Highly charged ions: optical clocks and applications in fundamental physics

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Recent developments in frequency metrology and optical clocks have been based on electronic transitions in atoms and singly charged ions as references. The control over all relevant degrees of freedom in these atoms has enabled relative frequency uncertainties at a level of a few parts in $10^{-18}$. This accomplishment not only allows for extremely accurate time and frequency measurements, but also to probe our understanding of fundamental physics, such as a possible variation of fundamental constants, a violation of the local Lorentz invariance, and the existence of forces beyond the Standard Model of Physics. In addition, novel clocks are driving the development of sophisticated technical applications. Crucial for applications of clocks in fundamental physics are a high sensitivity to effects beyond the Standard Model and Einstein’s Theory of Relativity and a small frequency uncertainty of the clock. Highly charged ions offer both. They have been proposed as highly accurate clocks, since they possess optical transitions which can be extremely narrow and less sensitive to external perturbations compared to current atomic clock species. The large selection of highly charged ions in different charge states offers narrow transitions that are among the most sensitive ones for a change in the fine-structure constant and the electron-to-proton mass ratio, as well as other new physics effects. Recent experimental advances in trapping and sympathetic cooling of highly charged ions will in the future enable advanced quantum logic techniques for controlling motional and internal degrees of freedom and thus enable high accuracy optical spectroscopy. Theoretical progress in calculating the properties of selected highly charged ions has allowed the evaluation of systematic shifts and the prediction of the sensitivity to the “new physics” effects. New theoretical challenges and opportunities emerge from relativistic, quantum electrodynamics, and nuclear size contributions that become comparable with interelectronic correlations. This article reviews the current status of theory and experiment in the field, addresses specific electronic configurations and systems which show the most promising properties for research, their potential limitations, and the techniques for their study.

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I. INTRODUCTION

In this review we cover current and new research directions that arise from high precision spectroscopy and novel optical clocks using trapped highly charged ions (HCI). The recent interest in high resolution optical spectroscopy of HCI has been triggered by their high sensitivity to a change in the fine-structure constant $\alpha$ (Sec. II). Since the required HCI physics is generally less well known compared to neutral and singly-charged atoms, Sec. III recapitulates the current status of theory, including quantum electrodynamics (QED), mostly dealing with few-electron HCI. In Sec. IV we present recent theory on more complicated electronic systems that are particularly interesting for frequency metrology, and discuss them in detail.

We present the current status of experimental methods in Sec. V, with a particular emphasis on the field of optical spectroscopy (Sec. V.E). Novel methods needed for high resolution optical spectroscopy with HCI are introduced in Sec. V.G and VI, and an analysis of clock shift systematics with HCI candidates follows in Sec. VII. Future directions of research are discussed in Sec. VIII.

A. Atomic clocks for exploring old and new physics

Celestial mechanics, based on the (for their time) exceptionally precise measurements of astronomy, became one of the most fruitful disciplines in theoretical physics and was the key for many discoveries in other fields. In the same way, atomic and optical clocks (Ludlow et al., 2015), aided by advances in atomic structure theory are evolving into an exceptional driving force for the search for new physics. Frequency measurements of narrow transitions in atoms, with their universal reproducibility that is paradigmatic in science, serve as benchmarks for the most subtle deviations from the theoretical framework of physics, while high-energy physics aims at testing the boundaries of our knowledge in huge facilities. These complementary approaches eventually aim at answering the same questions.

In atomic clocks, physics interactions appear as contributions to the electronic binding energies or the transition rates in a hierarchy now stretching over 18 orders of magnitude. Novel clocks are capable of addressing those in more and more depth, and their rapid development in the last decades heralds further advances. Progress in optical clocks is based on an improved control over all degrees of freedom, including the internal state, the motion, and external fields affecting the transition frequency, paired with increased accuracy of electronic structure calculations of atomic properties. This has been accomplished through the rapid development of suitable laser cooling and trapping techniques based on the pioneering work of Ashkin (1978); Aspect et al.
et al. (1986); Bollinger et al. (1985); Hänsch and Schawlow (1975); Lett et al. (1988); Metcalf and van der Straten (2007); Neuhauser et al. (1978); Phillips (1998); Phillips et al. (1985); Stenholm (1986); Wineland et al. (1978); Wineland and Itano (1979).

However, progress in atoms (such as most HCI), that do not possess the required properties for cooling and trapping could not profit from these advances. This situation has recently changed with the development of quantum logic techniques for spectroscopy in which a cooling ion, trapped together with the spectroscopy ion, provides sympathetic cooling as well as control and readout of the internal state of the spectroscopy ion. This arrangement forms a compound system combining the advantages of both species and makes previously intractable atoms, such as HCI, accessible for high resolution spectroscopy.

Similarly to the progress in experimental techniques, advances in atomic structure theory are required for exploiting the present and future experimental precision in order to improve our knowledge of the various fundamental interactions that are intertwined within the electronic shell. For the present status of optical clocks, we refer to the recent review of Ludlow et al. (2015), and for a general work on atomic physics methods for probing fundamental physics to Safronova et al. (2018). Within this review we will be concerned with the specific aspects related to the applications of HCI as novel atomic frequency references.

B. Atomic physics at the extremes: Highly charged ions

Since the epoch of reionization – roughly 13 billion years ago – atomic matter in the universe mostly appears as ions (Shull et al., 2012). Now, the majority of the chemical elements can be found as highly charged ions. Following Big-Bang nucleosynthesis and 400 million years of expansion, reionization was driven by strong radiation sources, stars coming into being by the gravitational collapse of cold neutral gas. Supernovae later infused space with heavy elements, heating interstellar matter in shocks to very high temperatures (Hitomi Collaboration et al., 2017). Furthermore, as a consequence of energy virialization in deep gravitational potentials, the translational temperature of the diffuse intergalactic medium containing most of the baryonic matter is also very high ($10^{5-7}$ K) (Reimers, 2002). Here, ions reign absolute, no matter how low the radiation temperature of the medium around them might be. Galaxy clusters, galaxies with their active galactic nuclei, binary x-ray systems and stars are extremely hot environments; hot winds and relativistic jets expel highly ionized material out of the galactic cores (Hitomi Collaboration et al., 2016). X-ray astronomy missions such as the present Chandra and XMM-Newton allow us to observe such environments, and they as well as the future ones XARM (Hitomi Collaboration et al., 2016) and Athena (Barcons et al., 2017) will produce more and more quantitative results. This emphasizes the need for laboratory data and advanced atomic structure calculations for their interpretation; therefore, studying HCI is essential for astrophysics diagnostics (Beiersdorfer, 2003). In addition, HCI play a central role in plasma physics (Beiersdorfer, 2015), and in various aspects of fundamental research such as tests of quantum electrodynamics (QED) (Beiersdorfer, 2010), developing relativistic atomic structure theory, and other applications (Beyer et al., 1997; Gillaspie, 2001; Martinson, 1989; Zou et al., 2016). In the present review we address novel avenues of research which have recently been proposed, and recapitulate about their foundation in the exciting atomic physics properties of HCI.

Due to their fundamental role in atomic structure theory and quantum mechanics, the most investigated iso-electronic sequences have been the hydrogenlike and lithiumlike ones, with one single ns electron being amenable to accurate theoretical calculations of the dominant terms of the energy Hamiltonian. The heliumlike sequence has also seen a wealth of calculations (see, e.g. (Andreev et al., 2001; Artemyev et al., 2005; Chen et al., 1993; Cheng and Chen, 2000; Cheng et al., 1994; Drake, 1979, 1988, 2002; Indelicato et al., 1987; Johnson et al., 1995; Lindgren et al., 2001, 1995; Plante et al., 1994; Yan and Drake, 1995)), since understanding the two-electron correlations is believed to be the gateway to the study of more complex quantum systems.

Relativistic fine-structure, QED and nuclear size effects (see Sec. III) show along any given iso-electronic sequence a much stronger dependence on the nuclear charge than electronic correlations. Advantageously, this tunability of the various terms of the Hamiltonian can be used to tailor studies capable of separating their relative contributions.

Owing to the reduction of the number of bound electrons, electronic structure theory becomes – in principle – less complicated. Nonetheless, in astrophysics and plasma applications (see, e.g., reviews by Beiersdorfer (2003, 2015)), which often deal with ions having more complex electronic structures, an accurate treatment of electronic correlations is as important as that of relativistic effects and QED. This is crucial in order to improve the quantitative understanding of plasmas.

In most cases, the strongest transitions observed in HCI are in the X-ray region. Nonetheless, they also display observable transitions in every spectral range, and in particular also in the optical regime, around which this review is centered. There are several possibilities for optical transitions arising in HCI (Crespo López-Urrutia, 2008). As a function of increasing charge state, fine- and even hyperfine structure splittings reach the optical regime. Furthermore, level crossings between different
Electronic configurations can result in transitions in the optical wavelength range.

Production of HCI in a laboratory environment is a long-standing problem. Few groups could routinely generate those ions, since the techniques were complicated and expensive. For these reasons, there is still an enormous scarcity of data and the majority of possible ions in this “spectral desert” remains unexplored. As for high-accuracy measurements, the best results in the field of HCI spectroscopy lag by more than ten orders of magnitude behind of what is now possible in atomic physics with neutral atoms, or singly charged ions. Compounding the lack of experimental data, theory encounters a rugged terrain when scouting beyond its usual range. Complex electronic configurations with several shell vacancies in the ground state configuration are still very hard challenges for advanced atomic structure theory.

Further development of both HCI theory and experiment became crucial in the past several years after a completely new avenue of research blossomed following the pioneering work by Berengut et al. (2010), which identified HCI optical transitions between states with different electronic configurations and proposed their applications for optical metrology and tests of variation of the fine-structure constant. This work and subsequent studies (Berengut et al., 2011a,b, 2012a,b; Derevianko et al., 2012; Dzuba et al., 2012a,b, 2013; Dzuba et al., 2015a,b; Kozlov et al., 2013; Safranova et al., 2014a,b,c; Yudin et al., 2014) demonstrated that despite very large ionization energies, certain HCI have very narrow transitions that lie in the optical range and can be used for the development of ultra high-precision clocks and tests of fundamental physics.

This new dimension in the parameter space of precision atomic physics opens a wide field of research opportunities. HCI are less sensitive to external perturbations than either neutral atoms or singly charged ions due to their more compact size. Recent studies of systematic uncertainties (Derevianko et al., 2012; Dzuba et al., 2012a, 2013) have shown that the achievable fractional inaccuracy of the transition frequency in the clocks based on HCI may be smaller than $10^{-19}$ using shift cancelation schemes. At the same time, the clock transitions in HCI are more sensitive to the variation of $\alpha$ than those of neutral atoms (Berengut et al., 2010). Therefore, HCI-based clocks may allow significant improvement of the current experimental limit on $\alpha$ variation on the level $\dot{\alpha}/\alpha \lesssim 10^{-17}$ yr$^{-1}$ (Godun et al., 2014; Huntemann et al., 2014; Rosenband et al., 2008). Moreover, optical clocks are sensitive not only to a linear variation of $\alpha$, but also to hypothetical oscillations and occasional jumps of this parameter. Such effects can be caused by cosmological fields (Stadnik and Flambaum, 2015, 2016) and topological defects (Derevianko and Pospelov, 2014), which are often considered as candidates for dark matter (Arvanitaki et al., 2015; Derevianko, 2016). In all these cases sensitivity to $\alpha$ variation is given by the same sensitivity coefficients. Therefore, HCI based clocks are also more sensitive to all these effects than state-of-the-art atomic clocks.

Two major obstacles on the way toward the realization of such proposals in 2010 were the lack of accurate theoretical descriptions of potential clock candidates and, even more importantly, lack of experimental techniques to decelerate, trap, cool, and control HCI to observe such weak transitions and support the development of the frequency standards.

At the present time, theoretical studies have identified a list of HCI candidates for optical clock development and provided extensive calculations of relevant atomic properties. In 2015, crucial experimental steps were achieved with a breakthrough demonstration of sympathetic cooling of $\text{Al}^{13+}$ with a laser-cooled $\text{Be}^+$ Coulomb crystal in a cryogenic Paul trap (Schm"oger et al., 2015b). This experiment heralded the start of a new era in exploration of HCI with the techniques previously reserved for neutral and singly-charged systems. Combined with quantum logic spectroscopy, in which another ion is used for cooling and readout of the clock transitions, as it is done in the $\text{Al}^+$ clock (Schmidt et al., 2005), cold trapped HCI suddenly become an experimentally-accessible resource for precision fundamental studies. These developments represented a turning point for HCI studies and this review aims to summarize both theoretical and experimental findings and to discuss possible directions of further research.

Both theory and experiment have to be improved in order to achieve the best possible scientific harvest from these investigations. On the other hand, this is a worthwhile endeavor given the plethora of available ground state configurations with laser-accessible transitions that HCI offer. Furthermore, studies along isoelectronic sequences in HCI afford a large degree of tunability concerning the systematics of the various binding energy contributions, aiding the identification of yet unassigned HCI spectra, as shown in (Windberger et al., 2015). New measurements will provide benchmarks of the theoretical predictions and help to further improve the theory.

II. BACKGROUND: VARIATION OF FUNDAMENTAL CONSTANTS

Variation of fundamental constants is predicted by many extensions of the Standard Model (SM). Experimental searches for $\alpha$-variation allow testing of these models and search for the new physics beyond the SM. Light scalar fields appear very naturally in cosmological models, affecting parameters of the SM including $\alpha$. Space-time variations of these scalar fields are expected because of the evolution of the Universe’s composition. Theories unifying gravity and other interactions predict
spatial and temporal variation of physical “constants” in the Universe (Calmet and Keller, 2015; Dent et al., 2008; Marciano, 1984). Moreover, all coupling constants and masses of elementary particles in such models can be both space and time-dependent, and influenced by the local environment (Uzan, 2011).

Searches for variation of fundamental constants are conducted in a very wide range of systems including astrophysical studies of quasar spectra and observation of the H I 21 cm line, atomic clocks, the Oklo natural nuclear reactor, meteorite dating, stellar physics, cosmic microwave background, and big bang nucleosynthesis (see e.g. reviews (Chin et al., 2009; Koziol and Levshakov, 2013; Uzan, 2011)). Here, we only briefly discuss the laboratory limits set on the variation of the fundamental constants by atomic clocks and focus on the HCI proposals.

The transition frequency \( \nu \) between two electronic energy levels in an atom is only dependent on the fine-structure constant:

\[
\nu \simeq c R_\infty A F(\alpha), \tag{1}
\]

where \( R_\infty \) is the Rydberg constant, \( c \) is the speed of light in vacuum, \( A \) is a numerical factor depending on the atomic number \( Z \) and \( F(\alpha) \) is a function which depends upon the particular transition. Based on their respective frequency ranges, current atomic clocks based on such electronic transitions are referred to as optical clocks, while clocks based on hyperfine transitions are referred to as microwave clocks. The frequency of the electromagnetic radiation associated with transitions between the hyperfine levels, such as the Cs transition defining the SI second, may be expressed as

\[
\nu_{\text{hfs}} \simeq c R_\infty A_{\text{hfs}} \times g_i \times \frac{m_e}{m_p} \times \alpha^2 F_{\text{hfs}}(\alpha), \tag{2}
\]

where \( m_e \) and \( m_p \) are electron and proton masses, respectively, \( A_{\text{hfs}} \) is a numerical quantity depending on the particular atom, and \( F_{\text{hfs}}(\alpha) \) is a relativistic correction specific to each hyperfine transition. The dimensionless quantity \( g_i = \mu_i/\mu_N \) is the g-factor associated with the nuclear magnetic moment \( \mu_i \), where \( \mu_N = e\hbar/2m_p \) is the nuclear magneton. The potential variation of g-factors may be reduced to more fundamental quantities, such as \( X_q = m_q/A_{\text{QCD}} \), where \( m_q \) is the average light-quark mass and \( A_{\text{QCD}} \) is the QCD energy scale. As a result, the hyperfine transition frequencies are sensitive to the variation in \( \alpha \), \( \mu = m_p/m_e \), and \( X_q \).

Measuring the ratios \( R = \nu_1/\nu_2 \) of optical to hyperfine clocks over time sets limits on the variation of \( \alpha \), the proton-to-electron mass ratio \( \mu \), and nuclear g factors, specifically \( g_{\text{Cs}} \) and \( g_{\text{Yb}} \), as these correspond to the two microwave clocks with the smallest uncertainties.

The ratio of frequencies of any two optical clocks depends only upon \( \alpha \). The sensitivity of the particular optical atomic clock to \( \alpha \)-variation depends on the parameter \( q \) that links variation of the transition energy \( E_0 \), and hence the atomic frequency \( \nu = E_0/h \), to the variation of \( \alpha \)

\[
\frac{\delta E}{E_0} = \frac{2q}{E_0} \frac{\delta \alpha}{\alpha_0} \equiv K \frac{\delta \alpha}{\alpha_0}, \tag{3}
\]

where

\[
K = \frac{2q}{E_0} \tag{4}
\]

is a dimensionless sensitivity factor.

The relationship between the ratio of two clock frequencies and the variation of \( \alpha \) is then given by the difference in their respective \( K \) values for each clock transition, i.e. \( \Delta K = |K_2 - K_1| \). The larger the value of \( K \), the more sensitive is a particular atomic energy level to the variation of \( \alpha \). Therefore, it is advantageous to select transitions with significantly different values of \( K \), preferably of the opposite sign. These \( K \) factors allow comparison of the sensitivity to \( \alpha \)-variation between transitions with significantly different frequencies.

The \( K \) factors are small for most clocks currently in development, \( \text{Al}^+ (0.008), \text{Ca}^+ (0.15), \text{Sr}^+ (0.4), \text{Sr} (0.06), \text{Yb} (0.3), \text{Yb}^+ \) quadrupole transition (0.88) (Dzuba et al., 2003; Dzuba and Flambaum, 2009). The \( K \) factors for \( \text{Hg}^+ \) and \( \text{Yb}^+ \) octupole clock transitions are \(-3\) and \(-6\), respectively, making them the best candidates for one member of a clock-comparison pair, with the other member taken from the previous group. A particular attraction of HCI is the availability of transitions with much larger \( K \) factors.

The most accurate single laboratory test of \( \alpha \)-variation comes from the \( \text{Al}^+/\text{Hg}^+ \) optical clock comparison (Rosenband et al., 2008), setting the limit

\[
\frac{\dot{\alpha}}{\alpha} = (-1.6 \pm 2.3) \times 10^{-17} \text{yr}^{-1}. \tag{5}
\]

The global limits to the present day variation of \( \alpha \) and \( \mu \) from all present clock comparisons and Dy measurements (Leefer et al., 2013) are given by Godun et al. (2014); Huntemann et al. (2014):

\[
\frac{\dot{\alpha}}{\alpha} = (-2.0 \pm 2.0) \times 10^{-17} \text{yr}^{-1} \tag{6}
\]

\[
\frac{\dot{\mu}}{\mu} = (0.2 \pm 1.1) \times 10^{-16} \text{yr}^{-1}. \tag{7}
\]

A number of optical and near-optical transitions in various HCI were shown to be very sensitive to the possible variation of the fine-structure constant (Berengut et al., 2010; Berengut et al., 2011a,b, 2012a,b; Derevianko et al., 2012; Dzuba et al., 2012a,b, 2013; Dzuba et al., 2015a,b; Koziol et al., 2013; Safronova et al., 2014a,b,c; Yudin et al., 2014). The energy scale for HCI levels is large (\( \sim (Z_a + 1)² R_\infty \)), where \( Z_a \) is the ionization charge.
Optical transitions arising due to a level crossing take place between states with accidental near degeneracy. If the orbital angular momenta of the corresponding energy levels differ by two units or more, these energies have a different dependence on $\alpha$. Relativistic corrections for HCI scale as $\alpha^2 Z^2(Z_a + 1)^2 R_{\infty}$, where $Z$ is the nuclear charge, while optical frequencies are of the order of a fraction of $R_{\infty}$. As a result, the frequencies of optical transitions depend on $\alpha$ as (Berengut et al., 2010):

$$\frac{\delta \nu}{\nu} \sim \alpha^2 Z^2(Z_a + 1)^2, \quad \Rightarrow \quad K \sim 2\alpha^2 Z^2(Z_a + 1)^2.$$ Therefore, the sensitivity of optical transitions in HCI to $\alpha$-variation is enhanced by the factor $(Z_a + 1)^2 \sim 10^2$ compared to similar transitions in neutral atoms. Brief reviews of $\alpha$-variation in HCI were recently published by Ong et al. (2014) and Dzuba and Flambaum (2015).

In 2011, a very large analysis of quasar absorption spectra that combined data taken by the Keck telescope in Hawaii and the Very Large Telescope (VLT) in Chile indicated $4\sigma$ spatial gradient in the value of $\alpha$ (Webb et al., 2011). A 2015 study of systematic distortions in the wavelengths scales of high-resolution spectrographs (Whitmore and Murphy, 2015) showed that instrumental error may weaken the spatial variation result, but can not explain all of the observed $\alpha$-variation. Calculated sensitivity coefficients of the optical transitions in HCI to $\alpha$-variation are indeed much higher than in neutral atoms or singly-charged ions. This opens the possibility to drastically improve present laboratory limits on $\alpha$-variation, or find such variation and explore new physics beyond the Standard Model.

