ns, 2.21 ns$^d$ |

| 1   | $4f^{14}$ | $^1S_0$   | 0       | 0      | 0$^d$ | $\infty$ |       | 6017 s$^d$ |
| 2   | $4f^{13}5d$ | $^3P_0^o$ | 29208   | 33386  | 39755$^d$ |         |         |
| 3   | $4f^{13}5d$ | $^3D_0^o$ | 33839   | 39141  | 44429$^d$ |         |         |
| 4   | $4f^{13}6s$ | $^3F_4^o$ | 35000   | 34656  | 36336$^d$ |         |         |
| 5   | $4f^{13}6s$ | $^1F_2^o$ | 36418   | 34991  | 36764$^d$ |         |         |
| 6   | $4f^{13}5d$ | $^3P_1^o$ | 35288   | 39721  | 39762$^d$ | 250 ns  | 230(20) ns$^c$ | 166 ns, 270 ns$^e$ |
| 7   | $4f^{13}5d$ | $^3P_0^o$ | 41059   | 45277  | 49469$^d$ | 0.133 s | 181 ns$^d$ |

$^a$ Ref. 28.
$^b$ Ref. 31; the first calculated value was obtained using the length gauge and the second calculated value was obtained using the velocity gauge.
$^c$ Ref. 28.
$^d$ Ref. 31; the value was obtained using the RMBPT method.
$^e$ Ref. 32; the first calculated value was obtained using the RHF method+CP effects; the second calculated value was obtained using the same procedure with including 5s, 5p, and 4f to the CP effects.

B. Polarizabilities and Blackbody Radiation Shifts

Static scalar polarizability $\alpha_v(0)$ of an atom in state $v$ is given by

$$\alpha_v(0) = \frac{2}{3(2J_0 + 1)} \sum_n A^2_{vn} \omega_{vn}$$  \hspace{1cm} (12)

where $J_0$ is the total angular momentum of state $v$, $A_{vn}$ are the amplitudes (reduced matrix elements) of the electric dipole transitions, $\omega_{vn}$ is the frequency of the transition. Eq. (12) is valid when all wave functions $v$ and $n$ are many-electron wave functions of the whole atom. It can also be used to calculate valence contributions to the polarizability if $v$ and $n$ are many-electron wave functions for the valence electrons only. Then the contribution from core electrons should be calculated separately. For the closed-shell core (or closed-shell atom or ion like Cu II or Yb III in the ground state) eq. (12) can be reduced to

$$\alpha_v(0) = \frac{2}{3} \sum_c \langle \hat{d} | \delta \psi_c \rangle$$  \hspace{1cm} (13)

where $\hat{d}$ is the operator of the electric dipole moment and $\delta \psi_c$ is the RPA correction to the core state $c$ (see Eq. (3)). The summation goes over all states in the core.

To calculate the polarizabilities of the clock states, we use the approach developed in Ref. 42 for atoms or
ions with open shells. It is based on Eq. (12) and the Dalgaro-Lewis method [43], which reduces the summation over the complete set of states to solving a matrix equation (see Ref. [42] for details). This approach treats the 3d electrons in Cu II and 4f electrons in Yb III as valence electrons. To calculate the contributions of the core electrons below the 3d or 4f shells, we use the Eq. (13), in which summation over core state is limited to states below 3d or 4f. To minimize the error in the difference between the ground state and clock state polarizabilities, we use the same approach for both states of both ions.

The results are presented in Table III. Our results for the ground state polarizabilities are in excellent agreement with previous calculations. To the best of our knowledge, the polarizabilities of the excited states of Cu II and Yb III ions were never calculated before.

The shift of the frequency of the clock transition due to black-body radiation (BBR) is given by [46]

$$\delta \nu_{\text{BBR}} = -1.6065 \times 10^{-6} \times T^4 \times \Delta \alpha(0),$$  (14)

where $T$ is a temperature (e.g., room temperature $T = 300 \, K$), $\Delta \alpha(0) = \alpha_{\text{CS}} - \alpha_{\text{GS}}$, is the difference between the clock state and ground state polarizabilities. The calculated frequency shifts are presented in Table III. The fractional BBR shifts for our Cu II are close in value to those of Zn: $-2.5 \times 10^{-16}$, Cd: $-2.8 \times 10^{-16}$ [47], and Cu: $-3.4 \times 10^{-16}$ [20] and smaller than some other atomic clocks, such as Ca [48] and Sr [49] where fractional BBR shift is at the level of $10^{-15}$. As for the BBR shift in the Yb III clock transition, its fractional value, $-5.95 \times 10^{-17}$, is one of the smallest among optical clock transitions.

