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Recent advances in precision spectroscopy of ultracold atoms and ions

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Abstract. New methods and approaches in precision spectroscopy of ultracold atoms and ions are reviewed with an emphasis on contributions of Institute of Laser Physics SB RAS.

1. Introduction
Presently, laser spectroscopy and fundamental metrology are among the most important and actively developed directions in modern physics. Frequency and time are the most precisely measured physical quantities, which, apart from practical applications (in navigation and information systems), play critical roles in tests of fundamental physical theories (such as QED, QCD, unification theories, and cosmology) [1, 2]. Now, laser metrology is confronting the challenging task of creating an optical clock with fractional inaccuracy and instability at the level of $10^{-17}$ to $10^{-18}$. Indeed, considerable progress has already been achieved along this path for both ion-trap- [3, 4] and atomic-lattice-based [5, 6] clocks.

Work in this direction has stimulated the development of novel spectroscopic methods such as spectroscopy using quantum logic [7], magnetically-induced spectroscopy [8], hyper-Ramsey spectroscopy [9], spectroscopy of “synthetic” frequency [10] and others [11]. Part of these methods was developed in order to excite and detect strongly forbidden optical transitions. The other part fights with frequency shifts of various origins. In the present paper we review both parts with a special emphasis on methods developed and studied in Institute of Laser Physics SB RAS, Novosibirsk.

2. Magnetically-induced spectroscopy of strongly forbidden optical transitions
Initially experimental work on optical lattice clocks [12] focused on the transition in the odd isotopes of Sr and Yb [13-16], which is weakly allowed due to the hyperfine mixing. In contrast to their even counterparts that have zero nuclear spin, however, the odd isotopes have an uncomfortably large sensitivity to magnetic fields (MHz/T) and lattice light polarization. They also have multiple ground state sublevels that considerably complicate spectroscopic line shapes. The method described in this section [8] uses a small magnetic field ($\sim 1$ mT) to mix a small, controllable fraction of the nearby $^3P_1$ state into the $^3P_0$ state, thereby allowing single-photon excitation of the $^1S_0 \rightarrow ^3P_0$ clock transition for the even isotopes. In this way we can replace the odd isotopes with the even in lattice-based atomic clocks, which should greatly accelerate their progress. Estimates for Yb using experimentally realistic linewidths (1 Hz) show that induced frequency shifts can be controlled at a level that could enable a
fractional frequency uncertainty of below $10^{-17}$ for a lattice clock. Our method is equally effective for all alkaline-earth-like clock candidates (Yb, Sr, Ca, and Mg).

To excite the strongly forbidden $|1\rangle \rightarrow |2\rangle$ clock transition at frequency $\omega_{21}$ as shown in figure 1, we apply a static magnetic field $B$ that couples the states $|2\rangle$ and $|3\rangle$. These states are split by a frequency $\Delta_{32}$ and have a coupling matrix element $\Omega_B = \langle 2 | \mu \cdot B | 3 \rangle$, where $\mu$ is the magnetic-dipole operator. According to first-order perturbation theory the state $|2\rangle$ acquires a small admixture of the state $|3\rangle$ due to the presence of the static magnetic field:

$$|2'\rangle = |2\rangle + \frac{\Omega_B}{\Delta_{32}} |3\rangle.$$  \hspace{1cm} (1)

As a result the transition $|1\rangle \rightarrow |2\rangle$ becomes partially allowed. An optical field with amplitude $E$ and frequency $\omega$ acts via the $|1\rangle \rightarrow |3\rangle$ transition (see figure 1). We assume that this transition is at least weakly allowed. The corresponding coupling matrix element is the Rabi frequency, $\Omega_L = \langle 3 | d \cdot E | 1 \rangle / \hbar$. Because of the slight admixture of state $|3\rangle$ into the bare state $|2\rangle$, a resonance will be observed on the forbidden transition $|1\rangle \rightarrow |2\rangle$ when $\omega \approx \omega_{12}$.

![Figure 1](image.png)  \hspace{1cm} Figure 1. Magnetic field-induced excitation of a strongly forbidden transition in a generic three-level atomic system.