Up to now, most laboratory searches of $\alpha$-variation were focused on smooth drifts during the whole duration of the experiment (Godun et al., 2014; Huntemann et al., 2014; Rosenband et al., 2008), or on annual variations, which can be linked to the variations of the gravitational potential of the sun (see Blatt et al., 2008; Leefer et al., 2013) and references therein). However, some modern models of dark matter predict oscillations of the fundamental constants at the Compton frequency of the cosmological field, or even random jumps when the Earth passes domain walls, or other topological defects, associated with such a field (Arvanitaki et al., 2015; Derevianko, 2014; Derevianko and Pospelov, 2014; Stadnik and Flambaum, 2015). In the first approximation the sensitivity coefficient of a given optical transition to $\alpha$-variation is the same for gradual variation and for periodic variation if its frequency is much smaller than transition frequency. Because of that, HCI can be used to search for such variations and to test predictions of this class of theoretical models of dark matter. Recently, HCI have also been identified as potential candidates for significant improvement for tests of Lorentz symmetry (Shaniv et al., 2017). New experimental techniques for HCI described in this review combined with an improved theoretical description will allow for more stringent QED tests.

**III. ELECTRONIC STRUCTURE THEORY AND TESTS OF QED**

**A. Theoretical treatment of QED in HCI**

QED laid the foundation of the modern formalism of the Standard Model as the first relativistic quantum field theory (Akhiezer and Berestetskii, 1965; Bjorken and Drell, 1964; Peskin and Schroeder, 1995). It is arguably the most stringently tested part of the Standard Model. Highly charged ions are extremely relativistic systems and an accurate prediction of their electronic structure has to include large QED contributions. The understanding of QED contributions is crucial for a number of precision tests of physics beyond the SM, including those described in this review. QED contributions are also needed for determining fundamental constants. Therefore, we start the discussion of HCI electronic structure with the chapter on QED calculations in HCI and briefly review recent bound-state QED (BSQED) tests. We refer the reader to reviews by Beiersdorfer (2010); Drake and Yan (2008); Eides et al. (2001); Indelicato and Mohr (2017); Karshenboim (2005); Shabaev et al. (2015); Sturm et al. (2017, 2013b); Volotka et al. (2013) for detailed discussion of QED calculations and tests of QED. The electronic structure of HCI specific to the metrology applications and searches for the variation of fundamental constants is discussed in Section IV.

While in heavy atoms the QED contributions to the binding energy of the inner-shell electrons are equally strong to those in HCI, their investigation is hindered by the presence of filled outer shells. This causes, on one side, noticeable energy shifts, and, on the other side, reduces the lifetime of excited states through Auger decay coupling the initial state to the ionization continuum (Zimmerer et al., 1991). The resulting broadening of the electronic transitions of interest reduces spectral accuracy. In addition, theoretical methods are best developed for few-electron systems, and therefore the research quest was primarily the study of hydrogenlike and lithiumlike heavy HCI, and experimental efforts have also focused on such systems (Beiersdorfer, 2010).

Since the expansion parameter $Z\alpha$ in perturbative theory would approach a value close to 1 for heavy elements, it was not clear how far the usual expansion-based approximations would remain valid, and if contributions from two-loop QED (Yerokhin et al., 2003) could be appropriately be accounted for. To address this, non-perturbative, all-order methods have been developed, e.g., Lindgren et al. (2001); Shabaev (2002), and two-loop calculations carried out by e.g., Artemyev et al. (2005); Yerokhin et al. (2003).
A consistent QED approach is possible only within 1/Z perturbation theory for systems with up to three, or four electrons (Artemyev et al., 2005; Sapirstein and Cheng, 2011; Yerokhin et al., 2007, 2003; Yerokhin and Shabaev, 2015). For many-electron ions, which are of most interest to this review, the use of mean-field approximations (such as Dirac-Fock approximation) is necessary, and correlations are treated within relativistic quantum mechanics. In this case, QED corrections can be included by means of model potentials (Blundell, 1992; Cheng et al., 1993; Flambaum and Ginges, 2005; Ginges and Berengut, 2016; Roberts et al., 2013; Shabaev et al., 2013, 2015; Tupitsyn and Berseneva, 2013). In such calculations, the electron-electron interaction is usually treated within the Coulomb-Breit approximation, see e.g. (Konovalova and Kozlov, 2015; Schwerdtfeger et al., 2015).

Electron-electron correlation effects in many-electron ions, can be included with the help of several corrections: (i) many-body perturbation theory (MBPT) (Johnson, 2007); (ii) configuration interaction (CI) (Fischer et al., 2007; Fritzsche et al., 2002; Kotochigova and Tupitsyn, 1987; Yerokhin and Surzhykov, 2012), or multiconfiguration Dirac-Hartree-Fock (MCHF) (Fischer et al., 2007); (iii) coupled cluster (CC) method (Eliev et al., 1994; Hubac and Neograd, 1994); (iv) combinations of CI and MBPT (CI+MBPT) (Dzuba et al., 1996; Kozlov et al., 2015; Savukov and Johnson, 2002), or CI and all-order (CI+AO) methods (Kozlov, 2004; Safronova et al., 2009). Recently Tupitsyn et al. (2016) incorporated four of the most popular effective QED potentials into the CI+AO method, and tested them for several HCI. Recent developments of these theoretical methods have considerably improved the accuracy and reliability of newer calculations for HCI, and raised the predictive power of theory. We discuss the QED studies in HCI with one to three valence electrons (i.e. H-like to Li-like) in Section III.B below and return to the subject of many-electron HCI in Section IV.

B. Tests of QED effects in HCI

1. Lamb-shift studies in the x-ray region

In first order, the Lamb shift – understood as the difference between the Dirac binding energy and the actual one – of a hydrogenic ion scales with $(\alpha Z)^2/n^3$, and rises for the 1s electron of U$^{92+}$ to more than 425 eV (Johnson and Soff, 1985, 1988; Mohr, 1974). For this reason, very soon after the development of experimental methods for the production of HCI (Mokler et al., 1985), they were seen as potentially very interesting probes of QED calculations (Blundell, 1992; Johnson et al., 2004; Mohr, 1985, 1992; Mohr et al., 1998; Persson et al., 1997; Shabaev, 2002; Volotka et al., 2013) and, accordingly, studied in many experiments (Beyer et al., 1985, 1991, 1995; Briand et al., 1990, 1983a, b; Deslattes et al., 1984; Gumberidze et al., 2005; Gumberidze et al., 2004; Marmar et al., 1986; Richard et al., 1984; Tavernier et al., 1985). In fact, one of the strongest drives for research with heavy HCI in large facilities such as Bevalac at Lawrence Berkeley National Laboratory, GSI in Darmstadt, Germany, and GANIL in Caen, France, was testing QED in the non-perturbative regime. The HITRAP facility (Rodriguez et al., 2010) at GSI continues pursuing this type of research.

For the ground state of hydrogenlike uranium (U, Z = 92), the most recent Lamb-shift measurement by Gumberidze et al. (2005) has yielded 460.2±4.6 eV, to be compared with predicted 463.99(39) eV. Radiative corrections from QED contribute 265.2 eV, and a shift of -1.26(33) eV results from 2nd order QED (Beiersdorfer et al., 2005; Yerokhin et al., 2003). A comparably large correction arises from finite nuclear-size effects, with a total of 198.54(19) eV (Kozhedub et al., 2008). These results confirm QED theory predictions at the 2% level in the strongest stationary electromagnetic fields that nature provides, an extreme regime where the rest mass of the electron is only four times larger than its binding energy to the nucleus. Given the high accuracy of theory, hydrogenic systems have been proposed as calculable x-ray standards (Flowers et al., 2001).

For two-electron systems, and specifically for helium-like ions, there is abundant theoretical literature (Andreev et al., 2001; Cheng and Chen, 2000; Indelicato et al., 1987; Johnson et al., 1995; Lindgren et al., 2001, 1995). At medium Z, relativistic configuration interaction and perturbative many-body methods (Chen et al., 1993; Cheng and Chen, 2000; Cheng et al., 1994; Plante et al., 1994) as well as unified-method calculations (Drake, 1979, 1988, 2002; Yan and Drake, 1995) have yielded reasonably accurate results in close agreement with measurements of the $1s - 2p$ x-ray transitions (Amaro et al., 2012; Beiersdorfer and Brown, 2015; Briand et al., 1984; Bruhns et al., 2007; Epp et al., 2015; Indelicato et al., 1986; Kubíček et al., 2012; Machado et al., 2018; Rudolph et al., 2013; Kubíček et al., 2014; Widmann et al., 1996).

A controversy arising from a claimed Z-dependent divergence between earlier experimental data and calculations (Chantler et al., 2013, 2012; Gillaspy, 2014), soon disputed by Epp (2013), has been settled, with all newer results agreeing very well both with older calculations and advanced theory (Artemyev et al., 2005). Nonetheless, better measurements will be needed to test higher-order QED as well as interelectronic contributions to the binding energy in more detail.

In lithiumlike systems, the $2s_{1/2} \rightarrow 2p_{1/2, 3/2}$ transition energies display the largest relative QED contributions (up to 15%), and have been studied in detail both experimentally (Andreev et al., 2012, 2001; BosseLMANN et al., 1999; Brandau et al., 2002, 2003; Epp et al., 2010,
particular by means of sympathetically cooled HCI (Schnöger et al., 2015b).

The first direct observation of a hyperfine splitting (HFS) in the optical range was achieved by resonant laser excitation of the M1 transition coupling the two hyperfine levels of the ground state of hydrogen-like $^{209}$Bi$^{82+}$ ions circulating at relativistic velocities in the GSI heavy-ion storage ring ESR (Klaft et al., 1994), followed by spontaneous-emission measurements of $^{187}$Ho$^{66+}$ (holmium, Z = 67) ((Crespo López-Urrutia et al., 1996)), $^{185,187}$Re$^{74+}$ (rhenium, Z = 75) ((Crespo López-Urrutia et al., 1998a)), and $^{203,205}$Pb$^{80+}$ (thallium, Z = 81) (Beiersdorfer et al., 2001) ions trapped in an EBIT, and a further experiment on $^{207}$Pb$^{81+}$ (Seelig et al., 1998) at ESR. In all those experiments, systematic effects, low resolution and statistics limited the relative wavelength accuracies to about $1 \times 10^{-4}$.

On the theoretical side, the one-loop self-energy correction to the first-order hyperfine interaction in hydrogenic ions for various nuclear charges was theoretically studied by Persson et al. (1996). Vacuum-polarization corrections to the HFS of Bi HCI were analyzed by Labzowsky et al. (1997), and leading non-recoil radiative corrections to the HFS including effects of extended nuclear magnetization calculated by (Sumnergren et al., 1998). As for the nuclear recoil effect, Shabaev (1998); Shabaev et al. (1998, 2000); Shabaev et al. (2001) performed a sophisticated analysis of its influence on the various transitions.

3. Nuclear-size effects: Charge radius and magnetization distribution

The uncertainty of the leading radiative terms in all mentioned above calculations seems to be small compared with that of finite nuclear-size effects (NSE) appearing at the few % level in the HFS splitting (Shabaev et al., 1997). Since the finite charge radius can be independently measured in scattering experiments, its contribution (at the 10% level of the transition energy!) to the HFS could be reasonably inferred. However, the nuclear magnetization distribution, or Bohr-Weisskopf (BW) effect (at the level of 1% of the total HFS), is extremely difficult to determine independently. Basically, the only other method that can measure this quantity is $\gamma$ spectroscopy, and more recently also laser spectroscopy, on muonic atoms. Therefore, in most cases the BW effect is accounted for based on uncertain models of the nuclear magnetic structure. The situation in the BSQED tests with HCI is akin to that of the laser spectroscopy of hydrogen and the proton-size puzzle (Beyer et al., 2017; Pohl, 2016; Pohl et al., 2010, 2013, 2016): our limited knowledge of the nucleus is the frontier for the most stringent tests of QED.

In order to suppress the uncertainties stemming from finite NSE, Shabaev et al. (2001) introduced the concept of the specific isonuclear difference between the ground-
state HFS of the Li-like ion, $\Delta E(2s)$, and the H-like ion, $\Delta E(1s)$:

$$\Delta'E = \Delta E(2s) - \xi \Delta E(1s), \quad (8)$$

where the parameter $\xi$ is theoretically chosen to cancel the NSE in this difference.

By scaling with $1/n^3$ and applying relativistic corrections, $\xi$ can be calculated with high precision. For Bi (bismuth, $Z = 83$) ions, the method achieves now a relative uncertainty of $\approx 10^{-4}$ following better calculations (Volotka et al., 2012) of the two-photon exchange corrections. If HFS were measured at the $10^{-6}$ level, many-body QED effects could be benchmarked at a few percent level (Volotka et al., 2013). Experiments are already approaching this level of accuracy, e.g. for the $2s_{1/2} \to 2p_{1/2}$ EUV hyperfine transitions in Li-like and Be-like ions of $^{141}$Pr (Beiersdorfer et al., 2014).

Karpshein and Zhzaiaskovskaya (2015) have proposed the opposite approach, namely to investigate the nuclear magnetization distribution based on the HFS experimental data for various isoelectronic sequences, as had been demonstrated by Beiersdorfer et al. (2001); Crespo López-Úrrutia et al. (1998a) for the cases of Re and Tl HCl.

In order to solve some open questions, Lochmann et al. (2014) repeated the HFS measurements in hydrogen-like and lithium-like Bi, and obtained values in disagreement with earlier experimental work by Klaft et al. (1994). Recently, Ullmann et al. (2017) re-measured the HFS transitions in $^{209}$Bi$^{82+}$ and $^{209}$Bi$^{80+}$, and obtained $\xi$ with more than an order of magnitude improvement in precision. Its theoretical value of $\xi = 0.16886$ would allow to cancel the BW correction for $^{209}$Bi (Shabaev et al., 2001). However, the experimental result $\Delta'E = -61.012(5)(21)$ meV (statistical and systematic uncertainties given in parentheses) disagreed by $7\times$ with the predicted value of $-\Delta E(2s) + \Delta E(1s)$ (Volotka et al., 2012) (uncertainties in first and second parentheses arise from uncalculated higher-order terms and the uncertainty of the complete cancelation of all nuclear effects, respectively). This result was considered a challenge to bound-state strong-field QED theory (Ullmann et al., 2017). However, the explanation which was found soon after was rather mundane: the value of the nuclear magnetic moment for $^{209}$Bi that was used to analyze the data was simply wrong, as recently found out by Skripnikov et al. (2018). Chemical shifts which are difficult to be taken into account have now been properly included. This was a suspicion that Gustavsson and Mårtensson-Pendrill (1998a,b) had expressed in their analyses of the results of Klaft et al. (1994).

In this context, it is important to mention that the ubiquitous atomic diamagnetism modifies the magnetic field experienced by the nucleus in every determination of the nuclear gyromagnetic ratio. This intrinsic effect is always present when bound electrons surround the nucleus. Calculations of the diamagnetic shielding factors that result from this effect have theoretical uncertainties. Even more problematic are chemical shifts that appear in molecules imbedded in chemical samples. Therefore, the accuracy of the derived ‘corrected’ nuclear magnetic moments is reduced, and the interpretation of experiments becomes problematic. As an example, the nuclear magnetic shielding factors by the single bound electron in hydrogenic systems (Yerokhin et al., 2011) has to be calculated to all orders of QED expansion in the nuclear binding strength parameter. In principle, solving these issues is a prerequisite for the intended high-level QED tests, as pointed out by Gustavsson and Mårtensson-Pendrill (1998a,b).

4. Microwave studies of the bound-electron $g$ factor

Hitherto, the most stringent benchmark of QED calculations, and thus of the Standard Model, comes from the very good agreement of the measurements of the fine-structure constant $\alpha$ (a parameter of the model that cannot be calculated from the first principles) by strictly different methods. In the first method, the experimental value of the free-electron magnetic-moment anomaly $a_e$ (Mohr et al., 2016, 2012) is measured in a Penning trap (Hanneke et al., 2008) and combined with exact QED calculations that include electroweak and hadronic contributions using expansions in powers series of $\alpha/\pi$ with calculable coefficients. The second approach is based on the measured Rydberg constant $R_\infty$ (Bouchendira et al., 2011; Cadoret et al., 2008; Wicht et al., 2002) obtained by atom interferometry of recoiling atoms upon photon absorption.

For BSQED, the steep scaling laws governing the spin-orbit interaction make trapped HCI extremely sensitive probes. The $g$ factor of the bound electron (for a theory review see Shabaev et al. (2015)) is determined to a very high precision also in Penning traps (Sturm et al., 2013a, 2013b), to 10 significant digits in the case of H-like $^{28}$Si$^{13+}$, as demonstrated by Schabinger et al. (2012); Sturm et al. (2013a, 2011). Here, the experimental relative uncertainty is only $4 \times 10^{-11}$, leaving theoretical, uncalculated two-loop QED corrections of order $\alpha^2 (\alpha Z)^5$ and higher (Pachucki et al., 2005) as the largest source of uncertainty. These results could be further improved by combining theoretical and experimental values for two different H-like ions (Sturm et al., 2014). This idea of combining precise $g$-factor measurements and QED calculations (Czarnecki and Szafron, 2016; Sturm et al., 2013a; Yerokhin and Harman, 2013), has recently yielded a 13-fold improvement on the electron mass determination (Köhler et al., 2015; Sturm et al., 2014; Zatorski et al., 2017).

The most stringent BSQED experimental test of the
metals. This is the ion charge. Therefore, one would expect optical transitions in H-like ions taking place only between highly excited Rydberg states, being broadened by competing X-ray transitions branches. Certainly, electric-dipole (E1) transitions from the ground state lie in the extreme UV or X-ray wavelength regime. Nonetheless, optical transitions of interest to metrology in H-like ions electronic states occur within the ground state configuration due to fine structure, HFS, and also near level crossings, when the ions in the isoelectronic sequence change between ground state configurations. We will now consider this latter case.

First calculations of HCI systems which display such level crossings were done by Berengut et al. (2010). The general idea of that paper is as follows: the order of shells in neutral atoms follows the \( n + l \) rule and is different from that of the hydrogen-like ions (see Figure 1). For example, in hydrogen the 4\( f \) shell immediately follows 4s, 4p, and 4d shells, while in the periodic table it starts to fill after the 6s shell at \( Z = 58 \) (cerium). The energy of the 4\( f \) levels decreases much faster than energies of other levels if we move along isoelectronic sequences. As a result, we can expect a re-ordering of electron configurations (level crossings) near some value of \( Z \). When such crossings involve the ground state of an ion, we get low energy transitions, which may lie in the optical range. If these transitions are of \( p - f \), or \( s - f \) type (i.e. high order multipole transitions), they are very narrow and suitable for high precision metrology. Note that the \( s - d \) crossing may also lead to narrow optical transitions, but such crossings happen at a relatively low ionization stage. For example, the 6\( s - 5d \) crossing takes place in Tm-like sequence between Ta\( ^{4+} \) and \( \text{W}^{5+} \) Berengut et al. (2011a).

Alternatively, one can consider transitions between the levels of the ground state multiplet of an HCI. Such transition energies are of the order of \( (Z\alpha)^2(Z_{\alpha} + 1)^2 R_{\infty} \). For moderately heavy HCI these M1 transitions may lie in the visible range. This is the case, for example, for Al-like ions \( \text{V}^{10+} - \text{Cu}^{16+} \) (Yu and Sahoo, 2016). Nandy and Sahoo (2016) studied the fine structure transition \( ^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2} \) in the configuration \( 4f^{13}\text{s}^2 \) of the ions \( \text{W}^{15+}, \text{Ir}^{16+}, \text{and Pt}^{17+} \). Windberger et al. (2016) studied M1 optical transitions between fine structure levels in \( \text{Sn}^{11+} - \text{Sn}^{14+} \) ions. All these fine structure transitions are of M1 type. For optical clocks we would like to have weaker transitions to allow for significantly narrower lines. Schiller (2007) and (Yudin et al., 2014) considered M1 transitions between hyperfine levels in heavier H-like HCI, such as \( ^{171}\text{Yb}^{69+} \), or \( ^{207}\text{Pb}^{81+} \), where these transitions lie in the optical range.

**IV. HCI ELECTRONIC STRUCTURE AND FREQUENCY METROLOGY**

As we discussed in the previous section, BSQED tests and the corresponding measurements of fundamental constants have to be carried out in HCl with a very few valence electrons. In contrast, the metrology applications and the search for the variation of fundamental constants discussed in Sec. II requires HCI with rather complicated electronic structures, with the special exception of the HFS in H-like ions. In this section, we discuss the electronic structure of HCI relevant to these new applications. At a first glance, the idea to use HCI for optical clocks may appear strange. The energy scale for HCI electronic levels is about \( (Z_{\alpha} + 1)^2 R_{\infty} \), where \( Z_{\alpha} \) is the ion charge. Therefore, one would expect optical transitions in HCI taking place only between highly excited Rydberg states, being broadened by competing X-ray transitionsbranches. Certainly, electric-dipole (E1) transitions from the ground state lie in the extreme UV or X-ray wavelength regime. Nonetheless, optical transitions of interest to metrology in HCI occur within the ground state configuration due to fine structure, HFS, and also near level crossings, when the ions in the isoelectronic sequence change between ground state configurations. We will now consider this latter case.

