Manipulation of the collisional frequency shift in caesium fountain clocks

K. Szymanieca, W. Chalupczaka, S. Weyersb, R. Wynandsb, E. Tiesingac, C.J. Williams
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aNational Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK
bPhysikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany
cJoint Quantum Institute and Atomic Physics Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899-8423, USA

ABSTRACT

The frequency shift due to atomic collisions is a major, and in some cases the dominant, limitation to the accuracy of caesium fountain primary frequency standards. A correction for this shift is usually obtained by measuring the frequency of the standard as a function of atomic density and performing an extrapolation to zero density. In general this means that additional measurement time is needed to reach a given statistical resolution. Recently, we have observed that, for a certain range of fountain parameters (i.e. the initial size of the atom cloud and its temperature at launch), the collisional frequency shift varies significantly when the population of the clock states (set by the first Ramsey interaction) is varied. In particular, the collisional shift can be zero for a certain value of the population ratio. This demonstration of collisional shift cancellation offers the intriguing prospect of operating the fountain at the zero-shift point, avoiding the need for extrapolation. In this contribution we provide further experimental validation of the theoretical model describing the collisional shift variation. We also discuss requirements for and benefits of the operation at the zero shift point. In addition, we point out the possible consequences of collisional shift variation for operation of a fountain standard at elevated microwave power, a mode of operation frequently used for the evaluation of other systematic frequency shifts.

Key words: primary frequency standard, cold collisions

1. INTRODUCTION

Atomic fountains, the modern primary frequency standards (PFS), which use laser cooled atomic absorbers [1] find applications not only in timekeeping but also in many fundamental tests where the highest experimental precision is needed. Examples include searches for the electron dipole moment [2], the nuclear anapole moment [3] or time variations of the fine structure constant [4]. With the fountain approach long interrogation times and narrow velocity distributions have been achieved, which helped to overcome many limitations of the earlier thermal beam standards. On the other hand, collisions between the atoms, usually negligible in the beam standards, have become a major issue because for the laser-cooled atoms the de Broglie wavelength is much larger than the range of inter-atomic potentials. In particular, for the Cs atom, the base of the SI definition of the second, the collision rate coefficients are large (compared to other alkalis) and also depend on collision energy in a non-trivial way [5]. In all operational Cs fountain standards the collisional frequency shift is one of the major factors limiting their accuracy.

The usual way of evaluating the collisional shift of a fountain based PFS is by operating the standard at different densities. However, running the fountain at other than the optimum density usually degrades its stability, which means that additional measurement time is needed to reach a specific statistical resolution. Several strategies have been implemented to find the best compromise between accuracy of the collisional-shift determination and clock instability (see, for instance, [6][7]). Because the atomic density is not measured directly, but evaluated from the number of detected atoms, the accuracy of the collisional shift correction may be limited by an uncertainty related to a deviation from perfect linearity in the relation between frequency shift and number of atoms [6][8]. While this uncertainty can be reduced by an implementation of the adiabatic passage technique linking unambiguously the density variation and the...
number of detected atoms [9] or by operating the fountain at very low densities [7], it would be preferable if the shift could be avoided or cancelled in the first place.

The possibility of cancellation of thecollisional shift has been studied earlier. The cancellation would be possible if the cross-sections of the frequency changing collisions of the two clock states \( |3,0 \rangle \) and \( |4,0 \rangle \) were of opposite sign. Then, if a certain composition of the clock states were excited the two contributions to the clock shift would cancel. In the 1990s the relevant cross-sections for various Cs isotopes were calculated and it was shown that the cancellation is possible for the radioactive isotopes \(^{133}\text{Cs}\) and \(^{137}\text{Cs}\), but not for \(^{133}\text{Cs}\), which is used to realise the SI second [10]. The calculations in Ref. [10] were based on a theoretical model developed in Ref. [11], predicting the Wigner threshold regime (i.e. where the collisional rates do not depend on collision energy) in Cs for microkelvin temperatures. More recently more accurate constraints for the Cs-Cs scattering parameters were given by calculations [5] based on new experimental data [12]. It was found that the Wigner threshold regime is reached only for temperatures (collision energies) below 0.1 nK. Thus, unlike previously assumed, the collision rate (and clock shift) do depend on the energy of the colliding atoms. The variation of the collisional shift with the clock state composition was predicted for temperatures below 0.2 \( \mu \)K.