The effective Rabi frequency of the clock transition can be written in three different forms. First of all, taking into account the vector nature of the applied fields and Zeeman degeneracy of the intermediate state $|3\rangle$, we obtain

$$\Omega_{12} = \frac{d \mu (E \cdot B)}{\hbar^2 \Delta_{32}},$$  \hspace{1cm} (2)

where $d$ and $\mu$ are the reduced matrix elements of the dipole and magnetic dipole moments, respectively. From the other side the effective Rabi frequency is obviously proportional to the magnetic field strength and to square root from the light intensity:

$$\Omega_{12} = \alpha \sqrt{I B \cos \theta}.$$  \hspace{1cm} (3)
Here \( \theta \) stands for the angle between \( \mathbf{E} \) and \( \mathbf{B} \) directions. Finally, it is useful to express the effective Rabi frequency in terms of the light shift \( \Delta_v = \kappa I \) and quadratic Zeeman shift \( \Delta_B = \beta B^2 \) produced by the probe fields:

\[
\Omega_{12} = \xi \sqrt{\Delta_v \Delta_B} \cos \theta,
\]

where \( \xi \equiv \alpha / \sqrt{\beta \kappa} \) is a dimensionless quality factor for the clock transition in this scheme, since it relates the strength of the excitation to the magnitudes of the induced field shifts. A larger value for \( \xi \) implies that for a given spectroscopic linewidth, the induced shifts will be smaller. Table I summarizes the relevant parameters for four different alkaline-earth-like atoms that have been considered as excellent clock candidates.

**Table 1.** The calculated parameters for four different atoms.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta_{32} ) [THz]</th>
<th>( \alpha ) [Hz/(T mW(^{1/2})/cm)]</th>
<th>( \beta ) [MHz/T(^2)]</th>
<th>( \kappa ) [mHz/(mW/cm(^2))]</th>
<th>( \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb</td>
<td>21</td>
<td>186</td>
<td>-6.2</td>
<td>15</td>
<td>0.6</td>
</tr>
<tr>
<td>Sr</td>
<td>5.6</td>
<td>198</td>
<td>-23.3</td>
<td>-18</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca</td>
<td>1.5</td>
<td>154</td>
<td>-83.5</td>
<td>-3.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Mg</td>
<td>0.6</td>
<td>98</td>
<td>-217</td>
<td>-0.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Using these values for Yb one can show that a magnetic field 1 mT with a probe light intensity 10 mW/cm\(^2\) will produce the effective Rabi frequency about 1 Hz, accompanying by the quadratic Zeeman shift of 10 Hz and the probe light shift of 0.1 Hz. These shifts can be controlled at the level of a few mHz that results in a fractional frequency uncertainty well below \( 10^{-17} \) level. Further improvements can be achieved by the use a special method of hyper-Ramsey spectroscopy described in the next section.

Note that the method of magnetically-induced spectroscopy has been successfully realized first in experiments with Yb atoms [8], then with Sr atoms [17-19], and very recently with Mg atoms [20].

### 3. Hyper-Ramsey spectroscopy

#### 3.1. Motivations

For some of the promising clock systems, one of the key unsolved problems is the frequency shift of the clock transition due to the excitation pulses themselves. For the magnetically-induced spectroscopy, these shifts (quadratic Zeeman and ac-Stark shifts) could ultimately limit the achievable performance. Moreover, for ultra-narrow transitions (e.g., electric octupole [21] and two-photon transitions [22, 23]) the ac-Stark shift can be large enough in some cases that it rules out high accuracy clock performance. A similar limitation exists for clocks based on direct frequency comb spectroscopy [24, 25] because ac-Stark shifts are induced by large numbers of off-resonant laser modes.

In this section, we describe a general solution to this important problem, which is based on the development and generalization of the Ramsey method [26]. We have found that in contrast with the single-pulse (Rabi) technique, multi-pulse Ramsey spectroscopy offers several ways (e.g., pulse durations, frequencies, and phases) to significantly manipulate (due to interference effects) the induced frequency shifts of the spectroscopy signals. In particular, for special excitation schemes (which we refer to as “hyper-Ramsey”) the resulting ac-Stark shift depends on the laser intensity in an essentially nonlinear way. Such unusual and unexpected behavior allows us to dramatically suppress these shifts and their uncertainties (most critical for clocks) by two to four orders of magnitude with strongly relaxed control requirements for the experimental parameters. Additionally, we have found that these schemes can have a greatly reduced sensitivity to the pulse areas, which makes the procedure robust and accessible experimentally. Thus, this method can be readily implemented in a variety of existing and proposed clock systems [3-7, 12-25, 27]. Our approach could lead to significant progress for
atomic clocks: it will improve several key existing optical clock systems and could enable new systems that were not previously thought to be competitive.