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Below we will mostly focus on level crossings, where transitions are of quadrupole, or even octupole type and the lines are extremely narrow. Calculations of the ion properties in the vicinity of the level crossing are technically very difficult. Interesting crossings happen for degrees of ionization higher than 10 \((Z_a \gtrsim 10)\), when binding energies are of the order of 1 keV. That means that we need atomic calculations with very high accuracy to identify optical transitions, which correspond to energy differences of the order of 1 eV. In order to get transition energies with 10\(^{-19}\) accuracy, one needs fractional accuracy of the theory on the order of 10\(^{-4}\) or better. This is very challenging for existing theoretical methods. As a result, the first theoretical paper (Berengut et al., 2010) was followed by intensive further research (Berengut et al., 2011a,b, 2012a,b; Derevianko et al., 2012; Dzuba et al., 2012a,b, 2013; Dzuba et al., 2015a; Kozlov et al., 2013; Yudin et al., 2014). The most accurate calculations were done using a state-of-the-art hybrid approach that combines coupled-cluster and configuration interaction methods (Dzuba et al., 2015b; Safronova et al., 2014a,b,c). The last three works specifically considered all HCI which satisfied the following criteria:

- the existence of long-lived metastable states with transition frequencies to the ground states ranging between \(0.1 \ldots 1.8 \times 10^{15}\) Hz,
- high sensitivity to \(\alpha\)-variation,
- the existence of stable isotopes, and
- relatively simple electronic structure, with one to four valence electrons.

Safronova et al. (2014a,b,c) found that only four isoelectronic sequences satisfy the criteria above: Ag-like, Cd-like, In-like, and Sn-like, which include ions with 46-electron core \([1s^2 \ldots 4d^{10}]\). Berengut et al. (2012b) and Dzuba et al. (2015b) considered heavier actinide ions which satisfy all criteria above with the exception of the existence of stable isotopes.

A suitable transition for laser cooling and internal state readout is not required for the HCI when using quantum logic spectroscopy in which a co-trapped singly charged ion provides for these features as described in more detail in Sec. VII.C. The dependence of the clock transition on external fields and their gradients causes systematic effects in atomic clocks. The size of HCI scales as \(1/(Z_a + 1)\) and their dipole and quadrupole moments and polarizabilities, both static and dynamic, are suppressed by an order of magnitude and up to several orders for level-crossing and hyperfine optical transitions, respectively. A number of papers provided detailed investigation of systematic effects in optical clocks based on HCI, reaching the conclusion that the next order of magnitude improvement in the accuracy of frequency standards to \(10^{-19}\) uncertainty may also be achievable with HCI (Derevianko et al., 2012; Dzuba et al., 2012a, 2013; Dzuba et al., 2015a; Yudin et al., 2014). The systematic effects in HCI clocks are discussed in more detail in Sec. VII.D.

In the remaining part of this section we discuss calculations of the spectra, lifetimes, and sensitivity to \(\alpha\)-variation for particular systems. The accuracy of theoretical predictions strongly depends on the number of valence electrons, as the valence-valence correlations are very strong and can not be accurately treated perturbatively. As a result, CI represents the best strategy to include valence-valence correlations. However, the number of configurations that has to be included into the CI calculations grows exponentially with the number of valence electrons, limiting accurate calculations to a few valence electrons. Systems with more valence electrons usually also have a much denser spectrum, leading to experimental difficulties in spectra identification, exacerbated by large uncertainties in the theoretical predictions.

We start with the discussion of the proposals with H-like ions, which are based on the narrow M1 hyperfine transitions. All other HCI optical clock proposals are grouped by the number of valence electrons, starting with the systems with one electron above the closed shells and then discussing systems with two, three, and four electrons. Finally, we discuss systems with one or more holes in almost filled shells and a case with a mid-filled 4\(f\) shell.

A. HFS of hydrogenlike ions

As already mentioned in Sec. III.B.2, in heavy H-like HCI with nuclear spin 1/2 the hyperfine transitions may lie in the optical and near-optical range. These transitions are of the M1 type and are very weak because they require a nuclear spin-flip. Schiller (2007) analyzed systematic effects for the cases of \(61\)Ni\(^{27+}\) and \(207\)Pb\(^{81+}\). Yudin et al. (2014) discussed hyperfine transitions in H-like Yb, Pt, Hg, Ti, and Pb ions with clock wavelengths below 3 \(\mu\)m and nuclear spin \(I = 1/2\), listed in Table I. For these ions, the ground-state hyperfine structure consists of only \(F = 0\) and \(F = 1\) levels, simplifying experimental realization since the \(F = 0\) level does not have Zeeman components. The authors evaluated systematic effects due to quadrupole shifts in inhomogeneous electric fields, Zeeman shifts, blackbody radiation (BBR) shifts and ac-Stark shifts induced by the clock laser. As a result, Yudin et al. (2014) concluded that systematic effects can be controlled at a level below \(10^{-20}\) fractional accuracy. However, the achievable instability even for \(^{171}\)Yb\(^{69+}\), which has the longest upper clock state lifetime of 0.37 s, is \(\sigma_{\chi}(\tau) \approx 5 \times 10^{-15}/\sqrt{\tau}\), requiring 9.5 months to reach \(10^{-18}\) fractional accuracy (see Sec. VII.E.1).

Hyperfine transitions are particularly interesting for the search for a variation of fundamental constants be-
cause, like the Cs clock transition, they depend on $\alpha$, the proton-to-electron mass ratio $\mu$, and nuclear $g$ factors, which can be interpreted in terms of the variation of $X_q = m_q/\Lambda_{\text{QCD}}$, according to Eq. (2). All other optical atomic clocks are sensitive only to the variation of $\alpha$. This means that by comparing such a HCI hyperfine clock with any other optical clock one can significantly improve the laboratory limit on $\mu/\mu$, which is constrained according to Eq. (7) at the level of $10^{-16}$ yr$^{-1}$. The present constraint is limited by the Cs clock accuracy and the long averaging times to reach low statistical uncertainties. Both limitations may be overcome using optical hyperfine transitions in HCI. Availability of different nuclei may also allow the setting of further constraints on the variation of $X_q$. Moreover, the sensitivity coefficients to $\alpha$-variation $K$ for heavy H-like HCI vary monotonically from 1 for $Z = 1$ to 4.3 at $Z = 92$ (Schiller, 2007), therefore exceeding the sensitivity of the Cs clock $K_{\text{Cs}} = 2.83$ clock for all ions listed in Table I.

### B. HCI with one valence electron

#### a. Ag-like ions

The single-valent systems are simplest from the theoretical point of view. It was pointed out already by Berengut et al. (2010) that the $5s - 4f$ crossing in the Ag-like iso-electronic sequence ($N = 47$) takes place near Pm$^{14+}$. The ions Nd$^{13+}$ ($Z = 60$) and Pm$^{14+}$ have the ground state configuration [1s$^2 \ldots 4d^{10}]5s$ and the closely lying first excited state configuration [1s$^2 \ldots 4d^{10}]4f$. These configurations exchange places in Sm$^{15+}$. Energies and $\alpha$-variation sensitivity coefficients $q$ relative to the ground state for Nd$^{13+}$ and Sm$^{15+}$ are listed in Table II. The table also lists the enhancement factors $K = 2q/E$, wavelengths $\lambda$ (in nm) for transitions from the ground states and total radiative lifetimes $\tau$ (in s). The experimental wavelengths from Sugar and Kaufman (1981) are given; the remaining values are from CI+AO calculation (Safronova et al., 2014c). Theoretical energy values are listed for consistency with the $q$ values. The Ag-like ions are among the very few HCI with near-optical transitions for which experimental measurements are available. The comparison of the theoretical and experimental energies relative to the ground state for Nd$^{13+}$, Sm$^{15+}$, and Ce$^{9+}$ is given in Table III, adapted from Safronova et al. (2014c). The experimental values are from Joshi et al. (2001); Sugar and Kaufman (1981). Ce$^{9+}$ has a $5s^2$ closed shell, so it can be considered as either a system with one or three valence electrons, as discussed below. Excellent agreement with experiment is observed for all levels. A detailed calculation of the Ag-like ion properties is given in (Safronova et al., 2014b).

The Pm$^{14+}$ ion has no stable isotopes and while the CI+MBPT calculation predicted that the $5s$ and $4f_{5/2}$ states are separated by 3973 cm$^{-1}$ (Berengut et al., 2010), the CI+AO calculations predicted only about 300 cm separation (Safronova et al., 2014b). Nd$^{13+}$ represents a particularly attractive case since the strongest transition from the metastable $4f_{5/2}$ level of this ion is E3, resulting in the extremely long lifetime of more than 15 days (see Figure 2). The wavelength of

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**Table I Clock transition wavelengths $\lambda$ (in $\mu$m) and natural linewidth $\gamma/2\pi$ (in Hz) for hyperfine transitions in H-like ions. The values are from Yudin et al. (2014).**

| Ion        | $\lambda$ (\(\mu\)m) | $\gamma/2\pi$ |
|------------|------------------------|---------------|
| $^{171}$Yb$^{69+}$ | 2.16                   | 0.43          |
| $^{195}$Pt$^{77+}$  | 1.08                   | 3.4           |
| $^{199}$Hg$^{73+}$   | 1.15                   | 2.8           |
| $^{203}$Tl$^{80+}$   | 0.338                  | 111.2         |
| $^{205}$Tl$^{80+}$   | 0.335                  | 114.2         |
| $^{207}$Pb$^{81+}$   | 0.886                  | 6.2           |

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**Table II Energies and $\alpha$-variation sensitivity coefficients $q$ relative to the ground state in cm$^{-1}$ for HCI with one and two valence electrons. $K = 2q/E$ is the enhancement factor. Wavelengths $\lambda$ (in nm) for transitions from the ground states and total radiative lifetimes $\tau$ (in s) are listed. Nd$^{13+}$, Sm$^{15+}$, Nd$^{12+}$, Sm$^{14+}$, and Es$^{17+}$ values are from CI+AO calculation Dzuba et al. (2015b); Safronova et al. (2014c). Nd$^{13+}$ and Sm$^{15+}$ wavelengths are experimental values from Sugar and Kaufman (1981). CI$^{17+}$ results are CI+MBPT calculations from Berengut et al. (2012b). * indicates cases with no stable isotopes.**

| Ion | Level | Energy | $q$ | $K$ | $\lambda$ | $\tau$ |
|-----|-------|--------|-----|-----|-----------|--------|
| Nd$^{13+}$ | 5$s_{1/2}$ | 0      | 4$f_{5/2}$ | 55706 | 104229 | 3.7 | 179 | 1.3 $\times$ 10$^{6}$a |
|       |       |        | 4$f_{7/2}$ | 60134 | 108243 | 3.6 | 166 | 0.996 |
| Sm$^{15+}$ | 5$s_{1/2}$ | 0      | 4$f_{5/2}$ | 6444  | 5910  | 1.8 | 1526 | 0.308 |
|       |       |        | 5$s_{1/2}$ | 60517 | -134148 | -4.4 | 166 | 3.1 $\times$ 10$^{5}$ |
|*CI$^{17+}$ | 6$p_{3/2}$ | 18686  | -49750  | -48 | 535  |
|       |       |        | 5$f_{7/2}$ | 21848 | 17900  | 1.6 | 458  |
| Nd$^{12+}$ | 5$s_{2}1S_{0}$ | 0      | 5$s_{4}3F_{2}$ | 79496 | 101461 | 2.6 | 126 | 8.5 $\times$ 10$^{10}$ |
|       |       |        | 5$s_{4}3F_{3}$ | 80769 | 102325 | 2.4 | 124 | 19.7 |
| Sm$^{14+}$ | 4$f_{2}3H_{4}$ | 0      | 5$s_{4}3F_{2}$ | 2172 | -127720 | -118 | 4600 | 5.6 $\times$ 10$^{13}$b |
|       |       |        | 5$s_{4}3F_{3}$ | 3826 | -126746 | -66 | 2614 | 8.51 |
|*Es$^{17+}$ | 5$f_{2}3H_{4}$ | 0      | 5$f_{6}3F_{2}$ | 7445 | -46600 | -13 | 1343 | 11000 |

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* This value includes E3 and M2 transitions. Inclusion of the hyperfine-induced E1 transition for $^{143}$Nd$^{13+}$ decreases the lifetime to $1.1 - 1.2 \times 10^{6}$ s, depending on the hyperfine component of the transition (Dzuba and Flambaum, 2016).  

b. The hyperfine quenching reduces this lifetime in $^{147}$Sm$^{14+}$ to $5 \times 10^{6}$ s - $2 \times 10^{6}$ s (Dzuba and Flambaum, 2016).
translated such hyperfine-induced transitions for on the nuclear spin and can be significantly enhanced. The amplitudes of such strongly forbidden transitions may depend on the hyperfine component of the transition (Dzuba and Flambaum, 2016). The contribution of the hyperfine-induced E1 transition to the lowest excited state lifetime of the $^{147}\text{Sm}^{15+}$ is only 1%. Dzuba et al. (2012b) carried out a detailed assessment of the systematic uncertainties for $\text{Nd}^{13+}$ and $\text{Sm}^{15+}$, including BBR shifts, Zeeman shifts, electric quadrupole shifts, and other perturbations, concluding that the fractional accuracy of the clocks based on these systems may reach $10^{-19}$ if efficient shift cancelation schemes are applied.

### Table III

| Ion          | Level     | Expt. | CI+AO | Diff. | Diff.% |
|--------------|-----------|-------|-------|-------|--------|
| $\text{Nd}^{13+}$ | $5s_{1/2}$ | 0      | 0     | 0     | 0      |
|              | $4f_{5/2}$ | 55870  | 55706 | 164   | 0.29%  |
|              | $4f_{7/2}$ | 60300  | 60134 | 166   | 0.28%  |
|              | $5p_{1/2}$ | 185066 | 185028| 38    | 0.02%  |
|              | $5p_{3/2}$ | 243864 | 243887| -23   | -0.01% |
| $\text{Sm}^{15+}$ | $4f_{5/2}$ | 0      | 0     | 0     | 0      |
|              | $4f_{5/2}$ | 6555   | 6441  | 111   | 1.69%  |
|              | $5s_{1/2}$ | 60384  | 60517 | -133  | -0.22% |
|              | $5p_{1/2}$ | 268488 | 268604| -116  | -0.04% |
|              | $5p_{3/2}$ | 333203 | 33335 | -182  | -0.05% |
| $\text{Ce}^{9+}$ | $5p_{1/2}$ | 0      | 0     | 0     | 0      |
|              | $5p_{3/2}$ | 33427  | 33450 | -23   | -0.07% |
|              | $4f_{5/2}$ | 54947  | 54683 | 264   | 0.48%  |
|              | $4f_{7/2}$ | 57520  | 57235 | 285   | 0.50%  |

Figure 2 Energy levels and radiative lifetimes of low-lying levels of Ag-like $\text{Nd}^{13+}$. Vertical intervals are not to scale. The lowest state lifetime includes E3 and M2 transitions. Inclusion of the hyperfine-induced E1 transition for $^{143}\text{Nd}^{13+}$ decreases the lifetime to 12.5 – 14 days, depending on the hyperfine component of the transition (Dzuba and Flambaum, 2016). From Safronova et al. (2014b).

the $5s - 4f$ transition in $\text{Nd}^{13+}$ is in the VUV. The amplitudes of such strongly forbidden transitions may depend on the nuclear spin and can be significantly enhanced for odd isotopes. Dzuba and Flambaum (2016) calculated such hyperfine-induced transitions for $^{143}\text{Nd}^{13+}$, $^{149}\text{Pm}^{14+}$, $^{147}\text{Sm}^{15+}$, and $^{147}\text{Sm}^{15+}$. The $^{143}\text{Nd}^{13+}$ lowest excited state value in Table II includes E3 and M2 transitions. Inclusion of the hyperfine-induced E1 transition for $^{143}\text{Nd}^{13+}$ decreases the lifetime to $1.1 - 1.2 \times 10^6$ s, depending on the hyperfine component of the transition (Dzuba and Flambaum, 2016). The contribution of the hyperfine-induced E1 transition to the lowest excited state lifetime of $^{147}\text{Sm}^{15+}$ is only 1%.

### C. HCI with two valence electrons

#### a. Cd-like ions

Cd-like ions $\text{Nd}^{12+}$ and $\text{Sm}^{14+}$ have two valence electrons and ground configurations $5s^2$ and $4f^2$, respectively. In both cases the first excited configuration is $4f5s$. The lowest multiplet of this configuration is $3\text{F}_{2,3,4}$. In $\text{Nd}^{12+}$ the levels of this multiplet lie at approximately 79500, 80800, and 83700 cm$^{-1}$ above the ground state, while for $\text{Sm}^{14+}$ they are much lower, at 2200, 3800, and 8800 cm$^{-1}$ respectively, as illustrated in Table II. Therefore neither of the ions have transitions in the visible range and Pm has no stable isotopes. The lowest level $3\text{F}_2$ is connected to the ground state by an M2 transition and has an extremely long lifetime, while the other levels of this multiplet have lifetimes of the order of seconds. The M2 lifetimes are strongly quenched by hyperfine-induced E1 transitions, by 4-6 orders of magnitude in $^{147}\text{Sm}^{15+}$, depending on the hyperfine component of the transition (Dzuba and Flambaum, 2016). Other details can be found in Dzuba and Flambaum (2016); Safronova et al. (2014a).

#### b. Pb-like californium and einsteinium

Cf$^{16+}$ has a very dense and complex spectrum with three closely lying configurations, $5f^2$, $5f6p$ and $6p^2$. According to the CI+MBPT calculation by Berengut et al. (2012b), the ground state is $J = 3(5f6p)$, with the first excited state...
Table IV  Energies and α-variation sensitivity coefficients $q$ relative to the ground state in cm$^{-1}$; enhancement factor $K = 2q/\omega_c$, wavelengths $\lambda$ (in nm) for transitions to the ground state, and lifetimes $\tau$ (in s) for HCI with three and four valence electron configurations. All values are obtained using the CI+AO method. CI$^{4s5}$ and Es$^{16s}$ values are from Dzuba et al. (2015b), the other data are from Safronova et al. (2014c). Energy values include QED and three-electron corrections from Kozlov et al. (2016); Tupitsyn et al. (2016). * indicates cases with no stable isotopes.

| Ion | Level | Energy | $q$ | $K$ | $\lambda$ | $\tau$ |
|-----|-------|--------|----|----|---------|-------|
| Ce$^{14+}$ | 5s$^2$5p$_{1/2}$ | 0 | | | | |
| | 5s$^2$5p$_{3/2}$ | 33450 | 37544 | 2.2 | 299 | 0.0030 |
| | 5s$^2$4f$_{5/2}$ | 54683 | 62873 | 2.3 | 182 | 0.0812 |
| | 5s$^2$4f$_{7/2}$ | 57235 | 65150 | 2.3 | 174 | 2.18 |
| Pr$^{10+}$ | 5s$^2$5p$_{1/2}$ | 0 | | | | |
| | 5s$^2$4f$_{5/2}$ | 3702 | 73849 | 40 | 2700 | 8.5$\times$10$^4$ |
| | 5s$^2$4f$_{7/2}$ | 7031 | 76833 | 22 | 1422 | 2.35 |
| | 5s$^2$5p$_{3/2}$ | 39141 | 44098 | 2.3 | 256 | 0.0018 |
| Nd$^{11+}$ | 5s$^2$4f$_{5/2}$ | 0 | | | | |
| | 5s$^2$4f$_{7/2}$ | 4180 | 3785 | 1.8 | 2392 | 1.19 |
| | 5s$^2$5p$_{1/2}$ | 53684 | -85692 | -3.2 | 186 | 0.061 |
| Sm$^{13+}$ | 5s$^2$4f $^2$F$_{5/2}$ | 0 | | | | |
| | 5s$^2$4f $^2$F$_{7/2}$ | 6203 | 5654 | 1.8 | 1612 | 0.367 |
| | 4f$^7$5s $^4$H$_{11/2}$ | 20254 | 123621 | 12 | 494 | 0.133 |
| Eu$^{14+}$ | 4f$^5$5s $^3$J=7/2 | 0 | | | | |
| | 4f$^3$ $^3$J=9/2 | 1262 | 137437 | 218 | 7924 |
| | 4f$^5$5s $^3$J=9/2 | 2594 | 1942 | 1.5 | 3855 |
| | 4f$^3$ $^3$J=11/2 | 5388 | 141771 | 53 | 1856 |
| *Cr$^{15+}$ | 5f$^6$p$^2$ $^2$F$_{5/2}$ | 0 | | | | |
| | 5f$^6$p$^4$ $^2$I$_{9/2}$ | 12898 | 38000 | 59 | 775 | 6900 |
| | 5f$^6$p$^2$ $^2$F$_{7/2}$ | 22018 | | | 454 | 0.012 |
| *Es$^{16+}$ | 5f$^6$6p$^4$ $^2$I$_{9/2}$ | 0 | | | | |
| | 5f$^6$p$^2$ $^2$F$_{5/2}$ | 6994 | -18000 | -53 | 1430 | 16000 |
| | 5f$^3$ $^2$H$_{13/2}$ | 10591 | | | 944 | 3.4 |
| Pr$^{17+}$ | 5s$^2$5p$^3$ $^3$P$_0$ | 0 | | | | |
| | 5s$^2$5p$^3$f $^3$G$_3$ | 20216 | 42721 | 4.2 | 475 | 6.6$\times$10$^4$ |
| | 5s$^2$5p$^3$f $^3$F$_2$ | 22772 | 42865 | 3.8 | 426 | 59.0 |
| | 5s$^2$5p$^3$f $^3$F$_3$ | 25362 | 47076 | 3.7 | 382 | 5.33 |
| Nd$^{18+}$ | 5s$^2$4f$^2$ $^4$J=4 | 0 | | | | |
| | 5s$^2$5p$^4$ $^4$J=3 | 1564 | -81052 | -104 | 16000 |
| | 5s$^2$5p$^4$ $^4$J=5 | 3059 | 3113 | 2.0 | 1.4 |
| | 5s$^2$5p$^4$ $^4$J=2 | 5060 | -60350 | -24 | 2200 | 25 |

$J = 0[6p^2]$ at about 5000 cm$^{-1}$ and $J = 4[5f^2]$ at roughly 10000 cm$^{-1}$. QED and high-order correlation corrections may shift levels enough to even change their order. Therefore, new studies are necessary to predict this spectrum more reliably. Note that the sensitivity coefficients $q$ are very large and have opposite signs: $q(J = 3) \approx -371000$ cm$^{-1}$ and $q(J = 0) = +415000$ cm$^{-1}$. Es$^{17+}$ was considered by Dzuba et al. (2015b) using the CI+AO method; the clock transition data are listed in Table II.