In this paper, we first recall our observation of the collisional shift variation and cancellation [13]. We then examine some specific predictions of the theoretical model presented in Ref. [13] providing a validation of that model. We show that the measurement of the collisional shift in a Cs fountain, in particular of the zero-shift point, allows one to distinguish between scattering parameters values of Refs. [14] and [15]. Further, we discuss in detail how the cancellation of the shift may improve the effective short-term stability (and hence shorten the averaging time) or the accuracy of a fountain standard. We use the aforementioned model to estimate an uncertainty of the (nominally zero) collisional shift for a set of realistic fountain parameters. We also describe a situation where the varying collisional frequency shift can be misinterpreted as a power-dependent shift affecting accuracy evaluations of caesium fountain primary frequency standards.

### 2. VARIABLE COLLISIONAL FREQUENCY SHIFT IN CS FOUNTAIN

Caesium fountain frequency standards (clocks) operate in a cyclic mode [1]. The Cs atoms from a background vapour or a beam are collected in a magneto-optical trap (MOT) or optical molasses. A cloud of about \( 10^7-10^8 \) atoms is formed, which has an approximately Gaussian distribution of density and atomic velocities. In the case of a MOT, the initial size \( r^{1/2} \) radius) is typically \( \zeta_0 \leq 1 \) mm; in the case of a molasses the cloud is larger \( (\zeta_0 = 3-5) \) mm. The collection phase typically lasts up to about 0.5 s. Then the atoms are accelerated in a moving molasses, thus launched to an apogee some 80-90 cm above the cooling region. During the cooling and launching process the Cs atoms are optically pumped to the \( |F=4, m_F = 0 \rangle \) sublevel; atoms in \( |F = 4, m_F = 0 \rangle \) are selected and transferred to \( |3,0 \rangle \) by a microwave pulse and those in \( |F = 4, m_F \neq 0 \rangle \) are removed by radiation exerted by a laser pulse. The interrogation of the ground state hyperfine transition (clock transition) is performed using the Ramsey technique of separated fields. During the ballistic flight the atoms pass twice, on the way up and down, a resonant microwave cavity installed approximately 30-40 cm below the apogee; the field inside is derived from a local oscillator (LO). Finally, the relative populations of the \( |F = 3 \rangle \) and \( |F = 4 \rangle \) states are detected by laser-induced fluorescence after the second microwave interaction, from which the transition probability is calculated. From the time-of-flight signal of the fluorescence also the number of detected atoms and their temperature can be extracted. The observed Ramsey interference fringes typically have a full-width at half-maximum of \( \Delta \nu \leq 1 \) Hz. The contrast of the fringes can be almost 100% when the field amplitude in the cavity is adjusted such that during each passage the atoms experience a microwave pulse with an area (time-integrated Rabi frequency) of \( \pi/2 \).

In order to measure the frequency of the clock transition, the difference between the frequency \( \nu \) of the LO and the centre of the central Ramsey fringe \( v_k \) is detected. In each fountain cycle the LO frequency is toggled between \( \nu + \Delta \nu/2 \) and \( \nu - \Delta \nu/2 \) (where \( \Delta \nu \) is the full width at half maximum of the fringe). Thus, the \( |3,0 \rangle \rightarrow |4,0 \rangle \) transition probabilities are measured on either side of the central fringe and, from the imbalance in the measured probabilities, the difference \( \nu - v_k \) is calculated or servoed back to zero.

The collisional frequency shift originates from the fact that the energy levels of an atom are shifted due to collisions or interactions with other atoms. The differential level shift of the two clock states is known as the clock shift. The atom-atom interaction, to good approximation, is determined by the interplay between two Born-Oppenheimer (BO)
potentials, which describe the electronic bonding between ground-state caesium atoms, the rotation of the di-atomic molecule, and the hyperfine interaction of each atom. As the depth of the BO potentials is orders of magnitude larger than the collision energies and the spatial extent of the BO potentials is much smaller than the mean distance between the caesium atoms the clock shift is expressible in terms of scattering amplitudes that depend on relative collision energy \( E \), relative orbital angular momentum, as well as the hyperfine states of the colliding atoms \([16],[17]\). In this theoretical framework the clock shift due to collisions at a single collision energy \( E \), at an instant \( t \) is given by:

\[
\Delta \omega(E, t) = n [ \hat{\lambda}_{30}(E, t) \rho_{30} + \hat{\lambda}_{40}(E, t) \rho_{40} ]
\]