3.2. The original proposal

The hyper-Ramsey spectroscopy schemes [9] (see in figure 2) are based on time-separated pulses that can have different durations, frequencies, and phases. The action of a single light pulse (with frequency \( \omega_p \), duration \( \tau \), and Rabi frequency \( \Omega_0 \)) on two-level atoms with ground \( |g\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \) and excited \( |e\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \) states, (separated by the unperturbed energy \( \hbar \omega_0 \)), is described by the following matrix:

\[
W(\tau, \Omega_0, \delta_p) = \begin{pmatrix}
\cos\left(\frac{\Omega_0 \tau}{2}\right) + i \frac{\delta_p}{\Omega} \sin\left(\frac{\Omega_0 \tau}{2}\right) & i \frac{\Omega_0}{\Omega} \sin\left(\frac{\Omega_0 \tau}{2}\right) \\
\frac{i \Omega_0}{\Omega} \sin\left(\frac{\Omega_0 \tau}{2}\right) & \cos\left(\frac{\Omega_0 \tau}{2}\right) - i \frac{\delta_p}{\Omega} \sin\left(\frac{\Omega_0 \tau}{2}\right)
\end{pmatrix},
\]

where \( \Omega = \sqrt{\Omega_0^2 + \delta_p^2} \) is the generalized Rabi frequency. The detuning during the pulse \( \delta_p = \omega_p - \omega_0 - \Delta_{sh} \) contains the excitation related shift \( \Delta_{sh} \) (see figure 2, level scheme) due to the influence of other (far-off-resonant) transitions.

\[\text{Figure 2.} \text{ Ramsey pulses with Rabi frequency } \Omega_0 \text{ of different duration } [\tau_1 \text{ and } \tau_2 \text{ (a)}]. \text{ During the pulses, we step the laser frequency } \omega \text{ by } \Delta_{\text{step}} \text{ [(b) and text]} \text{. Hyper-Ramsey scheme with composite second pulse } 3\tau \text{ [(c) and text]} \text{. Also shown is a two-level atom with splitting } \omega_0, \text{ detuning } \delta \text{ of the laser with frequency } \omega \text{ during dark time } T, \text{ and excitation related shift } \Delta_{sh} \text{ during pulses.}\]
During the dark period between the pulses, excitation-related shifts (which produce the total actual shift $\Delta_{sh}$) are absent (e.g., the ac-Stark shift from the laser) or can be turned off (like the Zeeman shift). If during the dark period $T$ the laser frequency is $\omega$, then the free evolution is described by the matrix with detuning $\delta = \omega - \omega_0$:

$$V(T\delta) = \begin{pmatrix} \exp(iT\delta/2) & 0 \\ 0 & \exp(-iT\delta/2) \end{pmatrix}$$

In the general case, the laser frequency during the pulse does not have to be the same as the frequency during the dark time, i.e., $\omega_p \neq \omega$ [27]. As we will see, at times it can be useful to approximately offset the induced shift $\Delta_{sh}$ by stepping the laser frequency only during the pulses by a fixed $\Delta_{step}$, i.e., $\omega_p = \omega + \Delta_{step}$ [see figure 2(b)]. Thus, in the general case the detuning during the pulses can be written as $\delta_p = \delta + \Delta$, where $\Delta = \Delta_{sh} - \Delta_{step}$ step is the effective frequency shift during the pulse. This manipulation allows us to stabilize the frequency $\omega$ under the controlled condition $|\Delta/\Omega_0| \ll 1$ (independently of the value $\Delta_{sh}$). This condition is very important, because the shift of the central Ramsey fringe has a form of decreasing series in terms of powers of the small value $\Delta/\Omega_0$ (see [9]).

Formulas (5) and (6) are sufficient for description of the signal in Ramsey spectroscopy. For example, if at $t = 0$ atoms are in the lower level $|g\rangle$, then after the action of two pulses of duration $\tau_1$ and $\tau_2$ separated by dark period $T$ [see figure 2(a)] the population $\pi^{(e)}$ of atoms in the excited state $|e\rangle$ is determined by

$$\pi^{(e)} = \langle e | W(\tau_2, \Omega_0, \delta - \Delta) V(T\delta) W(\tau_1, \Omega_0, \delta - \Delta) | g \rangle^2$$

This formula describes Ramsey fringes as a function of variable detuning $\delta$, but with fixed $\Delta$. The presence of the additional shift $\Delta$ in the course of the pulse action leads to the shift of the central Ramsey fringe with respect to the unperturbed frequency $\omega_0$.