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D. HCI with three valence electrons

Figure 3  Energy levels and radiative lifetimes of low-lying levels of In-like Pr$^{10+}$, From Safronova et al. (2014c).

a. In-like ions. There are two level crossings in the In-like isoelectronic sequence ($N = 49$). There is a crossing of the $5p$ and $4f$ shells near $Z = 59$ as well as a crossing of the $5s$ and $4f$ shells near $Z = 63$. The ground configuration at the first crossing is $5s^2nl$, where $nl = 5p$, or $nl = 4f$. Near the second crossing the $5s^24f$ and $4f^25s$ configurations have similar energies. Both crossings can be adequately studied using a three-electron model with the closed core $[1s^2\ldots 4d^{10}]$.

At the first crossing the order of levels changes from $5p_{1/2}$, $5p_{3/2}$, $4f_{5/2}$, and $4f_{7/2}$ for Ce$^{14+}$, to $5p_{1/2}$, $4f_{5/2}$, $4f_{7/2}$, and $5p_{3/2}$ for Pr$^{10+}$, and, finally, to $4f_{5/2}$, $4f_{7/2}$, $5p_{1/2}$, and $5p_{3/2}$ for Nd$^{11+}$. The all-order results from Safronova et al. (2014b,c) are compiled in Table IV. The theoretical spectrum of the Pr$^{10+}$ ion is shown in Figure 3. The energies of the $4f$ levels of Pr$^{10+}$ are very difficult to calculate accurately as they are very close to the ground state $5p_{1/2}$. The one-electron binding energies of the $5p_{1/2}$ and $4f_{5/2}$ states are $1.3 \times 10^6$ cm$^{-1}$, and these values cancel to 99.7% when two energies are subtracted to obtain a theoretical prediction for a transition energy, 3700(200) cm$^{-1}$ (Safronova et al., 2014b).

Theory predicts that a second crossing takes place between Sm$^{13+}$ and Eu$^{14+}$. Calculated energy levels are listed in Table IV. For the Sm$^{13+}$ ion, the closest configuration to the ground fine-structure multiplet $^2F_J[5s^24f^2]$ is $5s4f^2$. This leads to a very interesting level structure with a metastable $J = 7/2[5s4f^2]$ level in the optical transition range from both levels of the ground multiplet $^2F_{5/2,7/2}[5s^24f^2]$. For Eu$^{14+}$, the ground state belongs to the configuration $5s4f^2$ and the first excited level belongs to the configuration $4f^3$. These levels are very close and their theoretical uncertainty is comparable to the energy interval. For example, QED corrections for the configuration $4f^3$ exceed 1000 cm$^{-1}$ (Tupitsyn et al., 2016) and corrections from the effective three-electron interac-
tions are of similar size (Kozlov et al., 2016). It is possible that missing correlation corrections can change the ground state to $J = 9/2\ [4f^3]$. An experimental measurement of the spectrum of Eu$^{14+}$ would allow testing of the theory for such difficult cases.

b. Bi-like californium and einsteinium. Cf$^{15+}$ and Es$^{16+}$ were studied using the CI+AO method in (Dzuba et al., 2015b). Theoretical spectra of these ions are shown in Fig. 4 and Fig. 5. In both ions the first excited state is metastable and linked to the ground state by an E2 transition. For the Cf$^{15+}$ ion, this transition has a large sensitivity to $\alpha$-variation, $q = +380000 \text{ cm}^{-1}$. For the Es$^{16+}$ ion both levels belong to the same 5f$^2$6p configuration and the $q$-factor is smaller, $q = -184000 \text{ cm}^{-1}$. CI+AO results are listed in Table IV.

E. Sn-like ions with four valence electrons

Pr$^{9+}$ and Nd$^{10+}$ are the ions of interest in the Sn-like isoelectronic sequence. Pr$^{9+}$ is particularly interesting, because the lowest metastable state $J = 3\ [5p4f]$ is extremely long lived, with a 495 nm transition to the ground state in the optical range, see Figure 6. The strongest allowed transition for even isotopes is M3, making this ion a unique system. We expect that the lifetime of that level will be strongly quenched due to the E1 hyperfine transition in odd isotopes. The next two levels also have optical transitions to the ground state, and have lifetimes of 59 and 5.3 s respectively. In addition, there is a strong M1 transition to the ground state from the $3P_1\ [5p^2]$ level at 351 nm that may be useful for cooling and probing. The first excited state of Nd$^{10+}$ is so close to the ground state that the theoretical uncertainty is on the order of the transition energy. The atomic parameters are listed in Table IV. Further details are given by Safronova et al. (2014a,c).

F. Ions with holes in almost filled 4f shell

Berengut et al. (2011b) considered Ir$^{16+}$ and W$^{7+}$ ions with one hole in the 4f shell. The energies of the 4f$^{13}5s^2$ and 4f$^{14}5s$ configurations in Ir$^{16+}$ were predicted to be sufficiently close for an optical transition. According to the CI calculation of these authors the ion Ir$^{16+}$ has ground multiplet $^2F_{7/2,5/2}[4f^{13}5s^2]$ with huge fine-structure splitting $\Delta F_S \approx 259000 \text{ cm}^{-1}$ and excited state $^2S_{1/2}[4f^{14}5s]$ roughly at 37000 cm$^{-1}$ (see Table V). Later these levels were recalculated within MBPT method by Safronova et al. (2015) and by Nandy and Sahoo (2016) using CC approach. Both calculations gave the same ground doublet and the level $^2S_{1/2}[4f^{14}5s]$ approximately at 28 and 26 thousand cm$^{-1}$ respectively. All three calculations gave close values of the fine structure splitting between 25 and 26 thousand inverse centimeters.

A similar crossing between the one-hole configurations 4f$^{13}5p^6$ and 4f$^{14}5p^5$ takes place for W$^{7+}$ (Berengut et al., 2011b; Draganic et al., 2003). Theory predicts the following order of levels: $^2F_{7/2}[4f^{13}5p^6]$, $^2P_{3/2}[4f^{14}5p^5]$, $^2F_{5/2}[4f^{13}5p^6]$, and $^2P_{1/2}[4f^{14}5p^5]$. The fine splittings for two multiplets are about 18000 and 90000 cm$^{-1}$ respectively. At present only CI calculations are available and the accuracy of the theory is not sufficient to reliably predict the distance between the multiplets.

In addition to one-hole ions Berengut et al. (2011b) also considered the two-hole systems Ir$^{17+}$ and W$^{8+}$. The Ir$^{17+}$ ion has low lying levels of the 4f$^{12}5s^2$, 4f$^{13}5s$, and 4f$^{14}$ configurations. Spectra of these ions are much denser and, according to the calculation, include many optical lines. However, present theory may be rather unreliable for predicting the energy difference between different configurations. One needs to include more cor-
relations to reduce theoretical uncertainty. On the other hand, all such ions are particularly interesting because of the very large $q$-factors, which determine sensitivity to $\alpha$-variation. For Ir$^{17+}$ ions, spectra were recently studied by Windberger et al. (2015), along with the isoelectronic, Nd-like sequence ions of W, Re, Os, and Pt.

Other systems with two-hole $4f^{12}$ configuration were discussed by Derevianko et al. (2012) and Dzuba et al. (2012a). These authors point out that there are always optical transitions between levels of this configuration independently of the degree of ionization, and the first excited state is always metastable. For the HCI the two holes form the relativistic configuration $4f^2$. Allowed total angular momenta for this configuration are: $J = 6, 4, 2, 0$. According to Hund’s rules, the $J = 6$ state is the ground state and $J = 4$ state is the first excited state. These states are connected by an electric quadrupole transition. The configuration $5s^24f^{12}$ is the ground state configuration for Ce-like ions (Z=58) beginning from Re$^{17+}$. There are many ions of this type starting from Re$^{17+}$ to Ir$^{34+}$. An analysis of the systematic shifts of transitions within this configuration by Derevianko et al. (2012) shows that the largest ones are caused by magnetic fields and the zero-point-energy motion of the trapped ion. The former effect can be suppressed by averaging two transitions with different signs of the projections $M_J$. An estimate of the latter effect is based on the observation that trapping parameters are similar to those in the Al$^+/\text{Be}^+$ clock, but that HCI are about 10 times heavier than Al. This mass difference leads to a suppression of the time-dilation effects for heavy HCI, assuming a similarly efficient sympathetic cooling (see Sec. VII.B). Derevianko et al. (2012) concluded that all investigated systematic effects may be suppressed to a fractional level of $10^{-19}$ by applying efficient shift-suppression schemes. We note that the transitions between the fine-structure states are generally not sensitive to $\alpha$, since all multiplet states have similar $q$ coefficients.

The more complex Ho$^{14+}$ ion was proposed for metrology applications by Dzuba et al. (2015a). This ion has as its ground state configuration $4f^65s$, a first excited configuration $4f^55s^2$, and a very rich optical spectrum, which includes a potential hyperfine-induced clock transition at approximately 400 nm and a strong cooling and detection transition at 260 nm. The paper includes estimates of the transition rates and lifetimes. The values are listed in Table V. However, the clock state prediction has a very large uncertainty, probably as high as 10000 cm$^{-1}$. Sympathetic cooling of Ho$^{14+}$ is discussed by Okada et al. (2015). Their simulations show that at least 10 such ions can be cooled to sub-milli-Kelvin temperatures by sympathetic cooling with a single laser-cooled Be$^+$ ion.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Energy levels and radiative lifetimes of low-lying levels of Sn-like Pr$^{14+}$. From Safronova et al. (2014b).}
\end{figure}

Table V Energies and $\alpha$-variation sensitivity coefficients $q$ relative to the ground state in cm$^{-1}$; $K = 2q/\omega$ is the enhancement factor. Wavelengths $\lambda$ (in nm) for transitions to the ground states is listed. All values are from the CI calculations and are expected to have large uncertainties, see text. Ir$^{16+}$ and Ir$^{17+}$ values are from Berengu et al. (2011b) and Ho$^{14+}$ values are from Dzuba et al. (2015a).

| Ion     | Level          | Energy | $q$  | $K$  | $\lambda$ |
|---------|----------------|--------|------|------|------------|
| Ir$^{16+}$ | $4f^{13}5s^2$ | $2F_{7/2}$ | 0    |      |            |
|         | $4f^{13}5s^2$ | $2F_{5/2}$ | 25898 | 23652 | 1.8        | 386 |
|         | $4f^{14}5s$   | $2S_{1/2}$ | 37460 | 367315| 20          | 267 |
| Ir$^{17+}$ | $4f^{13}5s$  | $3F_4$   | 0    |      |            |
|         | $4f^{13}5s$  | $3F_3$   | 4838  | 2065  | 0.9        | 2067 |
|         | $4f^{13}5s$  | $3F_2$   | 26272 | 24183 | 1.8        | 381 |
|         | $4f^{14}$    | $1S_0$   | 5055  | 367161| 145        | 1978 |
|         | $4f^{12}5s^2$| $3H_6$   | 35285 | -385367| -22        | 283 |
|         | $4f^{12}5s^2$| $3F_4$   | 45214 | -387086| -17        | 221 |
| Ho$^{14+}$ | $4f^65s$    | $8F_{1/2}$| 23823 | -186000| -16        | 420 |

V. EXPERIMENTAL METHODS FOR HCI STUDIES

A. Early spectral observations

Experimental observations of forbidden optical transitions in HCI have a surprisingly long history. Actually, the first detections of forbidden lines were reported in the year 1869 by Harkness and Young, who saw during a total eclipse how the solar corona emitted green light at 530 nm from an unknown and extremely light element, as it was believed. In the 1940s Grotrian (Grotrian, 1939) and Edlén (Edlén, 1943; Edlén, 1947) hypothesized the presence of highly ionized atoms in the corona having fine structure transitions that would explain the observed lines. This implied coronal temperatures in the range of 1 MK, in contradiction with the then prevailing understanding of the Sun, and gave a first insight into the very
hot universe of modern astrophysics. Diagnostics of hot astrophysical plasmas was therefore the first application of forbidden optical transitions in HCI. The first laboratory experiments had to wait until the production of such ions became feasible in a controlled way.

B. First laboratory methods

After decades of research with large devices such as theta pinches that used powerful pulsed electrical discharges to generate ions in high charge states, the sliding spark method (Feldman et al., 1967) provided a source of comparatively small size and achieving ionization stages as high as Fe XVIII. In the 1970’s, the beam-foil method (Bashkin, 1968; Berry, 1977), was introduced. It starts with moderately charged ions that are accelerated to energies in the range 100 keV-10 MeV per unit of charge and sent through a submicrometer thin foil which strips further electrons and generates HCI in highly excited states (Berry, 1977). Spectroscopic investigations were carried out by observing the trail of excited ions exiting the foil in a mostly perpendicular direction. However, with HCI moving at speeds of a few mm/ns, allowed transitions with ps and ns range upper level lifetimes are predominantly detected, while the forbidden optical transitions with ms lifetimes do not produce sufficiently strong signals due to finite detector size. A severe handicap for precision measurements was the geometry-dependent Doppler shift, which in spite of various corrections could not be completely canceled. Another problem was the simultaneous presence of several charge states in a manifold of multiply excited configurations at the exiting channel. This hindered line identification and the assignment of electronic levels. Given those difficulties, the field achieved what was possible at that time, and produced pioneering systematic spectroscopic data.

Magnetic-fusion research devices such as tokamaks provided for the first time a limited number of forbidden optical observations (Edlén, 1984; Finkenthal et al., 1984; Kaufman et al., 1983; Suckewer et al., 1982). Calculations were made for identification and plasma diagnostic purposes (Feldman et al., 1985). Again, the Doppler width and the difficult control of the plasma composition and conditions hindered dedicated high-resolution studies. More recently, the analysis of Zeeman splitting and polarization of visible transitions has also been reported (Iwanae et al., 2007). Spectroscopy in general, and forbidden transitions in particular, offer opportunities for temperature and density diagnostics in magnetic fusion plasmas (Beiersdorfer, 2015).

C. Early laboratory sources of HCI

The development of stationary HCI sources solved most of those problems and made HCI more easily accessible to experimentalists. Among those, electron-cyclotron resonance ion sources (ECRIS) (Bechtold et al., 1980; Briand et al., 1975; Geller, 1970) based on the electron heating of a thin plasma by powerful microwaves in a magnetic bottle yielded microampere beams of HCI in moderate charge states, typically used to load accelerators. Optical access to the plasma volume was very constrained by the bulky and complicated magnetic structures surrounding it. As for the charge states of HCI produced in ECRIS, they have typically been limited to \( q < 28+ \) by the plasma conditions. Nonetheless, it was a flexible source and this was soon recognized. One of the first examples of optical spectroscopy was the observation by Prior (1987) of fine-structure transitions in ions with open \( p \) and \( d \) subshells by using beams from an ECRIS at the Lawrence Berkeley Laboratory. The very intense currents of HCI available there (tens of microamperes) made it possible to observe the decay of a small fraction of the metastable ions passing in front of a spectrometer equipped with a position-sensitive microchannel plate detector. In this way, intra-configuration fine-structure transitions from F-like ions (Ar\(^{9+}\), K\(^{10+}\), and Ca\(^{11+}\)), O-like ions (K\(^{11+}\) and Ca\(^{12+}\)), and B-like ions (Ar\(^{13+}\) and K\(^{14+}\)) were measured. The transitions 3d\(^{5}\)\(^{2}\)D\(_{5/2}\)\(\rightarrow\)3p\(^{3}\)\(^{2}\)P\(_{1/2}\) in Nb\(^{14+}\), 3d\(^{5}\)\(^{2}\)D\(_{4}\)\(\rightarrow\)3p\(^{3}\)\(^{2}\)P\(_{3/2}\) as well as the 3d\(^{5}\)\(^{2}\)F\(_{2}\)\(\rightarrow\)3p\(^{3}\)\(^{2}\)P\(_{1/2}\) in Nb\(^{15+}\), and the 3d\(^{5}\)\(^{2}\)F\(_{9/2}\)\(\rightarrow\)3p\(^{3}\)\(^{2}\)P\(_{3/2}\) in Nb\(^{16+}\) were also investigated. Spectral resolution and wavelength accuracy were both instrumentally and methodologically limited to a level of 0.1%.

Another step in the direction of higher charge states and better control was the introduction of electron beam ion sources (EBIS) by Arianer (Arianer et al., 1975; Arianer and Goldstein, 1976) and Donets (Donets, 1967, 1985, 1990; Donets and Pikin, 1975). An intense, narrow electron beam was generated through magnetic compression that compensated the mutual repulsion of the electrons in the beam. This development owed much to radar technology, which had made use of such beams to generate microwaves. Accumulation of multiply charged ions inside the electron beam space charge distribution was recognized as a factor for the beam neutralization. Unfortunately, due to technical difficulties, spectroscopy on EBIS devices was not strongly pursued although a few cases of in-source X-ray spectroscopy (Ali et al., 1991, 1990) were reported.

D. Production of HCI with electron beam ion traps

It was recognized that ion heating by electron beam instabilities was hindering the production of the highest charge states in EBIS devices (Levine et al., 1985).
Correcting this problem, the decisive invention of the electron beam ion trap (EBIT) by Marrs and Levine (Levine et al., 1989, 1988; Marrs et al., 1994a; Penetrante et al., 1992) at the Lawrence Livermore National Laboratory (LLNL) prepared the field for many long ranging developments. To mention some examples, we refer to investigations of QED effects in X-ray emission spectra (Beiersdorfer et al., 2005, 1995; Beiersdorfer et al., 1998; Beiersdorfer et al., 1993), studies of the dielectronic-recombination process (Beiersdorfer et al., 1992; Knapp et al., 1989; Watanabe et al., 2007) and of quantum interference in photo-recombination processes (González Martínez et al., 2005; Knapp et al., 1995; Nakamura et al., 2009), nuclear-size determinations (Elliott et al., 1996), lifetime measurements of forbidden transitions (Crespo López-Urrutia et al., 1998a, 2006; Wargelin et al., 1993), laser spectroscopy of the 2s − 2p He-like transitions (Hosaka et al., 2004), charge exchange (Allen et al., 2007; Beiersdorfer et al., 2003, 2000; Otranto et al., 2006; Wargelin et al., 2005), plasma-polarization spectroscopy (Amaro et al., 2017; Beiersdorfer et al., 1997; Nakamura et al., 2001; Shah et al., 2018; Shlyaptseva et al., 1997, 1998), effects of Breit interaction in x-ray emission (Hu et al., 2012), soft x-ray laser spectroscopy (Bernitt et al., 2012; Epp et al., 2007), photoionization of HCl with soft x-rays (Simon et al., 2010a), and mass spectroscopy (Ettenauer et al., 2011) as well as in-trap nuclear spectroscopy of radioactive isotopes (Lennartz et al., 2014).

These devices, for reasons we will see below, became true spectroscopy workhorses and produced an enormous scientific harvest. Experimentally, production of HCl in more or less arbitrary charge states is now routinely performed with EBITs, and therefore several groups worldwide started utilizing such devices (Biedermann et al., 1997; Böhm et al., 2007; Currell et al., 1996; Dilling et al., 2006; Fu et al., 2010; Gillaspy et al., 1995; López-Urrutia et al., 1999; Nakamura et al., 1997; Ovsyannikov and Zschornack, 1999; Silver et al., 1994; Takacs et al., 2015; Watanabe and Currell, 2004; Xiao et al., 2012). In view of their apparent advantages and of the large body of experimental results, in the following we will focus on the uses of the versatile EBITs.

1. Ionization and trapping mechanism

The principle of operation is the interaction of an intense (mA to A), strongly focused electron beam with atoms and their ions (for more details see, e.g., (Beyer et al., 1997; Currell and Fussmann, 2005; Currell et al., 2000; Gillaspy, 2001)). Ionization of neutrals injected as dilute atomic or molecular beams crossing it yields first singly charged positive ions which stay trapped by, and mostly within, the negative space-charge potential of the beam. This parameter has its strongest gradient at the beam edge. Between that point and the beam central axis at tens of micrometers from it a potential difference of tens of volts appears. From the point of view of a neutral injected from a room-temperature atomic beam with a kinetic energy of 25 meV, ionization to the first charge state within the beam means the sudden appearance of a thousand times stronger trapping potential. This results in instantaneous trapping of the ions produced. Subsequent beam-ion interactions raise the charge state until the physical limit is reached, namely when the binding energy of the remaining bound electrons is higher than the electron beam energy. Electron-beam energies in the range 40 eV to 200 keV, ions from N$^{3+}$ (Simon et al., 2010b) to U$^{92+}$ (Marrs et al., 1994b) have been studied with the EBIT method. Recombination of the HCI is reduced by having an excellent vacuum, suppressing charge exchange with residual gas. Efficient ionization takes place at energies well above the pertinent thresholds, but the long trapping times (seconds to hours) allow compensation for the small electron-impact ionization cross sections close to threshold.