where \( n \) is the atom number density, \( \rho_{30} \) and \( \rho_{40} \) are the fractions of atoms in the states \( |3,0 \rangle \) and \( |4,0 \rangle \), \( \hat{\lambda}_{30}(E) \) and \( \hat{\lambda}_{40}(E) \) are collision rate coefficients determined by scattering amplitudes. We assume that in the experiment only the states \( |3,0 \rangle \) and \( |4,0 \rangle \) are populated \( (\rho_{30} + \rho_{40} = 1) \). The calculated coefficients \( \hat{\lambda}_{30}(E) \) and \( \hat{\lambda}_{40}(E) \) are shown in Fig. 1. Most notable is that the energy dependence of the two rate coefficients is very different. The rate coefficient \( \hat{\lambda}_{30}(E) \) changes sign at \( E/k_B = 0.16 \mu K \) while \( \hat{\lambda}_{40}(E) \) is always negative. By controlling the atom fractions (or state composition) the collision energy at which \( \Delta \omega(E) \) changes sign can be controlled.

In the experiment there is a distribution of collision energies, which evolves during the ballistic flight. Thus the expression for \( \Delta \omega(E) \) must be modified to include an average over the spatial and velocity density \( n(x, v, t) \) of the spreading atom cloud and to find the instantaneous clock shift:

\[
\Delta \omega(E, t) = \frac{1}{N} \left( \langle \hat{\lambda}_{30}(E, t) \rho_{30} + \hat{\lambda}_{40}(E, t) \rho_{40} \rangle n(x, v, t) n(x, v', t) \right)
\]

where \( \langle \ldots \rangle \) denotes integration over spatial \( (x) \) and velocity coordinates, \( N = \langle n(x, v, t) \rangle \) is the total number of atoms, and \( n(x, v, t) \) is the density distribution of the cloud. Time \( t \) satisfies \( t_{up} < t < t_{down} \) (\( t_{up} \) and \( t_{down} \) are the instants of passage through the Ramsey cavity, respectively, and \( t = 0 \) is the launch time). Our observed clock shift is the instantaneous clock shift \( \Delta \omega(t) \) averaged over the time the atoms spend between the two microwave interactions at \( t_{up} \) and \( t_{down} \) (Ramsey time). We calculated the clock shift by performing 3D Monte Carlo simulations of the expanding cloud \([18]\).

The collision energies during the Ramsey time may be significantly lower than those derived from the launch temperature, typically 1-2 \( \mu K \). The low collision energies result from a purely kinetic effect, position-velocity correlations, which develop in the expanding atomic cloud \([19],[20]\). As the cloud expands, collisions are only possible for the atoms with small relative velocities \( v_{coll} < \zeta_0 / t \). For \( T_0 = 1 \mu K, \zeta_0 < 1 \text{mm} \) and \( t > t_{up} \) the collision energies divided by the Boltzmann constant are less than 300 nK. For these collision energies the rate coefficients \( \hat{\lambda}_{30} \) and \( \hat{\lambda}_{40} \) differ in sign (Fig. 1), which gives rise to a strong variation of the collisional clock shift if the composition of the clock states (after the first Ramsey interaction) is varied.
Our experiments to demonstrate the collisional shift variation were performed on two independent primary frequency standards: NPL-CsF1 at National Physical Laboratory and PTB-CSF1 at Physikalisch-Technische Bundesanstalt [21], [22]. The collisional shift is expected to vary linearly with $\rho_{40}$, which is changed by adjusting the amplitude of the microwave field in the Ramsey cavity ($\rho_{40} = 0.5$ corresponds to the $\pi/2$ pulses optimising the fringe contrast). The results are shown in Fig. 2. In both cases the linear function is an excellent fit to the experimental data. The cancellation point was found at $\rho_{40}^{(C)} = 0.396 \pm 0.012$ for the NPL case, and at $\rho_{40}^{(C)} = 0.298 \pm 0.006$ for the PTB case. The differences in $\rho_{40}^{(C)}$ and the slopes of the lines in Fig. 2 for the two experiments come from the differences in launch parameters, especially $\zeta_0$ and the timing of the Ramsey interactions ($t_{up}$ and $t_{down}$) for the two set-ups.

![Fig. 2](image_url)

**Fig. 2.** Measurement of the collisional frequency shift as a function of the population composition during the Ramsey time.

The experimental data are fitted by a linear function. Grey symbols - data from NPL-CsF1; black symbols - data from PTB-CSF1. Cancellation points are the zero crossings of the linear fits, respectively.