Hereafter we assume that the position of the central fringe $\omega_T$ is determined by stepping the phase of one of the pulses by $\pm \pi/2$ in the way [28] and equalizing these signals. This approach is of greater relevance for clocks, because it directly generates an error signal with high sensitivity. In respect to the signal (7), this method is formulated as following. Let us introduce the phase steps $\phi$ after the dark time $T$, then the excited state population $\pi^{(e)}(\phi)$ and the error signal $S^{(err)}$ can be expressed as:

$$\pi^{(e)}(\phi) = \langle e | W(\tau_2, \Omega_0, \delta - \Delta) V(\phi) V(T\delta) W(\tau_1, \Omega_0, \delta - \Delta) | g \rangle^2$$

$$S^{(err)} = \pi^{(e)}(\pi/2) - \pi^{(e)}(-\pi/2).$$

The shift $\delta_T$ of the stabilized frequency $\omega_T$ is determined from the solution of the equation $S^{(err)} = 0$ relative to the unknown $\delta$.

In the standard Ramsey spectroscopy both exciting pulses have equal duration $\tau_1 = \tau_2 = \tau$. In the case of $\Omega_0 \tau = \pi/2$ and $\tau \ll T$, the dominant contribution has the following linear dependencies on the small value $|\Delta/\Omega_0| \ll 1$:

$$\delta_T \approx \frac{2}{T} \frac{\Delta}{\Omega_0}$$

However, most interesting and important results can be obtained by the use of the hyper-Ramsey scheme [21,30] shown in figure 2(c). Here the main peculiarity is the composite pulse (with total duration $3\tau$), which consists of subpulse $2\tau$ with inverted phase ($-\Omega_0$) and subpulse $\tau$ with initial phase ($\Omega_0$). If for the error signal we apply additional phase $\pm \pi/2$ steps directly after dark time (as it was in [9]), then this method we will be referred to as HR1 [see in figure 1(c)]. In this case, we define the function $\pi_{HR1}^{(e)}(\phi)$ and the error signal $S_{HR1}^{(err)}$:
As it was first shown in [21], for the hyper-Ramsey pulse sequence the dominant contribution in the shift $\delta_T$ has a cubic dependence on the small value $|\Delta/\Omega_0| \ll 1$. For instance, if $\Omega_0\tau = \pi/2$ and $\tau \ll T$, we have

$$\delta_T \approx \frac{4}{T} \left( \frac{\Delta}{\Omega_0} \right)^3$$

(11)

The suppression of the probe-field-induced shift in the hyper-Ramsey spectroscopy is illustrated by figure 3. As is clearly seen, a cubic nonlinearity appears. Moreover, this character is not changed under variations of $\Omega_0$, $\tau$, and $T$, i.e., we do not need the rigorous condition $\Omega_0\tau = \pi/2$. This circumstance is a key point to successfully realize our method in atomic clocks, because in real experiments the value of $\Omega_0$ can not be controlled better than at the level of 1%–10%.

Figure 3. Numerically calculated shift of the central resonance $T \delta_T$ versus $\Delta/\Omega_0$ for the standard Ramsey spectroscopy (solid line) and the hyper-Ramsey method (dotted and dashed lines) at $\Omega_0\tau = \pi/2$; $\Omega_0 T = 20$. Dashed line: position of extremum of the excited-state population $\pi^{(e)}_{HR}(0)$; dotted line: estimate of center from the error signal with $\pm \pi/2$ phase steps.

The hyper-Ramsey method was experimentally realized for the first time in Yb single-ion system [9]. The probe-field frequency shift was suppressed by more than three orders of magnitude. The use of the hyper-Ramsey scheme was crucial in development of the best single-ion clock [4]. Recently, a successful realization of the hyper-Ramsey excitation in magnetically-induced spectroscopy of neutral Sr atoms was reported in [19].
3.3. Further modifications