2. Photorecombination and charge-exchange processes

Acting in the opposite direction, photorecombination of free beam electrons with the HCI under emission of a photon (so-called radiative recombination, RR) is rather weak for ions in relatively low charge states, but becomes intrinsically strong for ions with open L and K shells, in particular if the charge state is also very high. This process, RR, is akin to time-reversed photoionization. Another one is dielectronic photorecombination (DR) involving the resonant excitation of an inner-shell electron during the capture process and the subsequent relaxation of this intermediate state through photon emission. It is extremely effective at certain discrete energies, with several orders of magnitude larger cross sections. While it affects typically only one charge state at each beam energy, its total contribution can be several times larger than that of RR with thermal electron distribution functions. Charge exchange is the process by which HCI capture electrons from residual gas neutrals by overcoming their ionization potential in collisions at the range of several atomic units. The cross sections for this are rather large (on the order of $10^{-13}$ cm$^2$) and therefore an excellent UHV is typically needed to store HCI. The charge-state distribution found in an EBIT is, in general, ruled by a set of coupled rate equations (Penetrante et al., 1991a, 1992) containing all those ionizing and recombining terms. Under normal conditions it will be comprised of only a few charge states, and it can be optimized to contain a rather dominant ionic species (Currell et al., 2000).
3. Electron-impact excitation of transitions

An invaluable advantage of an EBIT is the fact that the electron beam also copiously excites the trapped HCI. This, together with the convenient geometry giving radial optical access to the trap region at few-centimeter distances allows for spectroscopic observations in all spectral ranges. The space charge potential forms a narrow (50 to 500 µm), few-cm long cylindrical ion cloud which can readily be imaged onto the entrance slit of a spectograph, or even serve as its substitute in many cases. Then, spectral dispersion combined with ion-cloud imaging maximizes the signal. The ion cloud normally contains HCI that compensate a large fraction of the negative space charge of the electron beam. Taking into account the charge state, this leads to ion densities from \(10^9/\text{cm}^3\) to \(10^{11}/\text{cm}^3\), surrounding or immersed in a negative space charge of \(10^{13}/\text{cm}^3\) electrons. Since, depending on temperature, the HCI may spend some time outside the electron beam. This reduces the effective electron density for the excitation rate, which may become one hundred times lower than the actual one inside the beam (Liang et al., 2009).

The total HCI count in charge states of interest can be from only a few (e.g., for the ‘ultimate’ \(\text{U}^{92+}\)) to hundreds of millions, with experiments covering the whole range. Appropriately designed experiments have been running with count rates of only tens of counts per hour for both visible or x-ray photons, but under favorable conditions tens of kHz have been possible. Due to the stability of normal EBIT operations, the more time-consuming measurements can be run for days and weeks with little intervention needed.

4. Preparation of neutrals for ionization and trapping

An additional source term may have to be considered in the charge-state distribution, if a steady-state atomic beam is used. If neutrals are not constantly injected but introduced in a pulsed mode, the charge state evolution is rather homogeneous. This is the case if one chooses a starting population of singly charged ions injected along the magnetic field axis. In the case of a very heavy HCI such as \(\text{U}^{92+}\), the charge-state distribution reached at 190 keV may encompass \(\text{U}^{86+}\) to \(\text{U}^{92+}\) with its maximum at \(q = 88\) (Marrs et al., 1994b), a small fraction in the hydrogenlike state, and a very small one in the bare state. In moderate charge states, recombination processes are weaker and the charge-state distribution becomes narrower than in the aforementioned case, and can easily be made to peak at the charge state of interest. This is the case for most of the ions in the context of the present review.

Concerning the choice of chemical elements, there is no limitation in sight. EBIT operation has been reported for basically all types of gaseous and solid stable elements, and radioactive isotopes have also been studied with them. A common and convenient approach is the use of gases or volatile compounds containing heavier elements. Very low vapor pressure, e.g., organometallic substances at the rate of microgrammes per day have been extensively used to produce molecular beams for injection into the EBIT (e.g., in Ref. (Watanabe et al., 2001)). External ion injection from laser-ion sources (Niles et al., 2006; Trinczek et al., 2006), oven-based Knudsen cells (Yamada et al., 2007) and vacuum-discharge sources (Brown et al., 1986) has also been reported.

Quantities of atoms needed to feed an EBIT are truly microscopic: operation with nanogramme (and even picogramme) probes electrochemically coated on needles positioned close to the electron beam was reported for HCI such as \(\text{U}^{88+}\) and \(\text{Cf}^{96+}\) (Beiersdorfer et al., 1997; Elliott et al., 1996; Elliott and Marrs, 1995).

More recently, direct injection of radioactive isotopes produced on-line by accelerators, and with lifetimes in the millisecond range, has also been reported. The experimental cycle lasting only a fraction of a second involved the extraction of the isotope from the target, generation of a beam of singly charged ions, transfer into an EBIT, ‘charge-breeding’ there to HCI state, extraction from the EBIT, and transfer to a Penning trap (Dilling et al., 2006). There, precision atomic mass measurements were carried out taking advantage of the increased precision afforded by the linear scaling of the cyclotron frequency with the HCI charge. Other experiments involved fundamental studies of \(\beta\) decay and bound-internal conversion processes (Ettenauer et al., 2011; Lennartz et al., 2014) in charge states relevant for nucleosynthesis in stellar and supernova environments. In general, these methods have considerably expanded the range of isotopes which can be made available for future optical clocks and precision atomic physics experiments.

5. Techniques for HCI delivery

Since HCI production relies on energetic interactions between neutrals and electrons inside a trap or source, methods for their transfer and re-trapping in Penning or radio-frequency Paul traps, have to be developed. As with other sources of ions, HCI have to be delivered by means of vacuum beamlines using electrostatic and magnetic guiding fields generated by appropriate electrodes and magnets. The key limitation is the very small production rate, resulting from the combined effect of minute ionization cross sections and the need to stepwise pass through many successive charge states. Typical HCI currents from EBITs are therefore in the range from pA to fA for individual charge states in steady-extraction mode; bunches of \(10^2\) to \(10^7\) HCI are standard in pulsed mode (Blessenohl et al., 2018; Currell, 2003; Gillaspy, 2001;
Micke et al., 2018).

Electron yields caused by the impact of slow HCI on clean surfaces (of up to 280 electrons per ion) were studied using EBIT-extracted $^{136}$Xe$^{21+}$...$^{51+}$ and $^{232}$Th$^{51+}$...$^{80+}$ ions (Aumayr et al., 1993; McDonald et al., 1992). For studies of the electronic charge-exchange process in collisions between HCI and neutrals, experiments have used HCI beams extracted from EBITs, and ranging from Ar$^{16+}$...$^{18+}$ to U$^{88+}$ (Otranto et al., 2006; Schneider et al., 1994; Xue et al., 2014). Charge exchange (CX) with residual gas leads to HCI losses, and thus ultra-high vacuum levels ($< 10^{-9}$ mbar) are required within the apparatus and beamline.

Due to the fact that translational temperature and spatial distribution of the ions at the source (usually parametrized using the so-called emittance in units of mm-mrad) can severely reduce the efficiency of the beamline transmission, ion transport is usually performed by applying accelerating potentials on the order of tens of kilovolts, and ion optics elements such as einzel lenses as well as electrostatic or magnetic quadrupoles are introduced at several places in order to re-focus the divergent ion beam and keeping it from hitting the guiding elements and vacuum chamber.

Buffer-gas pre-cooling of ions, sometimes applied to improve the emittance of ion sources, is prohibited with HCI due to CX. However, in spite of the high temperature of the HCI at birth (on the order of MK), EBIS and EBIT show rather good emittance parameters (a few mm-mrad), since the ions are produced in a small volume with a well defined magnetic field. Since the available number of HCI is small, various techniques have been proposed in order to optimize the yield of HCI at the delivery point, e.g., mixing HCI with cold electrons (Beier et al., 2005; Kluge et al., 2008; Poth et al., 1991; Quint et al., 2001) or evaporative cooling from a bunch of HCI oscillating inside a Penning trap (Hobein et al., 2011). One method successfully applied to HCI is pulsed extraction from an EBIT followed by phase-space cooling of the formed ion bunch by application of a time and position dependent sudden electric pulse (Schmögner et al., 2015a) to the moving HCI bunch. After the pulse, more kinetic energy is removed from the faster ions than the slower ones, and an additional time-focusing effect can be conveniently achieved. Then, the shorter and more velocity-homogeneous bunches have to overcome a potential barrier before entering a RF quadrupole electrode structure that guides them over a length of several cm having an electrostatic mirror at its end. Given that the HCI bunch now moves slowly, the entrance electrodes of the RF quadrupole can be quickly switched to a higher positive bias potential. HCI reflected from the mirror electrode cannot leave the RF quadrupole and perform a linear oscillatory motion back and forth along its axis. These steps can now be complemented with a dissipative process that removes kinetic energy from the oscillating HCI. For this purpose, a continuously laser-cooled ensemble of other ions is prepared within the RF quadrupole, thereby providing stopping power at the beginning, and sympathetic cooling at the end of the procedure as discussed in more detail in Sec. VI.B.

E. Optical spectroscopy of HCI

1. Measurements of the HFS of hydrogenic ions

As already mentioned, an important boost to the field of optical spectroscopy with HCI occurred as both ion storage rings (Klaft et al., 1994; Seelig et al., 1998) and EBITs (Beiersdorfer et al., 2001; Crespo López-Urrutia et al., 1996, 1998b) reported HFS measurements in hydrogenlike ions of heavy elements. It was clear that scaling laws would shift the 21 cm microwave transition of atomic hydrogen into the optical region, and reduce its enormous 11 million years lifetime to milliseconds. At the same time, relativistic, QED (Persson et al., 1996), and nuclear size effects were boosted to the level of 50%, 10% and 0.5% of the total ground state hyperfine transition energy (Shabaev, 1993, 1994), respectively. As detailed in Sec. III.B, tests of QED in strong fields were the main interest of the community, and theoretical work aimed at disentangling contributions from two-loop QED, nuclear recoil effects and nuclear magnetization distribution in the measured transitions. Lacking sufficient accuracy, models of nuclear magnetization were deemed far more uncertain than the dominant first order QED contributions, thus leading to the application of the HFS data to determining nuclear magnetic radii (Beiersdorfer et al., 2001; Crespo López-Urrutia et al., 1998b).
2. Other optical spectroscopic observations

A parallel development was the study of specific transitions in Ti-like ions (starting with Ba$^{34+}$ using optical spectrometers in the work of the NIST EBIT group (Morgan et al., 1995)) that showed an interesting behavior along that isoelectronic sequence. This was later also studied by other groups (Porto et al., 2000; Utter et al., 2000; Watanabe et al., 2001), namely the very weak dependence of their wavelengths on the atomic number $Z$ and thus the charge state of the ion. The reason for this is a competition of relativistic and correlation effects that results in a near cancelation of the otherwise very strong scaling of forbidden transitions to high photon energies with $Z$. Exploratory experiments showed the existence of many forbidden optical transitions which could be observed in emission with an EBIT (Bieber et al., 1997; Serpa et al., 1997). With increased wavelength resolution, optical measurements in EBITs at the Freiburg (later moved to MPIK in Heidelberg) EBIT became sensitive to QED contributions, relativistic nuclear recoil effects and the Zeeman structure of forbidden lines (Draganić et al., 2003; Soria Orts et al., 2007, 2006). In order to explore these possibilities, more and more sophisticated calculations were produced (Artemyev et al., 2007; Tupitsyn et al., 2003). Lifetimes of the metastable levels from which the optical transitions arise were measured (Serpa et al., 1997; Träbert, 2002, 2008), reaching accuracies at the 1% level (Breuner et al., 2009, 2007) and beyond, whereas QED contributions from the electron anomalous magnetic moment could be resolved (Lapierre et al., 2006, 2005).

F. Electronic structure determination in HCI

Since most of the ions of interest have never been investigated, thorough theoretical and experimental studies of their electronic structure will be required for clarifying the actual electronic structure and identifying the transitions of interest. Ritz-Rydberg analysis of optical transitions has been used for the ground state configuration of HCI in a few cases (Torretti et al., 2017; Windberger et al., 2016) and has helped clarifying the physics of EUV radiation sources for nanolithography, which are based on laser-produced plasmas containing tin HCI (Harilal et al., 2006; O’Sullivan et al., 2015).

Typically, optical measurements in an EBIT are carried out with the help of grating spectrometers, since the high temperature of trapped HCI does not support a spectroscopic resolving power $E/\Delta E \leq 30000$. One example of such a measurement is shown in Figure 7. A few measurements have been carried out by means of laser spectroscopy both in storage rings and, as proposed initially by Back et al. (1998), in EBITs by Mäckel et al. (2011); Schnorr et al. (2013). Both types of experiments suffer from the wide velocity distribution of the storage ring (at the level of $E/\Delta E \leq 10000$) and the aforementioned translational temperature inside EBITs ($E/\Delta E \leq 30000$). There have also been experiments using free-electron lasers and synchrotrons in combination with EBITs. These studies have progressively expanded the field of laser spectroscopy into the EUV and soft x-ray (Bernitt et al., 2012; Epp et al., 2007) and x-ray regions (Epp et al., 2015; Rudolph et al., 2013; Rudolph et al., 2013), however with the aforementioned limitations in spectral resolution.

G. Compact EBITs for novel spectroscopic applications

Laser spectroscopy, metrology and quantum computational studies with trapped ions are most frequently based on the in-trap production of the ions using electron impact ionization or photoionization of atoms. Less often, ions are brought into the system from an external source by means of an ion transfer beamline. The first approach offers a more compact setup but can cause certain problems of electrode contamination which may constitute a hindrance for long-term stability in metrological work. The second option, generation of ions in a separate setup, is more complex but has advantages: more versatility in terms of the types of ions available and lesser contamination of trap electrodes and optics by the atomic sources. In principle, HCI would be more amenable to this latter approach, although one could conceive both electron-beam ionization (as in, e.g., Schabinger et al. (2012)) and pulsed-laser based production schemes for moderately charged ions working within the trap chamber. The most convenient approach, however, is to separate production and spectroscopy while maintaining an overall compact envelope for the whole apparatus.

Easy availability of HCI is a prerequisite for these stud-
ies. Production of HCI in accelerator facilities will still remain restricted to a few groups worldwide. A widespread application of HCI to atomic physics research and metrology calls for small and compact sources with minimal setup and maintenance costs, and simple and reliable operation. There exist already a number of publications on small HCI sources which can be set up with moderate resources and effort within a student project, or purchased from a commercial provider.

Most of the spectroscopic and HCI-interaction experiments mentioned above were based on rather powerful cryogenic EBITs using superconducting magnets. Although far smaller than accelerator-based HCI research devices, they still need a dedicated laboratory room and a scientific team for operation. During the last decades several groups have been working on the development of more compact, and economic, systems.

The first EBIS based on permanent magnets (Khodja and Briand, 1997) were followed by other “warm-type” instruments not requiring superconducting magnets at cryogenic temperatures. The Tokyo group built an EBIT based on permanent magnets (Motohashi et al., 2000) for spectroscopic studies. Others followed (Kentsch et al., 2002; Nakamura et al., 2004, 2008; Sakaue et al., 2009; Takacs et al., 2015; Xiao et al., 2012). They can generate and trap ions having ionization potentials of a few keV, that will allow to reach charge states up to 60+ for heavy elements. Currently, such devices have typically a footprint of one square meter and operate unattended for extended periods of time both as sources of ions or for spectroscopic observation.

At NIST, HCI have been extracted from the EBIS and injected into compact Penning traps (Brewer et al., 2013), where Rydberg states of the HCI shall be prepared for laser spectroscopy. These experiments start with mass selected HCI pulses from the EBIS, extracted at energies of up to $4 \times 10^3 Q \times eV$, with $Q$ being the charge of the HCI. The Penning trap captured a significant fraction (up to several thousand) of those ions in a potential well of $(4-12)Q \times eV$ by opening and closing the axial trapping potential. This fraction has a much narrower kinetic energy distribution (FWHM $\approx 5.5 eV$) than the HCI inside the EBIT and in the extracted bunch. Other experiments with extracted ions have been performed there to measure the lifetime of the Kr XVIII $3d^2 D_{5/2}$ metastable state (Guise et al., 2014). A compact EBIT under construction will be used as a HCI source (Hoogerheide and Tan, 2015) in combination with the compact Penning trap.

Other compact devices based on the EBIT principle have recently appeared. A strong point-like magnetic focus generates HCI in charge states as high as Ir$^{55+}$ in a compact and simple device developed by Ovsyannikov and Nefiodov (2016a,b) with an overall dimension of less than $0.2 m \times 0.2 m \times 0.2 m$ length, for which HCI extraction in the radial direction was also demonstrated.

For operation of electron beams at lower energies of less than 1 keV suitable for the production of HCI predominantly in charge states with many optical transitions, and moreover offering good ion beam properties, special care has to be taken in the field design. Recently, novel EBITs using permanent magnets, schematically shown in Figure 8, have reached magnetic field strengths of 0.86 T and demonstrated excellent electron beam energy resolution for X-ray studies, ion extraction and optical spectroscopy (Micke et al., 2018). One of these devices has been installed at the German metrology institute Physikalisch-Technische Bundesanstalt (PTB) to operate an optical clock based on HCI. The magnetic cage of the EBIT has dimensions of $0.3 m \times 0.3 m \times 0.3 m$. It surrounds a vacuum system that is attached to a transport and deceleration beamline, and has an overall area of approximately 1 m$^2$. It operates at UHV conditions suitable for its connection with a cryogenic RF-trap, CryPTEx-PTB (Leopold and et al., 2017) based on the CryPTex design (Schwarz et al., 2012) in which very long HCI storage times will be required for optical clock applications.

One can expect that the rapid development in this field will probably bring even smaller EBIS and EBITs to the market and substantially reduce the barrier for the use of HCI in the laser spectroscopy community.

VI. PREPARATION OF COLD HIGHLY CHARGED IONS

A. Evaporative cooling of HCI

A key element for the success of spectroscopy experiments in EBITs was the very early introduction of evaporative cooling to their operation. The first proposal, modeling and realization of this technique by Penetrante at LLNL in 1990 (Marrs, 1999; Marrs et al., 1994b; Penetrante et al., 1991a,b; Schneider et al., 1991) preceded its application to Bose-Einstein condensates. There was an understanding that electron-ion collisions in the deep potential well caused by the negative space charge would lead to heating of the HCI, and to their eventual loss. Therefore, a cooling mechanism would be needed to keep the ions inside the trap for a long time. This was found in taking advantage of the fact that HCI from lighter elements could not reach the high charge states of co-trapped heavier elements. Ion-ion collision rates are extremely enhanced between HCI and the product of the squares of the individual colliding charges. Efficient thermalization across ion species thus redistributes energy from the heavier ions, subject to strongest electron-impact heating, and the lighter ones.

The relevant trapping parameter is the product of the charge state $Q$ (on the order of $Q \sim 20$) times the potential difference between the trap center and its edge ($\Delta V \approx 50 V$). This gives a trap depth of $\Delta V \times Q \approx 1000 eV$, corresponding to a “temperature” of
Figure 9 Schematic representation of an experiment using sympathetic cooling of HCI for optical clock applications (Schm"og er et al., 2015a,b). HCI are produced in an electron beam ion trap (left), extracted from it, decelerated and bunched, and implanted into a Coulomb crystal of singly carged ions at mK temperatures. The implanted HCI repel their fluorescing, laser-cooled Be$^+$ neighbors strongly. This provides information about the location and charge of the implanted ions.

12 MK. Therefore, light HCI with lower absolute charge states (say, Ne$^{10+}$) experience a shallow potential well (here of about 200 eV), while sharing a common temperature with the much more deeply trapped heavier ones reaching far higher charge states under the same electron beam energy conditions (for example, Ba$^{46+}$ would experience a trapping potential of 920 eV in the present example). As a consequence, lighter ions in the hot tail of the thermal distribution preferably escape from the trap. Thereby, each evaporating ion in charge state $Q$ removes from the thermal ensemble left behind an energy equivalent to the individual trapping potential, i.e., $\Delta V \times Q$. A very rough estimate of a typical heating rate for a single heavy HCI (Ba$^{46+}$) yields that the EBIT electron beam transfers a thermal energy of the order of 100 eV/s through collisions. This heating rate can easily be compensated by the removal of a lighter HCI every couple of seconds. A steady supply of light atoms, e.g., from an atomic beam to the trap center, will result successively in their ionization, thermalization and evaporation, accomplishing an efficient removal of the heat constantly generated by the elastic collisions of electrons from the beam with trapped HCI. Evaporative cooling was the key to achieve in principle unlimited trapping times for HCI from heavy elements, which are at the same time those really needing long storage times for reaching the highest charge states. In principle, evaporative cooling also works without the need of a mixture of elements. Regulation of evaporative cooling is rather unproblematic: The potential barrier which has to be overcome can be tuned by varying the electrostatic potential applied to one of the cylinder-shaped electrodes, or drift tubes in the EBIT. The use of the magnetic trapping mode (Beiersdorfer et al., 1996), in which the electron beam is turned off but the HCI remain trapped in the resulting Penning trap was also combined with evaporative cooling. In spite of these advantages, trapping-field inhomogeneities, space-charge effects, and voltage noise on the electrodes have until now limited the efficiency of the method, which in principle should achieve lower temperatures.