### 3. VERIFICATION OF THE THEORETICAL MODEL

The theoretical model presented in Ref. [13] and briefly recalled above provides a good quantitative explanation of the experimental results reported in the same paper. Here we present additional experimental verification of the model. Such more quantitative verification is desirable to validate the model, so that it can later be used to estimate the uncertainty of the collisional shift for a fountain operating at the shift cancellation point. We also show in this section that our experiments confirm the most recent theoretical calculations of $\lambda_{30}$ and $\lambda_{40}$ based on the scattering parameters of Ref. [15].

As mentioned in the previous section, the instantaneous clock shift depends on the collision energy and is weighted by the density in the atomic cloud, both decreasing rapidly during the ballistic flight in the fountain (Fig. 3). The evolution of the collision energy depends on $\zeta_0$ and, to a lesser extent, on $T_0$ [18], [20]. Unfortunately, varying $\zeta_0$ in the experiment may complicate interpretation of the results as it affects other parameters like the number of atoms trapped (hence the average density) and the launch temperature. Another avenue for testing of the theoretical model is a variation of the toss height. Changing the launch height does not affect the temporal evolution of the collision energy or the density in the cloud. However, for reduced toss height, set by choosing a different launch velocity, the atoms reach the (fixed) Ramsey cavity later and return sooner. The collisions between the two Ramsey interactions therefore take place under different effective temperature and density conditions (Fig. 3), leading to a measurable change in the average collision shift (for given $\rho_{40}$) as a function of toss height.
Fig. 3. Instantaneous collisional shift calculated according to Equation (2): \( \rho_{\text{40}} = 0.4 \) – black line; \( \rho_{\text{40}} = 0.6 \) – grey line. Marked are the times of Ramsey interactions for two toss heights (above the cavity centre) in NPL-CsF1: \( h_1 = 310 \) mm and \( h_2 = 125 \) mm. For lower toss height the cloud takes longer to reach the Ramsey cavity from below and returns to it sooner.

| Parameter                                      | NPL-CsF1 | PTB-CSF1 |
|------------------------------------------------|----------|----------|
| Launch height (above the Ramsey cavity centre) (mm) | \( h_1 \) | \( h_2 \) |
| 1\textsuperscript{st} cavity passage, \( t_{\text{up}} \) (ms) | 164      | 209      |
| 2\textsuperscript{nd} cavity passage, \( t_{\text{down}} \) (ms) | 669      | 528      |
| Ramsey fringe width (Hz)                        | 0.98     | 1.56     |
| Initial cloud size, \( \varphi_0 \) (mm)       | 0.55     | 0.4      |
| Temperature at launch, \( T_0 \) (\( \mu \)K)   | 1.5      | 2.0      |

Tab. 1. Details of the experimental set-ups NPL-CsF1 and PTB-CSF1. The respective passage times through the Ramsey cavity are given relative to the launch instant.

The dependence of the collisional shift on \( \rho_{\text{40}} \), for two toss heights (above the microwave cavity) was again tested in the two set-ups NPL-CsF1 and PTB-CSF1. The details of the two experiments are given in Table I. In Fig 4 we show the results of both numerical simulations and a measurement of the shift versus \( \rho_{\text{40}} \). The straight lines are generated by the model with only one free parameter, proportional to the initial number of atoms at launch, which may be not known accurately. This parameter is the same for the two sets of data corresponding to the two toss heights \( h_1 \) and \( h_2 \) and was fitted for the data set obtained for the height \( h_1 \). We have found a very good agreement between the theoretical lines and the experimental points obtained for \( h_2 \) for both the NPL and PTB set-ups.

In our theoretical model so far we have used scattering parameters from Ref. [15] originating from a measurement of some 60 Feshbach resonances for weakly bound states of the Cs\(_2\) dimer. The data presented in Fig. 4 can be also compared with a model using a different set of the scattering parameters based on an earlier measurement of only 25 Feshbach resonances [14]. Fig 5 shows the experimentally measured cancellation point, \( \rho_{\text{40}}^{(C)} \) for the two fountain heights in NPL-CsF1 (as in Fig. 4a) and the modelling with no free fit parameters based on the two sets of scattering parameters. The error bars of the experimental points represent a calculated uncertainty of \( \rho_{\text{40}}^{(C)} \) due to the uncertainty in the initial cloud size of 10%. We note that the experimental data are in a better agreement with the theory based on the parameters from Ref. [15].
4. OPERATION AT THE ZERO-COLLISIONAL SHIFT POINT