C. Zeeman Shift and Electric Quadrupole Shift

Clock transition frequencies might be affected by external magnetic and electric fields. Zeeman shift caused by magnetic field strongly depends on whether the atom or ion has a hyperfine structure. Both stable isotopes of copper ($^{63}$Cu and $^{65}$Cu) have non-zero nuclear spin.
TABLE III. Scalar static polarizabilities of the ground states, $\alpha_0$(GS), and clock states, $\alpha_0$(CS), and BBR frequency shifts for the clock transition of $^{63}$Cu II and $^{171}$Yb III. $\delta \nu_{BBR}/\omega$ is the fractional contribution of the BBR shift; where $\omega$ is the clock transition frequency.

| Transition | $\alpha_0$(GS)[a$_0^B$] | $\alpha_0$(CS)[a$_0^B$] | $\Delta \alpha(0)$ | $\delta \nu_{BBR}$/| $\omega$[Hz] | $\delta \nu_{BBR}/\omega$ |
|------------|--------------------------|--------------------------|-------------------|--------------------------|--------------------------|
| Cu II      | Present | Other Cal. | Present | 18.76 | -0.1616 | 6.57·10$^{-14}$ | -2.46·10$^{-16}$ |
| 2$\leftrightarrow$1 | 5.36 | 5.36 | 24.12 |  |  |  |
| 3$\leftrightarrow$1 | 5.36 | 5.36 | 24.05 | 18.69 | -0.1610 | 6.85·10$^{-14}$ | -2.35·10$^{-16}$ |
| Yb III     | Present | Other Cal. | Present |  |  |  |
| 2$\leftrightarrow$1 | 6.39 | 6.55 | 13.29 | 6.90 | -0.0595 | 1.00·10$^{-15}$ | -5.95·10$^{-17}$ |

\(^a\) Ref. \[14\]  
\(^b\) Ref. \[15\]

(I = 3/2) and non-zero hfs. On the other hand, five stable isotopes of Yb have zero nuclear spins, and in two isotopes, spin is not zero (for $^{171}$Yb $I = 1/2$, for $^{173}$Yb $I = 5/2$). For atoms with zero nuclear spin, the first-order Zeeman shift can be avoided by considering transitions between states with $J_z = 0$, while the second-order Zeeman shift is small due to the absence of the hfs.

Below we consider isotopes with non-zero nuclear spin, $^{63}$Cu and $^{171}$Yb.

The linear Zeeman shift is given by

$$\Delta E_{F,F_z} = g_F \mu_B B F_z,$$

where $g_F$ is the $g$-factor of a particular hfs state. It is related to the electron $g_J$-factor by

$$g_F = g_J \langle F, F_z = F, I, J | \hat{J}_z | F, F_z = F, I, J \rangle / F.$$  

Electron $g_J$ factors have values $g_3 = 1.32$, $g_2 = 1.16$ for Cu II, and $g_2 = 1.46$ for Yb III (calculated value). Linear Zeeman shift can be suppressed by averaging over the transition frequencies with positive and negative $F_z$.

Second-order Zeeman shift for transition between definite hfs components is strongly dominated by transitions within the same hfs multiplet. Note that in this approximation, the shift is zero for the ground state (because $J_z = 0$). For the clock states, the shift is given by

$$\delta E_{F,F_z} = \sum_{F' = F \pm 1} \frac{|\langle F' F' z_{\text{ij}} | \hat{F} F_{ij} | F, F_z \rangle|^2}{\Delta E_{\text{hfs}}(F, F')}.$$  

where $x = g_J \mu_B B_m$ (in which $g_J$ is electron $g$ factors, $\mu_B$ is the electron magnetic moment, and $B_m$ is a magnetic field), and $\Delta E_{\text{hfs}}(F, F') = E(F I J) - E(F' I J)$ is the hfs interval. For more detail, see Ref. \[20\].

To calculate this shift, we need to know the hfs of the clock states. We calculated the hfs using the CIPT and RPA methods as described above. The results for magnetic dipole hfs constants $A$ and electric quadrupole hfs constants $B$ are presented in Table \[IV\]. Using these numbers and Eq. \[17\] we calculate the second-order Zeeman shift for all hfs components of the clock states of the $^{63}$Cu II and $^{171}$Yb III ions. The results are presented in Table \[V\]. The shift is small and only slightly larger than in clock transitions of Cu, Ag, and Au \[20\]. As in the case considered in Ref. \[20\], the shift can be further suppressed by taking appropriate combinations of the transition frequencies. It might be even easier here since we need to worry only about suppressing the Zeeman shift for the clock state while it is already strongly suppressed for the ground state.