In the recent paper [19], the authors have proposed the use of $\pm \pi/2$ phase steps after inverted ($-\Omega_0$) subpulse $2\tau$ [see in figure 2(c)] to form an error signal for the hyper-Ramsey approach (we will denote this modification as HR2). For its theoretical description, we introduce the following function $\pi_{HR2}^{(e)}(\phi)$ and the error signal $S_{HR2}^{(err)}$:

$$\pi_{HR2}^{(e)}(\phi) = \left\{ e^{iW(\tau, \Omega_0, \delta - \Delta)V(\phi)W(2\tau, -\Omega_0, \delta - \Delta)V(T\delta)W(\tau, \Omega_0, \delta - \Delta)g} \right\}^2$$

$$S_{HR2}^{(err)} = \pi_{HR2}^{(e)}(\pi/2) - \pi_{HR2}^{(e)}(-\pi/2).$$

Then the shift $\delta_T$ of the stabilized frequency $\omega_T$ is determined from the solution of the equation $S_{HR2}^{(err)} = 0$ relative to the unknown $\delta$. In this case, our theoretical estimations give us (for $\Omega_0 \tau = \pi/2$ and $|\Delta/\Omega_0| << 1$):

$$\delta_T \approx -\frac{4}{T} \left( \frac{\Delta}{\Omega_0} \right)^3,$$

which almost coincide with equation (11), but with the opposite sign.

Besides HR2, Ref. [19] also describes the theory and successful experimental demonstration of a modified hyper-Ramsey (MHR) method, which is based on the combination of both protocols HR1 and HR2. In the case of MHR, the error signal is determined as

$$S_{MHR}^{(err)} = \pi_{HR1}^{(e)}(\phi) - \pi_{HR2}^{(e)}(\phi).$$

Again, the shift $\delta_T$ of the stabilized frequency $\omega_T$ is determined from the solution of the equation $S_{MHR}^{(err)} = 0$ relative to the unknown $\delta$. This equation leads to an unexpected result: $\delta_T = 0$ for arbitrary $\phi, \Delta, \Omega_0, \tau$, and $T$. In the other words : $\delta_T = 0$ in all orders with respect to $\Delta/\Omega_0$. An analogous result was also found for an alternative scheme (so-called generalized hyper-Ramsey (GHR)), presented in the theoretical paper [20].

At first glance, both MHR and GHR approaches [19, 20] are the best for frequency stabilization, because they allow us to totally eliminate probe-induced shifts. However, as it was shown in [29], MHR and GHR methods are unstable relative to the decoherence, which leads to an appearance of the shift $\delta_T \neq 0$. Moreover, this residual shift is very sensitive to variations of Rabi frequency $\Omega_0$. A proper modification of the hyper-Ramsey method robust with respect to the decoherence (which is present in any real system due to the finite laser line width and/or the finite lifetime of the excited state, see in [30, 31]) was proposed by us recently [29] and it is based on the use of the synthetic frequency protocol briefly described in the next section.

4. Synthetic frequency method

4.1. General formulation

The essence of our approach consists of the following. Let us consider two clock frequencies $\omega_1^{(0)}$ and $\omega_2^{(0)}$ (different in the general case). Assume that due to a certain physical cause we have the stabilized frequencies $\omega_1$ and $\omega_2$, which are shifted relative to the unperturbed frequencies by the values $\Delta_1$ and $\Delta_2$:

$$\omega_1 = \omega_1^{(0)} + \Delta_1; \quad \omega_2 = \omega_2^{(0)} + \Delta_2.$$

Also assume that the ratio $\varepsilon_{12} = \Delta_1 / \Delta_2 = const$ does not fluctuate, while the shifts $\Delta_{1,2}$ can vary during the experiment. In this case, we can construct the following superposition:
\[ \omega_{\text{syn}} = \frac{\omega_1 - \varepsilon_{12} \omega_2}{1 - \varepsilon_{12}} = \frac{\omega_1^{(0)} - \varepsilon_{12} \omega_2^{(0)}}{1 - \varepsilon_{12}}, \]  

which is insensitive to the perturbations \( \Delta_{1,2} \) and their fluctuations. We will call this frequency the “synthetic frequency.” A key advantage of this concept is that to construct the shift-free frequency \( \omega_{\text{syn}} \), we do not need to know the actual values of the shifts \( \Delta_{1,2} \). We only need to know their ratio \( \varepsilon_{12} \), which can be exactly calculated or measured for many cases.

4.2. Application to the problem of BBR shift

The largest effect that contributes to the systematic uncertainty of many atomic clocks is the interaction of the thermal blackbody radiation (BBR) with the atomic eigenstates. This effect was first considered in 1982 for cesium atomic clocks [32] but remains up to now a major problem for many modern atomic time and frequency standards. At present, there exist three approaches to tackle the BBR shift problem. The first one is the use of cryogenic techniques to suppress this shift to a negligible level. This approach is pursued for the mercury ion clock [33], for the Cs fountain clock [34], and for the Sr optical lattice clock [18]. The second approach is the precise temperature stabilization of the experimental setup in combination with theoretical and/or semiempirical numerical calculations of the shift at a given temperature [35, 36]. The third approach is based on the choice of an atom or ion where both levels of the reference transition have approximately the same BBR shift.