4.1 Reduction in averaging time

Let us consider a fountain operated alternately at high and low density $n_H$ and $n_L$ in order to determine the collisional-shift correction; $n_H / n_L = \kappa > 1$. The measured frequencies are $\nu_H$ and $\nu_L$, and the frequency $\nu_0$ extrapolated to zero density is given by:

$$\nu_0 = (\kappa \nu_L - \nu_H) / (\kappa - 1).$$  \hspace{1cm} (3)

Applying the rules of error propagation and assuming that $\kappa$ is known accurately, we find that the Allan deviation $\sigma_0$ of $\nu_0$ is:

$$(\kappa - 1)\sigma_0(2\tau) = \sqrt{\kappa^2 \sigma_L^2(\tau) + \sigma_H^2(\tau)},$$  \hspace{1cm} (4)
where \( \sigma_L \) and \( \sigma_H \) are the Allan deviations for the fountain operating at low and high density, respectively, and \( \tau \) is the averaging time for a single density (thus \( \sigma_0 \) is determined every \( 2\tau \)). In order to further simplify our analysis, we take \( \sigma_L \approx \sigma_H \), which is the case when the noise is dominated by the LO phase noise, and assume that the fountain cycle time is kept unchanged between high and low density operation. For \( \kappa = 2 \) we get:

\[
\sigma_0(\tau) = \sqrt{2} \sigma_0(2\tau) = \sqrt{10} \sigma_H(\tau).
\]

(5)

On the other hand, for operation at the zero-shift point the fountain could be run at optimum density \( n_H \) all the time, giving:

\[
\sigma_0(\tau) = \sigma_H(\tau).
\]

(6)

Because for white frequency noise the single Allan deviations are proportional to \( \tau^{-1/2} \), one finds that without density correction the measurement time to reach a specified statistical uncertainty \( \sigma(\tau) \) is reduced with respect to the case of Eq. (5) by a factor of 10. In most experiments \( \sigma_L \approx \sigma_H \) holds due to the quantum projection noise or the technical noise in detection [23]. In those cases the averaging time reduction factor would be even larger. One should note, however, that additional time is needed beforehand to determine the zero shift point \( \rho_{40}^{(C)} \) (see next subsection).

4.2 Determination of the zero-point shift

If a fountain operates at the \( \rho_{40}^{(C)} \) fractional population, the collisional shift is nominally zero. However, there are two groups of factors contributing to the uncertainty of the frequency shift: the accuracy of the initial determination of \( \rho_{40}^{(C)} \) and the stability of its realisation during the fountain operation period. Using the theoretical model presented in Refs. [13] and [18] and further verified experimentally as shown in section 3 of this paper, we have analysed those factors, aiming to estimate an uncertainty related to a residual collisional shift in a fountain operating at the zero-shift point. The zero-shift point only exists if the initial cloud size \( \zeta_0 < 1 \text{ mm} \) (for temperatures \( T_0 \approx 1 \mu\text{K} \) [13]). This requirement sets a limit on the maximum atom number in the MOT to less than \( 10^6 \) [24], of which number about 10% end up in the \( |3, 0 \) state after state selection. Assuming that 20% of the selected atoms are detected after the Ramsey interaction, with a 1 Hz fringe width and a cycle time of 1 s, the best short-term stability would be \( \sigma_0 = 0.3 \times 10^{-13} (\tau s)^{1/2} \) if the detection were limited by atomic shot-noise. In many cases, however, where the PFS uses a room temperature dielectric oscillator as a LO, the short-term stability is limited at about \( 10^{-13} \tau^{1/2} \) due to an aliasing effect (the so called Dick effect) [25] and very large atom numbers (large \( \zeta_0 \)) are not needed. Therefore, in the numerical examples following here we will consider a fountain with \( 2 \times 10^7 \) atoms collected in a MOT (2 \( \times \) 10^6 atoms selectively transferred to \( |3, 0 \) and \( 4 \times 10^5 \) detected) and of a short-term stability limited at \( 10^{-13} \) (1 s) by LO noise (\( \sigma_{\text{LO}} \approx \sigma_L \)). We further assume \( T_0 = 1.5 \mu\text{K} \), \( \zeta_0 = 0.55 \text{ mm} \), launch height \( h_l = 31 \text{ cm} \) and cavity position as in NPL-CsF1 (Table I).