The electric quadrupole shift is due to the interaction of the atomic quadrupole moment $Q$ with trapping electric field gradient, and a corresponding term in the Hamiltonian is

$$H_Q = -\frac{1}{2} Q_0 \frac{\partial^2}{\partial z^2}.$$  

Here $z$ is the quantization axis determined by the externally applied B field. The spherical components of the quadrupole moment operator $Q_m = |e| \mu^2 r_m^{(2)}$ are the same as for the electric quadrupole (E2) transition. The energy shift of a state with total angular momentum $J$ is proportional to the atomic quadrupole moment of this state. It is defined as twice the expectation value of the spherical component $Q_0 = Q_{zz}/2$ of the quadrupole operator in the stretched state

$$Q_J = 2\langle J, J_z = J | \hat{Q}_0 | J, J_z = J \rangle.$$  

TABLE IV. Hyperfine structure constants $A$ and $B$ in (MHz) of $^{63}$Cu II and $^{171}$Yb III ions. Nuclear spin $I$ of $^{63}$Cu$= 3/2$ and $I$ of $^{171}$Yb$= 1/2$, nuclear magnetic moment $\mu(63$Cu$)= 2.2236(4)$$\mu_N$ and $\mu(171$Yb$)= 0.49367(1)$$\mu_N$ \[52\]; nuclear electric quadrupole moment $Q(63$Cu$) = -0.220(15)$ for $^{63}$Cu and $Q(171$Yb$) = 0$.

| No. | Conf. | Term | $E ($cm$^{-1}$) | $hfs$ 'A' | $hfs$ 'B' |
|-----|-------|------|----------------|----------|----------|
| $^{63}$Cu II | 1 | $3d^44s$ | $^3D_3$ | 21932 | -186.46 | -1.970 |
| 2 | $3d^64s$ | $^3D_2$ | 22733 | -34.62 | -1.097 |
| $^{171}$Yb III | 1 | $4f^{13}5d$ | $^3F_{2}$ | 33350 | -41.46 | 0 |
D. Sensitivity of the Clock Transitions to Variation of the fine structure constant.

Dependence of frequencies of atomic transitions on the fine structure constant in the vicinity of their physical values can be presented as

\[ \omega = \omega_0 + q \left( \frac{\alpha}{\alpha_0} \right)^2 - 1 \]  \hspace{1cm} (20)

where \( \alpha_0 \) and \( \omega_0 \) are the present-day values of the fine structure constant and the frequency of the transition and \( q \) are sensitivity coefficients that come from the calculations [15]. When one atomic frequency is measured against another over a long period of time, their relative time-change is related to the time-change of \( \alpha \) by

\[ \frac{\dot{\omega}_1 - \dot{\omega}_2}{\omega_1 - \omega_2} = (K_1 - K_2) \frac{\dot{\alpha}}{\alpha}. \]  \hspace{1cm} (21)

The dimensionless value \( K = 2q/\omega \) is usually called the enhancement factor. To calculate \( q \) (and \( K \)), we run computer codes at two different values of \( \alpha \) and calculate the numerical derivative

\[ q = \frac{\omega(\delta) - \omega(-\delta)}{2\delta}, \]  \hspace{1cm} (22)

where \( \delta = (\alpha/\alpha_0)^2 - 1 \) (see Eq. (20)). The value of \( \delta \) must be small to ensure linear behavior but sufficiently large to suppress numerical noise. Using \( \delta = 0.01 \) usually gives accurate results. The calculated values of \( q \) and \( K \) for clock transitions of Cu II and Yb III are presented in Table VI. As one can see, the sensitivity of the clock transitions of Cu II to variation of \( \alpha \) is not very high, so they may be used as anchor lines for a comparison with a high K transition (see eq. (21)). The sensitivity of the Yb III clock transition is one of the highest among the systems considered so far. It is close to the sensitivities of recently suggested clock transitions in Yb II [22] and Hg II [17], and slightly smaller than the sensitivity of the most sensitive clock transitions in Yb II and Hg II [17].

IV. CONCLUSION

We have investigated a possibility to use Cu II and Yb III ions as optical ion clocks of high accuracy. Energy levels, lifetimes, transition rates, scalar static polarizabilities of the ground and clock states, and the BBR shifts have been calculated using the CIPT method. We have obtained a good agreement with previous data that are available to compare. Sensitivity to "new physics" such as variation of the fundamental constants has been studied. The uncertainty estimates for the Yb III ion and its high sensitivity to new physics indicate that Yb III atomic clock may successfully compete with the latest generation of clocks.

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