Furthermore, compared with other ion traps operating in the mK and $\mu$K regime by means of laser cooling, actual HCI temperatures after evaporative cooling only go down to the level of 0.2 MK (Beiersdorfer et al., 1996; M"ackel et al., 2011; Schnorr et al., 2013). The insufficient cooling causes Doppler broadening and relativistic Doppler shifts, and is the main reason for the lack of data on HCI with a precision better than a few parts-per-million (ppm), an astounding gap of 12 orders of magnitude to the $10^{-18}$ accuracy of the best optical clock data. Unfortunately, all other HCI sources are also limited in similar ways. In some cases, like in accelerators, storage rings and beam-foil methods, the ion beam temperature results from its momentum distribution. In plasmas, both high ion temperatures and electron-density effects broaden transitions to the same level. For these reasons, highest-resolution spectroscopy is carried out nowadays in traps under application of laser cooling and related techniques. This calls for transferring the HCI from their source to another type of trap more amenable to those methods.

**B. Sympathetic cooling of HCI**

Overcoming the difficulty of the high HCI temperatures borne by the violent HCI production processes has...
been a long-standing aim. Laser cooling, the tool of choice with atoms and singly charged ions, is impossible with HCI due to the lack of the necessary fast cycling optical transitions.

Attempts to solve this shortcoming using sympathetic cooling in Penning traps were already proposed in the 1990’s, and two groups, LLNL and GSI started working on them with the aim of achieving enhanced spectroscopic measurements. At LLNL, resistive cooling schemes (Church et al., 1999; Gruber et al., 2001) for HCI re-trapped in a Penning trap after extraction from an EBIT were implemented, and sympathetic cooling was achieved (Gruber et al., 2001). The team at GSI worked at the development of sophisticated deceleration and cooling schemes (Beier et al., 2005; Kluge et al., 2008; Poth et al., 1991; Quint et al., 2001; Rodriguez et al., 2010; Winters et al., 2005) needed to bring HCI produced with a relativistic heavy ion accelerator to stillstand in order to load precision ion traps.

Recently, a combination of HCI production in an EBIT and sympathetic cooling inside of a Coulomb crystal of laser-cooled Be$^+$ ions contained in a linear RF trap (Schwarz et al., 2012; Versolato et al., 2013) has demonstrated how to bring the temperature of HCI by 8 orders of magnitude down to the mK regime, and opened the possibilities afforded by RF traps to the study of HCI. An artist’s impression and schematic are shown in Figure 9 and Figure 10, respectively. The different components of the system are: an EBIT for the ion production, a transfer beamline for mass selection and deceleration, and a cryogenic RF trap. Figure 11 shows the Doppler-cooling scheme applied for preparation of the Coulomb crystals. Within the work reported by Schmöger et al. (2015a,b), the HCI transferred to the RF quadrupole were finally embedded in a Coulomb crystal. Due to the high charge state, HCI tend to occupy the positions along the RF trap axis, where micromotion is minimized. The laser-cooled Be$^+$ ions are displaced from those positions and surround and sympathetically cool the HCI.

In order to theoretically explore other possible Coulomb crystal configurations, the full Coulomb interaction and cooling with a thermal bath and laser interaction molecular dynamics simulations were carried out by J. Pedregosa (Pedregosa, 2017) using a Velocity-Verlet algorithm implemented in Fortran90. Three phases were analyzed: in the first, no cooling was applied; in the second, a thermal bath was added, and in the third, laser cooling by two lasers counterpropagating in the axial direction was turned on. The simulations probed parameters like $q/m$, the absolute as well as relative number of cooling ions and sympathetically cooled HCI and the role of the thermal bath temperature. An example in which Ar$^{5+}$ ions are cooled by 300 Be$^+$ ions is displayed in Figure 12. Further simulations were performed for Ar$^{13+}$ ions using the parameters shown in Table VI. The results indicate for the co-trapped HCI higher radial and axial trap frequencies, arising from the much steeper potential gradients experienced by those ions. This could benefit reaching appropriate Lamb-Dicke parameters for the HCI.

These simulations would imply that in a very large trap stable configurations containing 300 Be$^+$ ions and up to nearly 20 thousand Ar$^{13+}$ sympathetically cooled to 100 mK are possible. However, the resulting ensembles would also become rather long and wide (several mm) and thus would suffer from micromotion.

Experimental temperature determinations in (Schmöger, 2017) yielded values of 10 mK and below for the HCI. For faster capture of the HCI in the Coulomb crystals, it was expeditive to use large ensembles of several hundred Be$^+$ ions. Expelling most of them by means of changes in the trapping parameters leads to the ideal configuration for high resolution quantum logic spectroscopy: a single Be$^+$ cooling a single Ar$^{13+}$, as shown in Figure 13 a) and b), respectively. An effect which has not yet been fully quantified is the partial shielding of the RF field at the HCI positions by Ar$^{13+}$ ions surrounding them.

In Figure 13a) a Be$^+$ Coulomb crystal containing implanted Ar$^{13+}$ is shown. Schmöger (2017) used these in a first attempt to detect fluorescence from those HCI upon excitation with a low-drift laser system (Leopold et al., 2016) developed for this purpose. Due to insufficient knowledge of the exact frequency of the $2p_{3/2} \rightarrow 2p_{1/2}$ transition at approximately 441.255 nm, and the faintness of the expected signal in comparison with technical background noise, the experiment has not yet been successful. In the near future, an enlarged detection solid

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### Table VI Parameters for a molecular dynamics simulation of a Coulomb crystal containing sympathetically cooled HCI

| Parameter | Value | Unit |
|-----------|-------|------|
| $\rho$    | 3.5   | mm   |
| $\Omega_{RF}$ | 3.96  | MHz  |
| $V_{DC}$  | 5.0   | V    |
| $V_{RF}$  | 36.25 | V    |
| $dt$      | 2.52  | ns   |
| $z_0$     | 2.7   | mm   |
| $\kappa$  | 0.259 |      |
| $q_{Ar^{13+}}$ | 0.047 |      |
| $q_{Be^+}$ | 0.21  |      |
| $a$       | 0     |      |
| $\omega_{x,y,Ar^{13+}}$ | 760   | kHz  |
| $\omega_{x,y,Be^+}$ | 531   | kHz  |
| $\omega_{x,Ar^{13+}}$ | 180   | kHz  |
| $\omega_{x,Be^+}$ | 310   | kHz  |
For one single $\text{A}^{13+}$, the fluorescence rate at saturation for this M1 transition is approximately 100 Hz (Lapierre et al., 2006, 2005). With a detection solid angle of the order of 1%, and including the photomultiplier detection efficiency and other losses, a few ions should provide a signal rate of 0.1 Hz, which in principle could be measured against a PMT dark count rate of 4 Hz. These limitations in signal-to-noise ratio can be overcome by more elaborate quantum state detection systems, e.g. based on quantum logic (Hempel et al., 2013; Schmidt et al., 2005; Wan et al., 2014) as discussed in VII.C. These techniques are crucial for addressing even more-forbidden transition types (E2, M2, E2M3) for optical clocks.

Since trapping of a single HCI with a single cooling $\text{Be}^+$ ion has been demonstrated, the possibility of sideband cooling to the ground state of motion as discussed in Sec. VII.B will allow for advanced detection schemes addressing very slow clock transitions. Sympathetic cooling overcomes the main difficulty for high-resolution laser spectroscopy and frequency metrology with HCI. In this way, the plethora of quantum manipulation techniques available in the atomic physics community gains a wide class of experimental target beyond the much-studied alkali-like ions. In essence, a working technique combining HCI source and RF trap as needed for these transitions of $\text{M}1$ type, as shown by Windberger et al. (2015).
studies is now within reach for high precision frequency-metrology groups. Optical clocks (Ludlow et al., 2015) based on trapped singly-charged ions have achieved accuracies which in science have only that of optical lattice clocks as peers. The introduction of HCI as pacemakers will open up new opportunities for further enhancement of accuracy and sensitivity for fundamental physics searches.

Figure 12 Simulation (Pedregosa, 2017) of a Coulomb crystal containing 300 laser-cooled Be⁺ ions cooling six Ar¹³⁺ with a very close charge-to-mass ratio Q/m. The thermalization in this case is very good, and the radial and transversal temperatures of all components are about 4 mK.

Figure 13 Images of Be⁺ Coulomb crystals with implanted HCI. a) Ellipsoidal crystal containing 5 Ar¹³⁺ ions; b) Single Ar¹³⁺ ion cooled by a single Be⁺ ion (Schmöger et al., 2015b). This latter configuration allows for best sympathetic cooling conditions and eventually for ground-state cooling, which is required for quantum-logic detection (Schmidt et al., 2005).

VII. TOWARDS HIGH-RESOLUTION SPECTROSCOPY

Several challenges need to be addressed to make HCI accessible for high precision spectroscopy and optical clocks. The main goal of an atomic frequency standard is the realization of the unperturbed frequency of the reference or clock transition. In this context, two types of uncertainties are important: the statistical uncertainty (sometimes also called instability or uncertainty type A) and the systematic uncertainty (sometimes also called inaccuracy or uncertainty type B). While the systematic uncertainty quantifies how well we believe we are able to reproduce the unperturbed transition frequency, statistical uncertainty tells us for how long we need to average frequency measurements to achieve a certain resolution. Systematic uncertainties of clocks beyond the current accuracy of a few parts in 10⁻¹⁵ of the best Cs frequency standards (Guéna et al., 2017) can only be estimated by considering all possible shifts to the measured frequency. This includes changes to the atomic structure due to interaction with external fields, but also relativistic effects from motion and gravity. The instability of a frequency standard in which N uncorrelated atoms are probed simultaneously is ultimately limited by quantum projection noise (Itano et al., 1993). In the simple case of Ramsey interrogation (Ramsey, 1985) of a transition with frequency ν₀ using perfect pulses and a probe time Tᵣ, we get a fractional frequency uncertainty expressed in the form of an Allan deviation (Allan, 1966; Riehle, 2004; Riley, 2008) of

$$\sigma_y(t) = \frac{1}{2\pi\nu_0\sqrt{NT_Rt}}.$$  \hspace{1cm} (9)

From this equation it becomes clear that a high transition frequency, many atoms and a long probe time reduce the averaging time t to achieve a certain resolution. The probe time is a special case, since it can either be limited by the lifetime of the excited clock state, or by the coherence time of the probe laser (Leroux et al., 2017; Peik et al., 2006; Riis and Sinclair, 2004). The currently best lasers achieve a flicker noise floor-limited instability of 4 × 10⁻¹⁷ (Matei et al., 2017) and support probe times of several seconds. For a single atom, the best possible statistical uncertainty is achieved for a probe time equal to the excited state lifetime τ of the clock transition. It is given by (Peik et al., 2006)

$$\sigma_y(t) = \frac{0.412}{\nu_0\sqrt{\tau t}}.$$  \hspace{1cm} (10)

In the remainder of this section, we will discuss the technical issues and systematic frequency shifts, their measurement, and suppression, specific to HCI. Frequency shifts arise from motion and from external fields causing a differential shift of the two clock levels. For evaluating the performance as a frequency reference, we need to know the atomic parameters (from theoretical atomic structure calculations or measurements) and the strength of the external field. In some cases suppression techniques exist to reduce the influence of external perturbations on the clock transition. While recent reviews have addressed these issues for single-ion clocks (Ludlow et al., 2015; Poli et al., 2013), we will provide the scaling of these effects to HCI. Some effects, such as electric and magnetic field shifts will be reduced, while others (collisional shift, motion-induced shifts) may be enhanced. The section will end with an assessment of potential HCI optical clock candidates and their expected performance.
A. Trapping

Radio-frequency Paul traps have been the workhorse in all areas of ion-based research that require isolation from external fields, such as ion optical clocks, quantum information processing, quantum simulation and quantum metrology (Major et al., 2006; Wineland et al., 1998). In spherical Paul traps, a 3D oscillating quadrupole field provides confinement in all directions. At the center of the quadrupole, a single ion can be stored almost perturbation free. To trap more ions, linear Paul traps have been invented in which an oscillating 2D radial electric field combined with a static axial field provides trapping. In both cases harmonic trapping at secular frequencies between 100 kHz up to a few MHz can be achieved with rf drive frequencies $\Omega_{rf}$ oscillating typically at least one order of magnitude higher. A huge variety of electrode geometries and material choices exist for ion traps, ranging from microfabricated surface traps providing a scalable approach with multiple segments (Britton et al., 2006; Chiaverini et al., 2005; Seidelin et al., 2006), sometimes even in a cryogenic environment (Labaziewicz et al., 2008) to macroscopic traps for optical clocks with ion-electrode distances on the order of one millimeter (Doležal et al., 2015). The latter provide large optical access for efficient detection and probing the ion from various directions. They feature deep trapping potentials on the order of a few eV for storage times of many hours up to a few months. They offer moderately large motional frequencies of up to several MHz to allow recoil-free spectroscopy in the Lamb-Dicke regime while maintaining potentially low motional heating rates of only a few motional quanta per second (Brownnutt et al., 2015). Recently even linear multi-ion traps for precision spectroscopy and optical clocks have been developed (Doležal et al., 2015; Herschbach et al., 2012; Keller et al., 2016, 2015; Pyka et al., 2014), with trap-induced shifts below $10^{-19}$ fractional frequency uncertainty (Keller et al., 2017). While most single-ion frequency standards in the past are room temperature systems, with the notable exception of the Hg$^+$ clock (Rosenband et al., 2008), cryogenic Paul traps are mandatory for HCI to achieve a sufficiently long lifetime through excellent vacuum conditions (Schwarz et al., 2012). Conveniently, at the same time the BBR shift (see Sec. VII.D.2) becomes negligible. One typically distinguishes two types of motion of an ion in a Paul trap: fast micromotion at frequency $\Omega_{rf}$ and so-called secular motion at lower oscillation frequencies. Paul traps support only stable trajectories for certain charge-to-mass ratios for a given geometry and rf trapping field (Drakoudis et al., 2006; Major et al., 2006). In the simplest case, stable trapping in linear Paul traps is achieved if the radial oscillation frequency, $\omega_r$, is significantly smaller than the trap drive frequency $\Omega_{rf}$, or $q \approx 2^{3/2} \omega_r / \Omega_{rf} < 1$. This has to be taken into account when trapping HCI, in particular when trapping them simultaneously with singly-charged atomic ions as discussed in the next section. Since the stability criterium scales with the charge-to-mass ratio, $Be^+$ is a suitable cooling ion species for many medium-charged HCI. As an example, Fig. 14 shows the stability parameter for two of the radial modes of a $^9Be^+$-$^{40}Ar^{Q+}$ ion crystal. For sufficiently small $q$, secular motion decouples from micromotion and it can be assumed to be harmonic in all three directions (Dehmelt, 1968), which is what we assume from now on. Residual effects of micromotion have to be included separately, as discussed in Sec. VII.D.4.

![figure 14](image)

Figure 14 Stability parameter for a HCI in a linear Paul trap. The stability parameter $q$ is plotted for the radial modes of a 2-ion crystal consisting of a singly-charged $^9Be^+$ and an $^{40}Ar^{Q+}$ ion as a function of the Ar-ion’s charge $Q$ for a single $Be^+$ radial trapping frequency of $\omega_r = 2\pi \times 2.2$ MHz and $\Omega_{rf} = 2\pi \times 50$ MHz. All charge states satisfy the stability criterion $q < 1$.

B. Sympathetic cooling

One of the key ingredients for the success of atomic systems over the past 25 years is the control of their motion through Doppler laser cooling and other advanced cooling techniques (Chu, 1998; Cohen-Tannoudji, 1998; Phillips, 1998). The first laser cooling concepts were in fact developed and experimentally demonstrated for trapped ions (Drullinger et al., 1980; Wineland and Itano, 1979). Since then, laser cooling has become mandatory for all optical ion clocks, since it allows localization of the ion to well below the wavelength of the spectroscopy light, which is equivalent to the condition of recoil-free absorption in the Lamb-Dicke regime (Dicke, 1953). For HCI optical clock candidates that do not have a sufficiently fast (MHz linewidth) and closed transition suitable for laser cooling, sympathetic cooling can be provided by another atomic species that is laser coolable. This is implemented by trapping the HCI together with the cooling ion into the same trapping potential and taking advantage of their mutual Coulomb repulsion (Barrett et al., 2003; Larson
et al., 1986; Wan et al., 2015). While initial stopping and Doppler cooling of HCI is performed in clouds of laser-cooled atomic ions (Schmöger et al., 2015b) as described in Sec. VI.B, precision spectroscopy demands smaller ion crystals, consisting in the simplest case of two ions.

The strong Coulomb repulsion between two cold ions with charges $Q_{1,2}$ in a linear Paul trap results in equilibrium positions $d_{1,2}$ away from the center of the trap according to

$$d_{1,2} = Q_{2,1}/(4\pi\varepsilon_0 u_0 (Q_1 + Q_2)^2)^{1/3}.$$  \hspace{1cm} (11)

Here, $u_0 = m_2\omega_z^2/Q$ quantifies the strength of the axial trapping potential in terms of a single reference ion with mass $m$, charge $Q$ and oscillation frequency $\omega_z$.

The ions perform a coupled motion around these equilibrium positions appropriately described in a normal mode framework. For two ions, we have two modes in each direction, the in– and out–of–phase mode (indices $i,o$) with mode frequencies $\omega_{i,o}$. We can thus write the oscillation $z_{1,2}(t)$ of the two ions along a selected direction as a superposition of the contributions from the two modes along this direction (James, 1998; Kiepinski et al., 2000; Morigi and Walther, 2001; Wübbena et al., 2012)

$$z_1(t) = (\hat{z}_1 b_{1,i} \sin(\omega_{i} t + \phi_i) + \hat{z}_1 b_{1,o} \cos(\omega_{o} t + \phi_o))/\sqrt{m_1},$$

$$z_2(t) = (\hat{z}_2 b_{2,i} \sin(\omega_{i} t + \phi_i) + \hat{z}_2 b_{2,o} \cos(\omega_{o} t + \phi_o))/\sqrt{m_2}.$$  

Here, $\hat{z}_i/o/\sqrt{m_{1,2}} = 2\sqrt{2\varepsilon_{i,o}/\omega_{i,o}}$ is an excitation amplitude that depends on the kinetic energy $E_{i,o}$ in each mode, and $b_{k,i/o}$ are mode amplitudes normalized to $b_{2,o} = -b_{1,i}$ and $b_{2,i} = b_{1,o}$ with $b_{1,i}^2 + b_{2,i}^2 = 1$. The modes have phases $\phi_{i,o}$ that depend on the initial conditions. While identical ions have (anti-)symmetric mode amplitudes for the in–phase (out–of–phase) mode in each direction, a difference in mass and/or charge results in one ion having a large mode amplitude, while the other has a small amplitude for one mode and vice versa for the other mode along the same direction.

Figure 15 shows the axial and Fig. 16 one set of radial mode frequencies $\omega_{i,o}$ and the square of the amplitudes $b_{1,2,1,2}^2$ of a 2-ion crystal consisting of a singly-charged $^9\text{Be}^+$ and an $^{40}\text{Ar}^{+Q}$ ion as a function of the $\text{Ar}$-ion’s charge $Q$. A single $\text{Be}^+$ ion would have an axial (radial) mode frequency of $\omega_z = 2\pi \times 1$ MHz ($\omega_r = 2\pi \times 2.2$ MHz). While the axial modes remain strongly coupled for all charge states, this is not the case for the radial modes. The radial mode frequency corresponding closely to the single $\text{Be}^+$ ion mode remains almost constant for all charge states, while the other mode frequency increases as a function of the HCI charge state. Similarly, one of the mode amplitudes remains almost constant near a value of one, while the other one is close to zero. An exception is $Q = 4$, for which the charge-to-mass ratio of $^9\text{Be}^+$ and $^{40}\text{Ar}^{+4}$ is almost equal. Thus, away from this “resonance” in the coupling the ions are radially only weakly coupled. A similar, but less pronounced effect is observed for singly-charged ions with different masses (Wübbena et al., 2012). The mode decoupling is more pronounced for HCI, since (in contrast to singly-charged ions with different masses) their distance ($d_1 + d_2$) increases with their charges according to Eq. (11), reducing the radial mode coupling. However, the resonances in the radial mode coupling can be exploited if a HCI with a suitable cooling transition and matching $Q/m$ can be found.

The reduction in coupling has two consequences for the two radial modes for which the Doppler cooling ion has only a small mode amplitude $b_r$. Firstly, the Doppler cooling rate scales with the square of the mode amplitude. Together with typical timescales to reach Doppler cooling temperature after a background gas collision on the order of milliseconds for a single ion (Wübbena et al., 2012), cooling a mode with $b^2 \sim 10^{-4}$ (see Fig. 16) would take up to 10 s, which is unacceptably long. However, cooling these radial modes can be made more efficient by tilting the ion crystal out of the axial alignment through application of a static electric field. This enhances the mode coupling and has already been successfully demonstrated in the $\text{A}^+ + \text{Be}^+$ quantum logic optical clock (Rosenband et al., 2008, supplementary information).