First we calculate the variable collisional shift as a function of \( \rho_{40} \) for the parameters specified above. For the zero-shift point we obtain \( \rho_{40}^{(C)} = 0.4 \) (black solid line in Fig. 4a). In order to keep the residual collisional shift small (e.g. \( < 4 \times 10^{-16} \)), \( \rho_{40}^{(C)} \) has to be determined with 2% accuracy. While the theoretical model reproduces well the observed data (as in Fig. 4) the accuracy of the \( \rho_{40}^{(C)} \) prediction is limited by uncertainties of the fountain parameters (e.g. \( \zeta_0 \)) and in practice \( \rho_{40}^{(C)} \) has to be found experimentally.

In principle, in order to find \( \rho_{40}^{(C)} \) one needs to obtain two points on the shift versus \( \rho_{40} \) plot (Fig. 6). One way to do it, which minimizes the averaging time, is to measure an absolute collisional clock shift \( f_1 \) at one point (for a population fraction \( \rho_{40}^{(1)} \)), and in addition to find the slope \( m \) of the linear dependence:

\[
m = \frac{\Delta f}{\rho_{40}^{(2)} - \rho_{40}^{(1)}}.
\]

(7)

The slope can be found by measuring a difference in the clock shift, \( \Delta f = f_1 - f_2 \) between \( \rho_{40}^{(1)} \) and \( \rho_{40}^{(2)} \). Experimentally, one needs to perform only three frequency measurements against a stable reference: at \( \rho_{40}^{(1)} \) with high atomic density, at \( \rho_{40}^{(1)} \) with low density and at \( \rho_{40}^{(2)} \) with high (or low) density. The zero-shift point is then given by:

\[
\rho_{40}^{(C)} = \rho_{40}^{(1)} - \frac{f_1}{m} = \frac{f_1}{\Delta f} (\rho_{40}^{(2)} - \rho_{40}^{(1)}).
\]

(8)
The residual clock shift \( u_{f_0} \) (deviation from zero shift) related to an inaccurate determination of the zero-shift point \( \rho_{40}^{(C)} \) (with uncertainty \( u_{\rho_c} \)) is given by:

\[
u_{f_0} = \frac{u_{\rho_c} \Delta \rho}{\rho_{40}^{(2)} - \rho_{40}^{(1)}}. \tag{9}
\]

The values of \( \rho_{40}^{(1)} \) and \( \rho_{40}^{(2)} \) can be known accurately enough, so that \( u_{\rho_c} \) (obtained from eq. (8)) is dominated by the clock shift uncertainties \( u_{f_1} \) and \( u_{\Delta f} \):

\[
u_{f_1} = f_1 \left[ \frac{u_{f_1}}{f_1} \right]^2 + \left[ \frac{u_{\Delta f}}{\Delta f} \right]^2. \tag{10}
\]

It is advantageous to choose \( \rho_{40}^{(1)} \) in the vicinity of the expected \( \rho_{40}^{(C)} \) value, and \( \rho_{40}^{(2)} \) so that \( f_1 \ll \Delta f \). In this case, the residual collisional clock shift is approximately \( u_{f_0} \approx u_{f_1} \).

![Diagram](image)

Fig. 6. Procedure for the determination of the zero-shift point \( \rho_{40}^{(C)} \). The error bars for the point at \( \rho_{40}^{(1)} \) are equal to \( u_{f_1} \) and for the point at \( \rho_{40}^{(2)} \) are equal to \( \sqrt{u_{f_1}^2 + u_{\Delta f}^2} \).

For the example of NPL-CsF1, the averaging time required in order to achieve \( u_{f_1} \leq 10^{-15} \) (\( \rho_{40}^{(C)} \) determination time) is approximately \( \tau_{\text{determin}} \approx 17 \) hours (or 2.7 days for \( u_{f_1} \leq 5 \times 10^{-16} \)). After the initial determination of the \( \rho_{40}^{(C)} \), the fountain is expected to operate without extrapolation of the collisional shift, providing a number of accurate frequency measurements over a period \( \tau_{\text{oper}} \), before the next determination of \( \rho_{40}^{(C)} \) is required. The expected shortening of the averaging time in individual frequency measurements will only be realised if the determination remains valid for \( \tau_{\text{oper}} >> \tau_{\text{determin}} \).