Here the most promising candidate is \( ^{2}\text{S}_1/2 \) with a fractional BBR shift of the reference transition frequency of \( 10^{-12} \) at 300 K [3], followed by \( ^{115}\text{In}^+ \) [37]. However, the latter approach limits the choice of candidates for tests of fundamental theories.

Our approach is based on the fact that, for the large majority of atomic transitions that are of interest as frequency standard reference transitions, the temperature dependence \( \Delta(T) \) of the BBR shift is very well approximated by the law \( \propto T^4 \). Consider now two clock transitions with frequencies \( \omega_1 \) and \( \omega_2 \) exposed to the same thermal environment. The BBR shifts on each frequency can be represented as a temperature dependence given by

\[ \omega(T) = \omega^{(0)} + a_i T^4, \]

where \( \omega^{(0)} \) is the unshifted frequency (at \( T = 0 \) K) and \( a_i \) is an individual characteristic of the \( j \)-th transition, which is proportional to the differential static polarizability of working levels. Introducing the coefficient \( \varepsilon_{12} = \Delta_1(t)/\Delta_2(t) = a_1/a_2 \), one can easily see, that the following superposition does not experience the BBR shift:

\[ \omega_{\text{syn}} = \frac{\omega_1(T) - \varepsilon_{12} \omega_2(T)}{1 - \varepsilon_{12}} = \frac{\omega_1^{(0)} - \varepsilon_{12} \omega_2^{(0)}}{1 - \varepsilon_{12}}, \]

Thus, one can use the frequency \( \omega_{\text{syn}} \) as a new clock output frequency which is immune to the BBR shift and to fluctuations in the operating temperature, while the thermal shifts \( \Delta_i(t) \) of the reference frequencies \( \omega_i \) can be large.

As an example that permits the practical realization of the ideas presented above, we consider the ion \( ^{171}\text{Yb}^+ \). As shown in figure 4, the level system of \( ^{171}\text{Yb}^+ \) provides two narrow-linewidth transitions from the ground state in the visible spectral range, which can be used as reference transitions of an optical frequency standard: the quadrupole transition \( ^2\text{S}_{1/2}(F = 0) \rightarrow ^2\text{D}_{3/2}(F = 2), \lambda \approx 436 \text{ nm} \) and the octupole transition \( ^2\text{S}_{1/2}(F = 0) \rightarrow ^2\text{F}_{7/2}(F = 3), \lambda \approx 467 \text{ nm} \). It should be noted that the case of \( ^{171}\text{Yb}^+ \) is especially attractive because here both clock transitions lie in a technically convenient frequency range and experience exactly the same thermal environment if probed in the same ion.
The BBR shifts of the quadrupole and octupole transitions of Yb\(^+\) were calculated in [38]. The room-temperature (at 300 K) BBR shift of the quadrupole transition is calculated as \(a_{\text{quad}} = -0.35\) Hz (fractional shift \(5.1 \times 10^{-16}\)) and that of the octupole transition as \(a_{\text{oct}} = -0.15\) Hz (fractional shift \(2.4 \times 10^{-16}\)). Using the results of Ref. [21], for \(^{171}\text{Yb}^+\) we find, that \(e_{12} = a_{\text{oct}} / a_{\text{quad}} = 0.43\), and the synthetic frequency equals \(607\) THz, corresponding to the synthetic wavelength \(494\) nm, which is sufficiently close to the initial reference transitions at \(436\) and \(467\) nm. The higher-order contributions (\(\propto t^6\) and higher) to the BBR shift of the octupole reference transition are negligible compared to that of the quadrupole transition. As a result, we estimated that the BBR shift can be suppressed to the fractional level of \(2.7 \times 10^{-17}\) at 300 K with variations at the level of \(\pm 5 \times 10^{-18}\) in a broad interval of \(300 \pm 15\) K.