Secondly, in the presence of motional heating mecha-
nisms (in addition to photon scattering), the steady-state temperature will be larger than the Doppler cooling temperature (Wübbena et al., 2012). Anomalous motional heating from fluctuating electric fields is the most common heating mechanism in ion traps and HCI will be particularly sensitive to it owing to their high charge state. Although the exact origin of anomalous heating remains elusive, for most traps the heating rate is significantly reduced at cryogenic temperatures and for large ion-electrode distances (Brownmunt et al., 2015). Since for HCI macroscopic traps at cryogenic temperatures will be employed, it can be expected that the anomalous heating rate is sufficiently small to allow efficient sympathetic cooling. Assuming a typical heating rate of 1 phonon/s for a trap with around 0.7 mm ion-electrode separation (Keller et al., 2016), the temperature of the weakly coupled modes for the Be\(^+\)/Ar\(^{13+}\) example discussed above would be elevated by less than 10\% above the Doppler cooling limit. The reduction of cooling rates for modes with a small amplitude of the cooling ion also hold for all other cooling techniques, such as sideband or electromagnetically-induced transparency (EIT) cooling (Lechner et al., 2016; Lin et al., 2013; Roos et al., 2000; Scharnhorst et al., 2017), that allow reaching the motional ground state.

C. Quantum logic spectroscopy

In addition to providing sympathetic cooling, the singly-charged atomic ion can also be employed for preparation and read out of the internal state of the HCI during the spectroscopy sequence using quantum logic spectroscopy (Rosenband et al., 2008; Schmidt et al., 2005). In the original implementation, state detection is accomplished by applying a series of laser pulses to the HCI and atomic ion in the motional ground state that implement so-called sideband pulses changing the internal state while adding/removing a quantum of motion (Wineland et al., 1998). This way, a SWAP operation between the internal state of the HCI and the motion is implemented, followed by another SWAP between the motion and the internal state of the atomic ion. Such a sequence maps the internal state of the HCI faithfully onto the internal state of the atomic ion, where it can be detected with high fidelity (Hume et al., 2007; Schmidt et al., 2005). Similarly, internal state preparation can be accomplished by applying sideband pulses to the HCI to drive the HCI into the target state. Dissipation is provided through ground-state cooling on the singly-charged atomic ion, which makes the sideband pulses irreversible (Chou et al., 2017; Schmidt et al., 2005). An parallel quantum readout algorithm for multiple clock ions using as few logic ions as possible has also been developed (Schulte et al., 2016). Other forms of quantum logic spectroscopy are more suitable for fast transitions. For example, in photon recoil spectroscopy (Hempel et al., 2013; Wan et al., 2014), recoil upon photon absorption by the spectroscopy ion manifests changes the motional state, which can be detected with high efficiency on the logic ion. By employing a state-dependent optical dipole force, incoherent photon scattering can be significantly suppressed, which enables spectroscopy of species with non-closed broad transitions, such as molecules (Wolf et al., 2016). The same technique can be employed for an efficient search and identification of previously unknown lines in HCI. In summary, using a co-trapped singly-charged atomic ion for sympathetic cooling and quantum logic spectroscopy, any HCI can be spectroscopically investigated as long as sideband transitions can be driven with high fidelity on either the transition of interest or any another suitable transition. Therefore, the choice of HCI for an optical clock is entirely dictated by its atomic properties.

Figure 16 Coupled radial mode parameters for a HCI in a linear Paul trap.
D. Systematic frequency shifts

The evaluation of systematic frequency shifts is one of the most important tasks when developing a frequency standard. The most common shifts arise from external fields coupling differentially to the two clock levels. The shift is characterized by its magnitude and associated uncertainty. Its magnitude is given by the properties of the external field (ac/dc, strength, orientation, polarization, gradient, ...) and the atomic properties of the clock levels. The field can either be measured externally or through the atoms, or by using a combination of measurements and simulation, as is the case e.g. for modeling the thermal environment of the ion to evaluate the blackbody radiation shift (Doležal et al., 2015; Dubé et al., 2013). Similarly, the atomic parameters can either be measured or one can rely on accurate atomic structure calculations. The uncertainty of a shift is given by the combined uncertainty of all individual contributions, i.e. the uncertainty in the atomic properties and the uncertainty in the properties of the external field. In some cases, shifts can be suppressed by taking advantage of symmetries in the shift. Averaging frequency measurements involving different levels of the Zeeman substructure of the atomic energy levels, allows e.g. elimination of the linear and quadratic Zeeman shift and the electric quadrupole shift. In these cases the uncertainty in the shift is determined by its variation during the averaging process, which has to be determined experimentally. Choosing a clock ion species with advantageous atomic properties can be simpler to implement and may eventually result in smaller systematic uncertainties compared to an atom for which cancelation schemes are required. Following (Itano, 2000; Ludlow et al., 2015; Schmidt and Leroux, 2015), we discuss the dominant shifts and possible cancelation schemes in trapped ion frequency standards applied to HCI.

1. Magnetic field shifts

External magnetic fields couple to the magnetic moment of the electron, $\mu_B$ (order of magnitude $14\ \text{MHz/mT}/h$ shifts), and the nucleus, $\mu_N$ (7.6 kHz/mT/h shifts). The coupling with the external field is in competition with the internal coupling between the magnetic moments. This results in non-linear shifts of the corresponding Zeeman levels as a function of the magnetic field strength. Of interest for clocks is the differential frequency shift $\Delta f_B$ between a selected ground and excited state, which can be expressed as a Taylor expansion according to

$$\Delta f_B = C_{M1}B + C_{M2}B^2 + C_{M3}B^3 + \ldots .$$

It is usually sufficient to consider only the first two terms for typical magnetic fields of a few 100 $\mu$T that are applied to provide a quantization axis for laser cooling and optical pumping. Electronic states with a total angular momentum quantum number $J = 0$ exhibit only the small nuclear Zeeman effect, whereas states with $J > 0$ have the much larger electronic Zeeman shift. In both cases, the $C_{M1}$ term of $\Delta f_B$ scales linearly with the magnetic quantum number $m$. The linear Zeeman effect vanishes for transitions $m = 0 \rightarrow m' = 0$, where the (un)primed magnetic quantum number denotes the (ground) excited state. In all other cases, averaging two (or more) transitions with shifts of equal magnitude, but opposite sign, allows recovering the unshifted transition frequency. The quadratic Zeeman effect is the next largest contribution. It arises from the decoupling of nuclear and electronic magnetic moments as a function of the external magnetic field strength. For atoms with $J > 0$ and hyperfine structure, the external field mixes states of different hyperfine quantum numbers $F$. The corresponding quadratic shift can be derived from first order perturbation theory to be $C_{M2} \sim (g_I h h - g_I h N)/(\hbar^2 A)$, where $g_J$ and $g_I$ are the electronic and nuclear $g$-factors, respectively, and $A$ is the hyperfine constant, characterizing the splitting between $F$ states. For singly-charged ions, typical values for $C_{M2}$ range between a few to a few ten kHz/mT$^2$. Since the hyperfine splitting scales in HCI as $Z^3$ (Gillaspay, 2001), hyperfine constants become very large and the quadratic Zeeman shift correspondingly small. In case the clock transition is a hyperfine transition, the expression for the shift coefficient simplifies to $C_{M2} = 2\mu_B^2/(\hbar^2 \nu_0)$ (Yudin et al., 2014).

In the case of $J = 0$ levels, a quadratic Zeeman effect arises through external field-mediated mixing of fine-structure components. The shift is then again proportional to the difference of the involved magnetic moments, divided by the fine-structure splitting. In singly-charged ions the $C_{M2}$ coefficient is on the order of a few ten Hz/mT$^2$. Since the fine-structure splitting in HCI scales with $Z^4$ (even more strongly than the hyperfine splitting), the quadratic Zeeman shift is further suppressed. To evaluate the shift precisely, the magnetic field and its variation needs to be determined with high accuracy. Where available, transitions with large and calibrated $C_{M1}$ coefficients can be employed for this task. Alternatively, from the difference of the two transitions averaged to eliminate the linear Zeeman shift, the magnetic field can be derived. In fact, by averaging transitions involving all Zeeman components of a state eliminates linear and quadratic Zeeman shifts, as well as the electric quadrupole shift discussed below (Dubé et al., 2013).

The previous discussion applies to dc magnetic fields. For ac magnetic fields, the linear Zeeman shift averages to zero. However, the quadratic term $\Delta f_{M2} = C_{M2}(B - B_0)^2$ remains and may be significant. In ion traps ac magnetic fields can arise from the trap RF drive or from power line noise. In both cases, the shift needs
to be calibrated by either sideband spectroscopy or by extrapolation to zero field.

2. Electric field shifts

a. AC Stark shift  Ions are always located at the position of vanishing electric field. Therefore, the dominant electric field shifts arise from field gradients and oscillating electric fields. Oscillating electric fields couple to the polarizability of the atom’s states via the ac Stark effect, while field gradients couple to electric quadrupole moments a state might have. The quadratic Stark effect can be treated as a small perturbation to the linear Zeeman effect, resulting in a scalar shift for energy levels \( |\gamma J\rangle \) with \( J \leq 1/2 \) of

\[
\hbar \Delta f_S(\gamma, J, \vec{E}) = -\alpha_S(\gamma, J)|\vec{E}|^2/2. \tag{12}
\]

It is characterized by the scalar polarizability \( \alpha_S \) which depends on the atomic state and, in general, on the frequency of the oscillating electric field \( \vec{E} \). Atomic states with \( J > 1/2 \) and \( F > 1/2 \) have an additional tensor component of the polarizability, \( \alpha_T(\gamma, J) \). The tensorial part depends on the quantum numbers \( F, m_F \) and on the polarization of the electric field with respect to the quantization axis of the atom. Sources of ac electric fields are the trap rf drive field, thermal black-body radiation, the clock interrogation laser or the cooling laser for the atomic ion applied during interrogation. They all couple the clock states off-resonantly to other levels, resulting in a differential shift. For example, the root mean square (rms) electric field associated with BBR near room temperature is given by \( \langle E^2(T) \rangle = (831.9 \text{ V/m})^2(T(\text{K})/300)^4 \). While in singly-charged ions the shift from BBR of the ion’s environment can be significant, it is negligible for HCI. This has two reasons. Firstly, HCI traps are operated at cryogenic temperatures near \( T = 4 \text{ K} \) where the BBR shift is suppressed by more than seven orders of magnitude compared to room temperature operation owing to the \( T^4 \) scaling of the shift. Secondly, the size of the electron orbitals and thus the polarizability scale with \( 1/Z \), contributing to a further suppression. AC Stark shifts arising from the rf trapping field of the Paul trap will be discussed in Sec. VII.D.4.

b. Electric quadrupole shift  Atomic states with \( J, F > 1/2 \) are no longer spherically symmetric, but exhibit higher order electric multipole moments that couple to the corresponding electric field components. The largest contribution is the quadrupole moment which interacts with electric field gradients according to the Hamiltonian (Itano, 2000)

\[
H_Q = \vec{\nabla}E^{(2)} \cdot \vec{\Theta}^{(2)}, \tag{13}
\]

where \( \Theta^{(2)} \) is the electric-quadrupole operator for the atom and \( \nabla E^{(2)} \) is a symmetric traceless tensor of second rank describing the electric field gradient at the position of the ion. It should be noted that even for states with \( J = 0, 1/2 \), a small quadrupole moment from mixing of other electronic states and nuclear quadrupole moments exists, which is usually negligible at a frequency uncertainty level above \( 10^{-19} \) (Beloy et al., 2017). The quadrupole shift depends on the total angular momentum \( F \) and its projection \( m_F \) along the quantization axis (Itano, 2000), according to

\[
\Delta f_Q \hbar \propto \frac{3m_F^2 - F(F+1)}{\sqrt{(2F+3)(2F+2)(2F+1)(2F(2F-1))}}. \tag{14}
\]

Furthermore, it depends on the orientation of the quantization axis with respect to the electric field gradient.

An electric field gradient is inherent to the axial trapping mechanism in linear ion traps and can become larger if more than one ion is trapped. Even in spherical ion traps, that can in principle be free of electric field gradients, spurious electric fields typically result in gradients of up to a few \( \text{V/mm}^2 \), resulting in shifts of a few Hz for a typical atomic quadrupole moment of \( e a_0^2 \), where \( e \) and \( a_0 \) are the electric charge and the Bohr radius, respectively. Quadrupole shift reduction or cancelation schemes are based on minimizing Eq. (14) or averaging frequency shifts of different transitions to zero. For example, selecting suitable hyperfine components \( F \) for the clock transition, the quadrupole shift can be made small. The dependence of the shift on the quantum number \( m_F^2 \) and the orientation of the gradient with respect to the quantization axis is identical to other tensorial shifts, such as the tensor component of the ac Stark effect. Therefore, averaging suitable pairs of Zeeman transitions cancels these shifts together with the linear Zeeman shift. Using such schemes, a suppression of the quadrupole shift by more than four orders of magnitude has been achieved in a singly-charged ion (Dubé et al., 2005, 2013). Alternatively, the quadrupole shift can be canceled by averaging the same transition over three mutually orthogonal magnetic field directions. The level of suppression using this technique can reach a factor of 100 if the magnetic field direction is determined to better than \( \pm 1^\circ \). Since the electric quadrupole moment scales with the square of the size of the electron orbitals \( a \sim 1/Z \), the quadrupole shift in HCI is reduced between one and several orders of magnitude compared to singly-charged ions.

3. Motion-induced shifts

An atom in motion experiences special relativistic frequency shifts with respect to an atom in the laboratory frame. Consider the case of an atom moving with velocity \( v_h \) along the direction of the clock laser with fre-
quency $f$ in the laboratory system probing the reference transition. According to special relativity, the atom observes the clock laser with a first order Doppler shift of $\Delta f_{D1}/f = \langle v\rangle/c$, where the average is taken over typical timescales required for stabilizing the probe laser frequency to the atomic transition frequency. For an ion oscillating in an ion trap that is fixed to the laboratory frame, this shift averages to zero. However, thermal drifts in the relative position of the trap with respect to the probe laser phase or probe-synchronous shifts in the ion’s position in the trap can result in fractional frequency drifts of $10^{-17}$ for a relative velocity of only 3 nm/s. Therefore it may be required to phase-stabilize the laser to the position of the trap using interferometric schemes (Falke et al., 2012; Ye et al., 2003). Since HCI are particularly sensitive to electric fields, displacements synchronous to the clock interrogation that may arise from motion in all directions, which is directly related to the total kinetic energy $E_{\text{kin}}$ of the ion in the trap. This shift can be difficult to quantify, since one has to make assumptions about the velocity distribution (Chen et al., 2017). Heating of the ion during interrogation can increase the shift and result in additional uncertainty, making this shift one of the largest contributions to the uncertainty budget, e.g. of the $\text{Al}^{+}$ and $\text{Yb}^{+}$ clocks (Chou et al., 2010; Huntemann et al., 2016; Rosenband et al., 2008). Assuming a constant thermal distribution over the probe time, characterized by a mean occupation of motional levels, $\bar{n}$, the kinetic energy in a linear Paul trap is given by the sum over all modes with frequencies $\omega_j$

$$E_{\text{kin}} \approx \left(\frac{1}{2} + \frac{1}{2}\right) \sum_{j \in \text{radial}} \hbar \omega_j \left(\bar{n}_j + \frac{1}{2}\right)$$

$$+ \frac{1}{2} \sum_{j \in \text{axial}} \hbar \omega_j \left(\bar{n}_j + \frac{1}{2}\right).$$

The first sum is over all radial modes. One of the $1/2$ prefactors reflects the fact that kinetic energy makes up only half the total energy in a harmonic oscillator, and the second $1/2$ is from intrinsic micromotion of the ion in the trap (Berkeland et al., 1998). It will be discussed in more detail in Sec. VII.D.4. The second sum is over axial modes that ideally are not affected by micromotion. It is interesting to note that the zero point energy contributes to the time dilation effect and can be on the order of $10^{-19}$ for typical trap frequencies of a few MHz and light ion species, such as $\text{Al}^{+}$. For HCI, motional shifts will depend crucially on the performance of sympathetic cooling with the singly-charged cooling ion as discussed in Sec. VII.B, which in turn will depend on the rate of collisions with background gas (discussed in Sec. VII.D.5) and the anomalous motional heating rate in the trap. Since HCI will be trapped in a cryogenic environment, we expect that both effects can be made small to not be a limiting factor in clock accuracy.

4. Micromotion shifts

The trapping mechanism of Paul traps is based on a periodically oscillating electric quadrupole field with angular frequency $\Omega_{\text{rf}}$. This field vanishes in a spherical trap at a single point and in a linear trap along the (axial) nodal line, on which ideally the ion is located (see Sec. VII.A). Since an ion in the trap has a minimal size along each direction corresponding to the zero point wave function extent $x_0 = \sqrt{\hbar/2m\omega_r}$, it is always subject to an oscillating force leading to intrinsic (and unavoidable) micromotion in the radial $(x, y)$ direction in addition to any secular motion around its equilibrium position at the much lower frequency $\omega_{x,y}$ (Berkeland et al., 1998). This intrinsic micromotion grows with the oscillation amplitude and thus the temperature of the ion. Electric dc fields displace the ion from its equilibrium position and result in additional, so-called excess micromotion. Similarly, a phase difference between the rf applied to a pair of electrodes results in excess micromotion. The amplitude of excess micromotion scales in both cases with the charge $Q$ of the ion. Therefore, HCI are particularly sensitive to micromotion and excess micromotion needs to be avoided. This is typically achieved by probing micromotion using one of several techniques (Berkeland et al., 1998; Keller et al., 2015) and applying compensation voltages to steer the ion back to the position of vanishing rf field. Since HCI experience $Q$-times stronger micromotion, the corresponding signal is also $Q$-times stronger, allowing micromotion compensation to a level comparable to singly-charged ions. Therefore, excess micromotion will not pose a limitation to optical frequency standards based on HCI as long as the required compensation voltages can be controlled with sufficient precision and remain constant between micromotion probe cycles. Micromotion contributes to the second order Doppler shift in the radial direction as discussed in Sec. VII.D.3, Eq. (15). In thermal equilibrium with the sympathetic cooling ion, the second order Doppler shift of HCI is identical to singly-charged ions. However, the oscillating electric field also leads to an ac Stark shift of the clock states as discussed in Sec. VII.D.2. This shift depends on the differential polarizability $\Delta\alpha_S$ between the two clock states. One can show that both shifts exhibit the same scaling with the oscillating field $E_{\text{rf}}$ at the position of the ion. For some ion species, such as $\text{Ca}^{+}$ and $\text{Sr}^{+}$ with negative $\Delta\alpha_S$, a so-called “magic” rf drive fre-
5. Collisional shifts

Collisions with residual background gas atoms can result in a transient distortion of the electronic energy levels and thus to a shift in the clock transition frequency. An upper bound to this frequency shift \( |\Delta \omega| \leq \sqrt{\gamma_g \gamma_e} \) is given by the total collision rates \( \gamma_g, \gamma_e \) for the ion in the ground and excited state, respectively (Vutha et al., 2017). These rates can either be calculated from scattering theory, or measured experimentally by observing decrystallization and re-ordering of a two-ion crystal (Rosenband et al., 2008). Since HCI are operated at cryogenic temperatures, background gas pressure is significantly reduced compared to room temperature setups, thus minimizing collisional shifts. Furthermore, collisions of neutral background gas atoms or molecules with a HCI almost always result in charge-transfer reactions, with the HCI capturing one electron from its neutral collision partner at a relatively far distance of several atomic units. The sudden mutual repulsion of the ionized neutral and the HCI imparts a momentum kick to both particles, and this usually removes the down-charged HCI from the trap. In this case the systematic uncertainty from collisional shifts vanishes.

E. Evaluation of HCI clock candidates

In this section, we will assess HCI candidates proposed for optical clocks and frequency references. Ideally, HCI clock candidates would outperform their neutral and singly-charged counterparts in the atomic properties that are responsible for systematic frequency shifts and the statistical uncertainty of the clock. Unfortunately, for many of the HCI candidates proposed as optical clock references not enough atomic data for a proper evaluation are available. This illustrates the strong demand for more detailed and more accurate atomic structure calculations and measurements. Therefore, we provide a list of primary clock ion selection criteria and order of magnitude values for the most important atomic parameters, inspired by Al\(^{1+}\) and Yb\(^{1+}\), two of the currently most advanced ion clock candidates:

- clock transition in a range accessible by current laser technology, i.e. 200 nm...2 \( \mu \)m
- transition with a large quality factor, i.e. high transition frequency and a long-lived excited state with a lifetime time \( \gtrsim 1 \) s to provide high stability
- small linear Zeeman shift coefficient, i.e. \( |C_{M1}| \lesssim 100 \) kHz/mT
- small quadratic Zeeman shift coefficient, i.e. \( |C_{M2}| \lesssim 100 \) Hz/mT\(^2\)
- small electric quadrupole moment \( \Theta \), i.e. \( |\Theta| \lesssim 0.1e\alpha_0^2 \)
- small differential polarizability, i.e. \( |\Delta \alpha_S| \lesssim 10^{-41} \) Jm\(^2\)/V\(^2\)
- sparse level structure to simplify initial state preparation and laser complexity
- long-lived isotopes with a lifetime exceeding years

The second requirement is often neglected in the literature. Assuming a transition wavelength of 500 nm (transition frequency \( \nu_0 = 600 \) THz) and an excited state lifetime of \( \tau = 1 \) s, we get according to Eq. (10) an instability of \( \sigma_y(T) \approx 7 \times 10^{-16}/\sqrt{\tau} \) s. This already corresponds to an averaging time of 5.5 days to achieve a relative frequency uncertainty of \( 10^{-18} \) for the measurement.