4.3 Stability of the shift cancellation point

The evolution of the effective collision energies in an expanding cloud (and hence the average clock shift) depends on the initial parameters \( \zeta_0 \) and \( T_0 \) as well as on the launch parameters and effectively on \( t_{\text{up}} \) and \( t_{\text{down}} \). Therefore, the instability of these parameters over \( \tau_{\text{oper}} \) will limit the stability of \( \rho_{40}^{(C)} \). Fig. 7 shows average clock shifts calculated as a function of the initial cloud size for three initial temperatures. From the slope of the 1.5 \( \mu \)K curve (black solid line) we find that a 3% drift in the cloud size around \( \zeta_0 = 0.55 \) mm results in a clock-shift variation of \( 4 \times 10^{-16} \). Experimentally,
the fluctuations and long-term drift in $\zeta_0$ can easily be monitored during fountain operation. Furthermore, it is possible to introduce a number of improvements in the experimental set-up (e.g. magnetic shielding of the trapping region, active stabilisation of amplitude and polarisation of the cooling beams) in order to reduce the fluctuations of $\zeta_0$.

To estimate the sensitivity of the clock shift to fluctuations of the initial temperature, we allow 10% variation of $T_0$, which is a realistic estimate based on experiment. We calculated $\rho_{40}^{(C)}$ corresponding to various values of $\zeta_0$ and then a residual clock shift at $\rho_{40} = \rho_{40}^{(C)}$ due to the 10% change of $T_0$. We found the residual clock shift to be less than $10^{-16}$ if in addition $\zeta_0$ is stable to 3%.

Our theoretical model also allows us to search for the bounds of the collisional shift variations due to instability of the microwave field amplitude in the Ramsey cavity, which defines the fractional population $\rho_{40}$. In order to keep the shift uncertainty at $10^{-16}$ or less, $\rho_{40}$ must be stable to 1% or better and the microwave field amplitude to 0.6%. While a microwave source output can achieve such stability, the coupling efficiency of the microwaves to the cavity also depends on the cavity detuning. For example, for a cavity $Q$-value of $10^4$ the detuning is required to be stable within 60 kHz, if the cavity is tuned to the atomic resonance. This is equivalent to a cavity temperature stability of about 0.3 K, well within the range of a simple temperature servo.

As mentioned earlier, the collisional shift observed in the experiment is the time average of the instantaneous shift between the instants of the two Ramsey interactions. Any variation in the launch height (i.e. the averaging period for the instantaneous collisional shift) would result in variation of the observed overall collisional shift. We find that such variations would be of the order of $0.5 \times 10^{-16}$ if the launch height were stable to 2 mm. By measuring the time-of-flight to the detection region one can monitor possible fluctuations of the launch height and the required stability is normally achieved in the experiment.

5. ACCURACY OF THE COLLISIONAL SHIFT EVALUATION

In Table II we summarise the requirements regarding the stability of the key operational fountain parameters together with the possible residual collisional shift. We conclude that it should be possible to operate a MOT based fountain frequency standard without having to apply any corrections for cold collisions. When operating the standard at the zero collisional shift point the extrapolation to zero density would not be needed and the overall residual clock shift should not exceed parts in $10^{16}$. The related type-B uncertainty of the collisional shift would be dominated by the statistical resolution of the $\rho_{40}^{(C)}$ determination (averaging time $\tau_{determin}$) and the long-term stability of $\zeta_0$. While the allowed 3% instability of $\zeta_0$ may appear demanding, we have observed the same residual clock shift within a part in $10^{16}$ in two measurement campaigns performed in 6 months time interval [26].
Tab. II. Summary of the stability requirements for the key fountain parameters and their effect on the residual collisional shift at $\rho_{40}^{(C)}$.  

| Parameter | Permissible instability | Residual shift (fractional) |
|-----------|-------------------------|----------------------------|
| Initial cloud size, $\zeta_0$ | 3% | $4 \times 10^{-16}$ |
| Temperature at launch, $T_0$ | 10% | $1 \times 10^{-16}$ |
| Microwave field amplitude, $x$ (cavity temperature, $T_{\text{cav}}$) | 0.6% (0.3 K) | $1 \times 10^{-16}$ |
| Launch height | 2 mm | $0.5 \times 10^{-16}$ |

The required stability of the parameters may appear difficult to achieve in a particular realisation of a fountain standard. Nevertheless, the operation at $\rho_{40}^{(C)}$ with extrapolation to zero density may still help to reduce the systematic uncertainty of the collisional shift, often approximately proportional to the shift itself [8]. In fact, the collisional shift uncertainty could be reduced to parts in $10^{-17}$, although in the case of the extrapolating operation, the reduction of averaging time described in section 4.1 does not apply. In order to gain both in terms of accuracy and stability an additional leverage in the collisional shift measurement is necessary. As discussed above, increasing the atom number (or density) is limited by the condition $\zeta_0 < 1$ mm. We note, however, that the effective atom number is reduced by approximately a factor of 10 in the process of selecting the atoms in $m_F = 0$. It should be possible to transfer the atoms in $m_F \neq 0$ to $m_F = 0$ in an efficient way, e.g. by optical pumping, and hence increase significantly the number of colliding atoms.