The concept of a synthetic atomic frequency standard can also be extended to the case that both reference frequencies \(\omega_{1,2}\) lie in the microwave range. Atomic fountain clocks are based on transitions in the microwave range between the ground-state hyperfine sublevels of alkali atoms. For a synthetic atomic fountain frequency standard, for instance, the combination \(^{87}\text{Rb}\) \((\omega_1 = 6.8\) GHz\) and \(^{133}\text{Cs}\) \((\omega_2 = 9.2\) GHz\) can be considered. Here, at the synthetic frequency \(1.9\) GHz it is possible to suppress the fractional BBR shift of the individual standards by two orders of magnitude. It is interesting to note that nearly optimal conditions for the efficient suppression of the BBR shift are realized in the dual Rb/Cs fountain clock described in Ref. [39], because here both reference transitions are exposed to the same thermal environment.

**Figure 4.** Section of the energy level scheme of \(^{171}\text{Yb}^+\), showing the hyperfine levels of the \(^2S_{1/2}\) ground state and the two lowest-lying excited states, which are metastable.

4.3. Applications to the Ramsey and hyper-Ramsey schemes

Let us now show how to incorporate the synthetic frequency protocol in Ramsey spectroscopy for significant suppression of the probe-induced shifts in atomic clocks. Consider again an influence of the probe-induced shift \(\Delta_{\text{sh}}\), which arises only during the Ramsey pulses (see two-level scheme in figure 2), while this shift is absent during the dark time \(T\). As a result, the stabilized frequency \(\omega_T\) also becomes differing from unperturbed frequency \(\omega_0\): \(\omega_T = \omega_0 + \delta_T\), where the index \(T\) denotes the fixed time of the free evolution interval under frequency stabilization. It can be shown that the dependence \(\delta_T\) on the value \(T\) can be expressed as the following decreasing series in terms of powers of \(1/T\):

\[
\delta_T = \sum_{n=1}^{\infty} \frac{A_n}{T^n},
\]  

(19)
where the coefficients $A_n$ depend on the pulse parameters (durations, amplitudes, phases, and the value $\Delta_n$).

Since the dark time interval $T$ is precisely controlled in experiments, we can set a goal to eliminate the main contribution $\propto A_i/T$ in equation (19) using the synthetic frequency protocol. To solve this task we will apply two different dark intervals $T_1=T$ and $T_2=T/2$ (but with the same Ramsey pulses), which will give us the corresponding stabilized frequencies $\omega_{T}$ and $\omega_{T/2}$ . Using Eqs. (16) and (19), we easily find the synthetic frequency $\omega_{\text{syn}}^{(1)}$ and its residual shift $\delta_{\text{syn}}^{(1)}$ :

$$\omega_{\text{syn}}^{(1)} = 2\omega_{T} - \omega_{T/2},$$
$$\delta_{\text{syn}}^{(1)} = \omega_{\text{syn}}^{(1)} - \omega_0 = 2\delta_{T} - \delta_{T/2} = \sum_{n=2}^{\infty} \frac{B_n}{T^n}.$$  \((20)\)

Moreover, we can go further to define a synthetic frequency of the second order $\omega_{\text{syn}}^{(2)}$, for which both contributions $A_i/T$ and $A_{i/2}/T^2$ will be simultaneously canceled. Here we need to use three different time intervals ($T_1=T$, $T_2=T/2$, and $T_3=T/3$) with the corresponding stabilized frequencies ($\omega_{T}$, $\omega_{T/2}$, and $\omega_{T/3}$). The required superposition takes the form,

$$\omega_{\text{syn}}^{(2)} = 3\omega_{T} - 3\omega_{T/2} + \omega_{T/3},$$
$$\delta_{\text{syn}}^{(2)} = \omega_{\text{syn}}^{(2)} - \omega_0 = 3\delta_{T} - 3\delta_{T/2} + 3\delta_{T/3} = \sum_{n=3}^{\infty} \frac{C_n}{T^n}. \tag{21}$$

The main metrological advantage of the proposed synthetic frequency protocol in the Ramsey spectroscopy is an improvement of accuracy and long-term stability of the atomic clock, first of all. At the same time, we expect small deterioration in the short-term stability, because the averaging time to reach the same short-term instability in the measurement scheme based on Eqs. (20) or (21) is approximately two to three times longer than for a direct locking to the clock transition.

At first, let us consider the standard Ramsey spectroscopy, where the dominant contributions have the following linear dependencies on the small value $|\Delta/\Omega_0| \ll 1$:

$$\delta_{T} \approx \frac{2\Delta}{T\Omega_0}; \quad \delta_{\text{syn}}^{(1)} \approx \frac{8\pi\tau}{\pi\tau T\Omega_0}; \quad \delta_{\text{syn}}^{(2)} \approx \frac{48}{\pi^2 T^2} \left(\frac{2\tau}{T}\right)^2 \frac{\Delta}{\Omega_0}. \tag{22}$$

Here due to the smallness of the ratio $(2\pi \tau) \ll 1$ (i.e., for short Ramsey pulses) we have the chain of inequalities: $\delta_{\text{syn}}^{(2)} \ll \delta_{\text{syn}}^{(1)} \ll \delta_{T}$. Thus, the synthetic frequency protocol can significantly suppress the shifts even for the standard Ramsey spectroscopy.