The accuracy of the collisional shift evaluation for a fountain operating away from the $\pi/2$ excitation (required for $\rho_{40} = \rho_{40}^{(C)}$), might be affected by the effect of cavity pulling, which also causes a frequency shift proportional to the number of atoms (first-order effect) [27]. We estimate, however, that in the case discussed above this effect is small ($< 10^{-16}$). Also the second-order pulling effect, independent of the atom number [28], is negligible despite operating at excitation not optimised to $\pi/2$ pulse area.

Finally we point out that the ultimate limit of the collisional shift evaluation, in the non-extrapolating as well as in the extrapolating mode, will be related to collisions with atoms populating $|F = 3, m_F \neq 0\rangle$ (left over, e.g., due to optical pumping by the radiation pressure pulse after the state selection) [29]. Again, the effect is expected to be negligible for the number of atoms in the fountain considered in our example.

### 6. APPARENT POWER DEPENDENT FREQUENCY SHIFT

In this section we describe a situation where the varying collisional frequency shift can be misinterpreted as a power-dependent shift. This misinterpretation may affect analyses of fountains tested at multiple-$\pi/2$ microwave pulse areas. Such tests are typically performed in search for microwave and cavity related systematic frequency biases. In general, these effects may depend on the microwave power in a complex way, but in some special cases the dependence exhibits an oscillating signature, with the amplitude of the oscillations increasing with the field amplitude [30]-[32].

We first note that the average effect of the microwave excitation will vary depending on whether the atoms are ascending or descending in the fountain. The effect is evident when comparing excitation curves (population $\rho_{40}$ as a function of the microwave amplitude, initially $\rho_{40}=0$) observed in the following cases (Fig. 8): (i) microwave field on when atoms are ascending and off when descending (full grey circles); (ii) field off for ascending atoms and on for descending atoms (open grey circles). As shown in Fig. 8, the two curves dephase with respect to each other as the field amplitude increases. The third curve, for the oscillations of $\rho_{40}$ in the case of the Ramsey configuration ((iii) field continuously on, black circles), also dephases from (i). Note that choosing the microwave power for maximum transfer to $|4, 0\rangle$ in case (iii) results in $\rho_{40} = 0.5$ after the first Ramsey interaction (case (i)). The deviation from $\rho_{40} = 0.5$ increases with the field amplitude and changes sign for subsequent odd multiples of $\pi/2$ pulse area (arrows in Fig. 8).
Since the collisional frequency shift depends linearly on $\rho_{40}$, the varying collisional shift can be misinterpreted as a shift caused by microwave leakage, spurious components in the microwave spectrum, or cavity phase gradients. Misidentification of the collision-induced shift may thus lead either to overestimation of these effects or to a significant underestimation of the effect (i.e. when a null effect is observed as a result of destructive interference of the shifts) [33].

7. CONCLUSIONS

We have demonstrated theoretically and experimentally that the frequency shift due to collisions between cold atoms in a caesium fountain clock strongly depends on the proportion of the two clock state populations, $|3,0\rangle$ and $|4,0\rangle$, established after the first passage through the microwave cavity. At effective temperatures well below 1 $\mu$K the collision rates $\lambda_{30}$ and $\lambda_{40}$ have opposite signs, making it possible to cancel the collisional shift for a particular composition of the clock states. This offers the intriguing prospect of operating a fountain standard at the zero-shift point, hence without having to apply any corrections for cold collisions. Such operation of the fountain standard offers a much improved effective short-term stability and about a ten-fold reduction in averaging time.

We have estimated the expected improvements in the standard’s performance and derived relevant requirements for the key operational parameters of the fountain. The residual clock shift is likely to be dominated by long-term instabilities in $\omega_{0}$, but should not exceed a few parts in $10^{16}$. Alternatively, operation at $\rho_{40}^{(C)}$ with extrapolation to zero density would help to reduce the systematic uncertainty of the collisional shift, to parts in $10^{17}$.

Finally, we have shown that the variation of the collision-induced frequency shift has the potential to mask or at least alter any power dependence of the frequency of the standard, which may arise due to imperfections in the microwave part of the set-up.

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