However, the most interesting and important results are obtained by the use of the hyper-Ramsey sequences. For the pulse sequence HR1 the dominant contributions take the form:

$$\delta_{T} \approx \frac{4\left(\frac{\Delta}{\Omega_0}\right)^3}{T}; \quad \delta_{\text{syn}}^{(1)} \approx \frac{48\pi\tau}{\pi\tau T} \left(\frac{\Delta}{\Omega_0}\right)^5; \quad \delta_{\text{syn}}^{(2)} \approx \frac{865}{\pi^2 T^2} \left(\frac{4\pi\tau}{T}\right)^2 \left(\frac{\Delta}{\Omega_0}\right)^7, \tag{23}$$

and very similar results for the pulse sequence HR2:

$$\delta_{T} \approx \frac{4\left(\frac{\Delta}{\Omega_0}\right)^3}{T}; \quad \delta_{\text{syn}}^{(1)} \approx \frac{48\pi\tau}{\pi\tau T} \left(\frac{\Delta}{\Omega_0}\right)^5; \quad \delta_{\text{syn}}^{(2)} \approx -\frac{865}{\pi^2 T^2} \left(\frac{4\pi\tau}{T}\right)^2 \left(\frac{\Delta}{\Omega_0}\right)^7, \tag{24}$$

These formulas (23) and (24) demonstrate that the chain of inequalities $\delta_{\text{syn}}^{(2)} \ll \delta_{\text{syn}}^{(1)} \ll \delta_{T}$, can be realized due to the controlled smallness $|\Delta/\Omega_0| \ll 1$, first of all. Moreover, the condition $(4\pi \tau/T) \ll 1$ leads to an additional suppression of the shifts. Thus, the relatively small initial shift $\delta_{T}$ and its fluctuations can be suppressed by several orders of magnitude to metrologically negligible values.
To summarize, the synthetic frequency protocol in Ramsey spectroscopy is a novel technique that offers a spectroscopic signal that is virtually free from probe-induced frequency shifts and their fluctuations. Our method has broad applications for any types of clocks, especially those based on ultranarrow transitions, two-photon transitions, lattice clocks based on bosonic isotopes with controlled collision shifts [5, 40], CPT-Ramsey [31-44], and POP-Ramsey clocks [45]. Moreover, our approach opens a prospect for the high-precision optical clocks based on direct frequency comb spectroscopy. High resolution matter-wave sensors [46] are also expected to benefit from the suppression of phase shifts in the interference patterns due to the excitation pulses.

5. Conclusion
We have presented three methods for ultra-precise spectroscopy of ultracold atoms and ions, which were proposed, developed, and investigated at the Institute of Laser Physics SB RAS. It should be noted that the experimental research on magnesium atoms and single ytterbium ions, which is aimed at the practical realization of these methods, has been actively carried out in the Institute since 2012. We plan to reach a level of relative instability of our frequency standards better than $10^{-16}$ by 2016-2017.

To conclude, we would like to make a forecast for the development of the research in the field of optical frequency standards:

(1) further improvement of metrological characteristics for single-ion (Yb$^+$, Al$^+$, In$^+$, Sr$^+$, Hg$^+$) and lattice-based atomic (Sr, Yb, Hg, Mg, Tm) optical frequency standards by using special methods of control over the frequency field shifts of different natures (thermal radiation, trap and lattice fields, probe field); reaching the uncertainty level of $10^{-18}$ in the nearest future; redefinition of frequency and time units based on optical frequency standards; precise tests of fundamental physical laws by using optical frequency standards;

(2) development of fundamentally new optical frequency standards (for example, based on nuclear transitions, magnetic dipole transitions in highly charged ions, etc.) that would allow reaching the frequency relative instability of the order of $10^{-19}$ and lower;

(3) development of compact mobile optical frequency standards based on ultracold atoms and ions, including those working in space and used for high-precision navigation and geodesy systems;

(4) improvement of metrological characteristics of optical frequency standards by realizing quantum networks of atomic clocks and using fiber and space communication lines.

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