Despite the lack of atomic structure data, some general guidelines for suitable clock transitions are at hand and can be applied with caution, since exceptions may exist:

- vanishing electronic spin or availability of a \( m = 0 \rightarrow m' = 0 \) transition to eliminate the linear Zeeman shift
- small total angular momentum to reduce the number of hyperfine levels and magnetic substructure which simplifies initial state preparation and minimizes second order Zeeman and tensorial shifts
- large fine- and hyperfine-structure splittings to reduce second order Zeeman and ac Stark shifts

In addition to the primary criteria, one might apply secondary criteria such as the availability of a cooling transition, known level structure from experiment or accurate atomic structure calculations. Particularly important for possible applications is the sensitivity of the clock transition to a change in fundamental constants, QED tests or other physics beyond the Standard Model. This will result in a trade-off between achievable accuracy and the sensitivity to such effects.

In the following, we will discuss some selected species representative of a whole class of HCI with slightly different properties. In this assessment, we have taken into account the atomic properties and will discuss possible cancelation techniques that will further reduce systematic frequency shifts.
1. Hyperfine transitions

Optical clocks based on M1 hyperfine transitions in HCI have been discussed by (Schiller, 2007; Yudin et al., 2014). All investigated species with transitions between the \( F = 0 \leftrightarrow F = 1 \) hyperfine components of the \( ^2S_{1/2} \) electronic ground state with nuclear spin \( I = 1/2 \) have very favorable atomic properties concerning systematic frequency shifts. They have no electric quadrupole moment, feature a vanishing first order Zeeman shift by employing a \( m = 0 \rightarrow m' = 0 \) transition and have a very small second order Zeeman coefficient \( C_{2/2} \), since the hyperfine splitting is large compared to any Zeeman shift (see Sec. VII.D.1). Since all dipole-allowed transitions are in the XUV wavelength regime, only a small differential polarizability arises from M1 couplings between hyperfine components (Itano et al., 1982). As a consequence, all electric and magnetic field shifts are extremely small with a fractional frequency uncertainty below \( 10^{-20} \), rendering HCI based on hyperfine transitions ideal candidates for high-accuracy clocks. The only drawback in these systems is the achievable statistical uncertainty, since either the transition frequency is low with a long excited state lifetime, or vice versa. The longest investigated excited state lifetime for a transition near the optical regime is that of \( ^{171}\text{Yb}^{69+} \) with a transition wavelength of 2160 nm and an excited state lifetime of 0.37 s (Yudin et al., 2014). The achievable instability of \( \sigma_g(\tau) \approx 4.9 \times 10^{-15}/\sqrt{\tau/s} \) (Peik et al., 2006) is better by more than an order of magnitude compared to the best Cs fountain clocks. Given the high sensitivity of hyperfine transitions to changes in \( \mu, X_q, \) and \( \alpha \), as discussed in Sec. II, HCI clocks based on these transitions could help to significantly improve bounds on a possible variation of these quantities compared to what is currently possible with measurements involving Cs clocks. Since only motional and collisional frequency shifts have to be evaluated, they represent a promising starting point for HCI-based clocks.

2. Fine-structure transitions

At more moderate charge states, fine-structure transitions in the optical regime can be found and optical clocks based on one-valence electron (OVE) \( ^2P_{1/2} \leftrightarrow ^2P_{3/2} \) \((I = 3/2)\) and two-valence electrons (TVE) \( ^3P_0 \leftrightarrow ^3P_1 \) \((I = 1/2)\) transitions have been investigated in (Yudin et al., 2014). The sensitivity to frequency shifting effects are similar, but not quite as small compared to the hyperfine clocks discussed in the previous section. The electric quadrupole shift is non-zero for the excited clock state of the OVE systems. However, it can be made small by a proper choice of hyperfine components (see Eq. 14). Currently no estimates on the actual value of the quadrupole moment exist that would allow a proper evaluation of this shift. While for the OVE species \( m_F = 0 \rightarrow m'_F = 0 \) transitions are available, the large electronic linear Zeeman shift needs to be canceled by averaging suitable combinations of \( m_F \) transitions for the TVE systems. As a consequence of the smaller hyperfine splitting, the second order Zeeman effect and M1 transition-induced differential polarizability are somewhat larger compared to the hyperfine transition clocks, but still significantly smaller compared to clocks based on neutral or singly-charged atoms. Transitions between the \( ^2F_{5/2} \leftrightarrow ^2F_{7/2} \) fine-structure in \( ^{184}\text{W}^{13+} \) \((I = 1/2)\) and \( ^{191}\text{Ir}^{16+} \) \((I = 3/2)\) have been investigated in (Nandy and Sahoo, 2016). These transitions share the properties of the OVE systems discussed above and exhibit non-zero electric quadrupole moments on the order of \( 0.015e \alpha_0^2 \) that are smaller by a factor of 4 compared to the \( \text{Yb}^+ \) excited clock state due to common mode suppression between ground and excited state. While the accuracy of clocks based on fine-structure transitions is very promising, their achievable statistical uncertainty is a limiting factor. The best instability of \( \sigma_g(\tau) \approx 3.2 \times 10^{-15}/\sqrt{\tau/s} \) for the OVE species is found for \( ^{79,81}\text{Br}^{14+} \) with an excited state lifetime of \( \tau \approx 0.5 \) s and a transition wavelength of \( \lambda \approx 1642 \) nm. A similar instability of \( \sigma_g(\tau) \approx 4 \times 10^{-15}/\sqrt{\tau/s} \) is achieved e.g. by the TVE system \( ^{123,125}\text{Te}^{2+} \) with an excited state lifetime of \( \tau \approx 0.51 \) s and a transition wavelength of \( \lambda \approx 2105 \) nm.

3. Level crossing transitions

The largest investigated group of HCI optical clock candidates is based on level crossing transitions (Berengut et al., 2012a). Many of them feature a large sensitivity to a change in the fine-structure constant (Berengut et al., 2010; Berengut et al., 2011b, 2012b), which was the original motivation to study them and is discussed in more detail in Sec. II. This group can be divided into one-valence electron systems for which atomic structure calculations can provide estimates of the atomic properties required for a proper evaluation of the clock candidates, and systems with a more complicated electronic structure for which accurate data is currently unavailable. HCI clock candidates belonging to the former group include \( \text{Nd}^{13+} \) and \( \text{Sm}^{15+} \) (Ag-like isoelectronic sequence) that have optical transitions between the \( 5s_{1/2} \leftrightarrow 4f_{7/2} \) electronic states at wavelengths of 170 nm and 180 nm, respectively and excited state lifetimes of several days with zero nuclear spin \((I = 0)\) (Dzuba et al., 2012b) (see also Fig. 2). A partial systematic frequency shift evaluation reveals (Dzuba et al., 2012b) that the differential polarizability is with \( \Delta \alpha_S \approx 10^{-41} \text{Jm}^2/\text{V}^2 \) comparable to the \( \text{Al}^+ \) polarizability, the large linear electronic Zeeman shift needs to be canceled by averaging suitable transitions, whereas the second order Zeeman shift is extremely small with
$C_{M2} \sim 10 \text{ mHz/mT}^2$. The electric quadrupole moments of the $4f_{5/2}$ states have not been calculated, thus cancellation techniques as discussed in Sec. VII.D.2 need to be applied. While the transition itself has only a mild sensitivity to a change in the fine-structure constant, the $4f_{5/2}$ ground state in Sm$^{15+}$ may exhibit a large sensitivity to a violation of local Lorentz invariance (LLI) as discussed in Sec. VIII.A. In (Nandy and Sahoo, 2016), the same transition has been investigated in $^{195}\text{Pt}^{17+}$ ($I = 1/2$) at a wavelength of around 400 nm. This transition exhibits a long lifetime of 128 years, a strong linear Zeeman effect, a wavelength of around 400 nm. This transition exhibits ground state in Sm$^{15+}$ and quadratic Zeeman shifts. However, the excited electric quadrupole shift, and exhibits only small linear Zeeman shift. A representative of the Sn-like sequence with $I = 9/2$ and a transition between the $3^1\text{P}_0 \leftrightarrow 3^3\text{F}_4$ states with an excited state lifetime of around 37 s, mostly from E1 decay into other states. While the nuclear spin of $I = 7/2$ enables a $m_F = 0 \rightarrow m'_F = 0$ transition free of the linear Zeeman effect, the large number of hyperfine levels and small hyperfine splitting will result in a large second order Zeeman shift and complicates state initialization.

4. Intra-configuration transitions

Another category of HCI for optical clocks are based on optical intra-configuration transitions in the $4f^{12}$ shell that have been investigated with (Derevianko et al., 2012) and without (Dzuba et al., 2012a) hyperfine structure. One example with hyperfine structure is $^{209}\text{Bi}^{25+}$ with $I = 9/2$ and a transition between the $3^1\text{H}_6 \leftrightarrow 3^3\text{F}_4$ states with an excited state lifetime of about 3 h. This transition features a very small differential polarizability, large linear and quadratic Zeeman shifts and a quadrupole moment up to four times larger compared to the Yb$^+ \text{F}$-state. Through a proper choice of transition, the effective quadrupole moment can be reduced by two orders of magnitude, at the expense of complicated state initialization. While the transition is not particularly sensitive to a change in fundamental constants, the large angular momentum may exhibit a high sensitivity to a violation of LLI as discussed in Sec. VIII.A. HCI species of this kind without hyperfine structure ($I = 0$) have a much simpler level structure and consequently smaller quadratic Zeeman shift (Dzuba et al., 2012a). All other properties are similar compared to the case with hyperfine structure, except that a more conventional electric quadrupole suppression technique (see Sec. VII.D.2) has to be employed.

F. Evaluation summary

All discussed HCI clock candidates have rich features and partially fulfill the primary criteria listed above. However, it remains an open challenge to obtain sufficient information about the atomic properties of most of
the species that would allow a full assessment of their systematic frequency shifts and enable identification of a superior candidate. By employing systematic shift cancelation schemes, such as magic-drive frequency operation and averaging the frequencies of all Zeeman components, all magnetic- and electric-field shifts can be significantly suppressed and very likely brought to a level below the current best singly-charged ion optical clocks. This opens up exciting prospects for testing fundamental physics with HCI. As an example, transitions in $^{17}$Berengut et al. 2011b) and $^{15+}/^{17+}$ have more than an a factor of 20 higher sensitivity to a change in the fine-structure constant $\alpha$ compared to the Yb$^+$ E3 transition, which is the most sensitive system currently employed. Similarly, HCI clocks based on hyperfine transitions are sensitive to a change in the electron-to-proton mass ratio, providing more than an order of magnitude better statistical uncertainty compared to the currently employed Cs clocks. Other optical transitions in HCI may not be well-suited for clocks with ultimate performance, but rather are sensitive to other New Physics effects as discussed in the next section. Improving the bounds on such effects using HCI with their high sensitivity might turn out to be a much more efficient approach compared to improving the systematic uncertainty of conventional neutral or singly-charged atom clocks and performing frequency comparisons at a challenging level of below $10^{-18}$.

VIII. OTHER APPLICATIONS AND FUTURE DEVELOPMENTS

A. Tests of local Lorentz invariance

Local Lorentz invariance (LLI) is one of the cornerstones of modern physics: the outcome of any local non-gravitational experiment is independent of the velocity and the orientation of the (freely-falling) apparatus. The recent interest in tests of Lorentz symmetries is motivated by theoretical developments in quantum gravity suggesting that Lorentz symmetry may be violated at some energies, tremendous progress in experimental precision, and development of a theoretical framework to analyze different classes of experiments. Separate violations of LLI are possible for each type of particle, and the experiments include searches for Lorentz violation (LV) in the matter, photon, neutrino, and gravity sectors. In this section, we limit the discussion to specific LLI tests relevant to HCI applications.

Lorentz violation tests are analyzed in the context of an effective field theory known as the Standard Model extension (SME). The Data Tables for Lorentz and CPT Violation by Kostelecký and Russell (2011, 2017) gives tables of the measured and derived values of coefficients for Lorentz and CPT violation in the SME. In minimal SME, the Standard Model Lagrangian is augmented with every possible combination of the SM fields that are not term-by-term Lorentz invariant, while maintaining gauge invariance, energy–momentum conservation, and Lorentz invariance of the total action (Colladay and Kostelecký, 1998). A general expression for the quadratic Hermitian Lagrangian density describing a single spin-1/2 Dirac fermion of mass $m$ (electron, proton, or neutrion) in the presence of Lorentz violation is given by (Kostelecký and Lane, 1999)

$$\mathcal{L} = \frac{1}{2} ic\gamma^\mu \overleftrightarrow{\partial_\mu} \psi - Mc^2 \overline{\psi} \psi,$$

where $\psi$ is a four-component Dirac spinor, $c$ is the speed of light in a vacuum, $f \overleftrightarrow{\partial_\mu} g = f \partial_\mu g - g \partial_\mu f$,

$$M = m + a_\mu \gamma^\mu + b_\mu \gamma^5 \gamma^\mu + \frac{1}{2} H_{\mu \nu} \sigma^{\mu \nu}$$

and

$$\Gamma_\nu = \gamma_\nu + c_\mu \gamma^\nu \gamma_\mu + d_\mu \gamma^5 \gamma_\nu + e_\nu + i \gamma_5 J_\nu + \frac{1}{2} g_{\lambda \mu \nu} \sigma_{\lambda \mu}.$$

The $\gamma_\mu$ are Dirac matrices, $\mu = 0, 1, 2, 3$, $\gamma_5$ is a Dirac matrix associated with pseudoscalars, and $\sigma^{\mu \nu} = \frac{i}{2} (\gamma^\mu \gamma^\nu - \gamma^\nu \gamma^\mu)$. The first terms in the expressions for $M$ and $\Gamma_\nu$ give the usual SM Lagrangian. Lorentz violation is quantified by the parameters $a_\mu$, $b_\mu$, $c_\mu$, $d_\mu$, $e_\mu$, $J_\mu$, $g_{\lambda \mu \nu}$, and $H_{\mu \nu}$. The coefficients in Eq. (18) have dimensions of mass; the coefficients in Eq. (19) are dimensionless. The framework of interpreting the laboratory experiments involving monitoring atomic or nuclear frequencies in terms of the SME coefficients is described in detail by Kostelecký and Lane (1999); Kostelecký and Mewes (2002).

Violations of Lorentz invariance in bound electronic states result in a perturbation of the Hamiltonian that can be described by (Hohensee et al., 2013; Kostelecký and Lane, 1999)

$$\delta H = -\left( C^{(0)}_0 - \frac{2U}{3c^2 c_0} \right) \frac{p^2}{2m_e} - \frac{1}{6m_e} C^{(2)}_0 T^{(2)}_0,$$

where $p$ is the momentum of a bound electron. The second term in the parentheses gives the leading order gravitational redshift anomaly in terms of the Newtonian potential $U$. The parameters $C^{(0)}_0$ and $C^{(2)}_0$ are elements of the $c_{\mu \nu}$ tensor in the laboratory frame introduced by Eq. (19):

$$C^{(0)}_0 = c_{00} + (2/3) c_{jj},$$

$$C^{(2)}_0 = c_{jj} + (2/3) c_{33},$$

where $j = 1, 2, 3$.

The non-relativistic form of the $T^{(2)}_0$ operator is $T^{(2)}_0 = p^2 - 3p_z^2$. Predicting the energy shift due to LV involves the calculation of the expectation value of the above Hamiltonian for the atomic states of interest. The
larger the matrix elements, the more sensitive is this atomic state. In atomic experiments aimed at the LLI tests in the electron-photon sector (Hoehnese et al., 2013; Pruttivarasin et al., 2015), one searches for variations of the atomic energy levels when the orientation of the electronic wave function rotates with respect to a standard reference frame, such as the Sun centered celestial-equatorial frame (SCCEF). The rotation is simply supplied by Earth 24 h or year long periodic motion.

Pruttivarasin et al. (2015) performed a test of Lorentz symmetry using an electronic analogue of a Michelson-Morley experiment using the $^2D_{5/2}$ atomic states of $^{40}$Ca$^+$ ion with anisotropic electron momentum distributions. A pair of $^{40}$Ca$^+$ ions was trapped in a linear Paul trap, with a static magnetic field applied, defining the eigenstates of the system. The direction of this magnetic field changes with respect to the Sun as the Earth rotates. The Lorentz violation effects depend on the magnetic quantum number $m_J$. A test of LLI can be performed by monitoring the frequency difference between the LV shifts of the $m_J = 5/2$ and $m_J = 1/2$ substates of the 3$d^2D_{5/2}$ manifold

$$\frac{1}{\hbar} (E_{m_J=5/2} - E_{m_J=1/2}) = [-4.45(9) \times 10^{15} \text{ Hz}] \times C^{(2)}_{jK}$$

as the Earth rotates. The Ca$^+$ experiment limits to the $c_{jK}$ coefficients ($J, K = 1, 2, 3$) of the LV-violation in the electron-photon sector to the $10^{-18}$ level.

Further significant improvement of the LV constraints with such experiments requires another system with a long-lived or ground state that has a large $\langle j | T_0^{(2)} | j \rangle$ matrix element. Dzuba et al. (2016); Shaniv et al. (2017) calculated this matrix element in a variety of systems and identified the $4F^{13}S^{2} 2F_{7/2}$ state of Yb$^+$ and HCl as systems with large sensitivities to LLI. HCl ions of interest are among those already proposed for the tests of the $\alpha$-variation. The advantage of HCl for LLI tests is the possibility to use a ground rather than an excited state as the LLI probe state and larger matrix elements ($\langle j | T_0^{(2)} | j \rangle$). An experimental scheme for a search of Lorentz violation with HCl is described in Shaniv et al. (2017).

### B. Probing for new forces

Motivated by the failure of the Standard Model to e.g. describe dark matter or dark energy, searches for possible candidate fields or other, yet unidentified fields and their non-gravitational effects on atoms and molecules have commenced (Safronova et al., 2018). Precision spectroscopy measurements allow searches for new light scalar fields and constraining their couplings to ordinary matter (see e.g. (Ficke et al., 2017)). Recently, a technique based on isotope shift spectroscopy has been proposed to probe for such fields that mediate forces e.g. between electrons and neutrons (Berengut et al., 2017; Delaunay et al., 2017a,b; Delaunay and Soreq, 2016; Flambaum et al., 2017; Frugiuele et al., 2016). The idea is based on the observation of King (King, 1963) that appropriately scaled isotope shifts of two transitions exhibit a linear dependence. An additional force between neutrons and electrons would break this linearity. Two major effects result in a change of the transition frequency of a selected transition with the neutron number: the field and mass shifts. The field shift arises from a difference in the nuclear charge radius for the two isotopes. This results in a change in the overlap of the wavefunctions of the involved electronic states with the nuclear charge distribution and thus a change in their binding energy. The mass shift takes into account the change in recoil upon photon absorption by the electrons bound to the nucleus. Neglecting higher order effects, the isotope shift of transition $i$ between isotopes $A$ and $A'$ can thus be written as (Heilig and Steudel, 1974)

$$\delta \nu_i^{A,A'} = F_i \delta \langle r^2 \rangle_{A,A'} + k_i \alpha_{NP} X_i \gamma_{AA'}$$

where $F_i$ and $k_i$ are the field and mass shift constants, respectively, and $\delta \langle r^2 \rangle$ is the change in the nuclear charge radius. While optical spectroscopy can achieve very high fractional resolutions of better than $10^{-17}$, the change in nuclear charge radius is much less well known. By measuring at least two transitions $i, i'$ and introducing the modified isotope shift $m\delta \nu_i = \delta \nu_i^{A,A'}$, the dependence on $\delta \langle r^2 \rangle$ can be eliminated:

$$m\delta \nu_i = F_i m\delta \nu'_i + k_i F'_i$$

Plotting the two modified isotope shifts in one graph has become known as a King plot (King, 1963). A hypothetical new force carrier represented e.g. by a scalar field $\phi$ mediated by an unknown particle with mass $m_{\phi}$ that couples to neutrons and electrons adds an additional term to Eq. (24) (Berengut et al., 2017)

$$\delta \nu_i^{A,A'} = F_i \delta \langle r^2 \rangle_{A,A'} + k_i \frac{A - A'}{AA'} + \alpha_{NP} X_i \gamma_{AA'}$$

In this equation, $\alpha_{NP}$ is the new physics coupling constant, $X_i$ depends on the form of the potential of the scalar field $\phi$, while $\gamma_{AA'}$ depends only on nuclear properties. The additional frequency shift for a single transition will in general result in non-linearity in Eq. (25) that could be bounded experimentally by measuring at least two transitions on at least four even isotopes (without hyperfine structure). The highest sensitivity is obtained when comparing transitions for which two of the electronic states have very different orbitals to maximize the differential effect. To be able to distinguish between higher-order nuclear effects and $\alpha_{NP}$, the range of the scalar field should be larger than the size of the nucleus.
The sensitivity for massive fields is enhanced for electron orbitals that are concentrated just outside the nucleus. As a consequence, narrow optical transitions between electronic state of different character in HCI are ideal for this purpose. However, even fine- or hyperfine transitions can serve as narrow reference lines when combined with transitions in neutral or singly-charged atoms. Possible candidates for which narrow lines and at least four stable isotopes exist are Yb and in particular Ca, since experimental data for Ca\(^+\) is already available (Gebert et al., 2015; Shi et al., 2017; Solaro et al., 2017). Once nonlinearities in the King plot have been observed, the challenge remains to isolate \(\alpha_{\text{NP}}\) from all other standard physics higher order effects neglected in Eq. (24) (Flambaum et al., 2017).

### C. Towards higher transition frequencies

Science based on frequency metrology experienced a tremendous boost with the development of optical frequency combs which enabled the counting and comparison of optical frequencies (Hall, 2006; Hänsch, 2006). Moving from microwave to optical frequencies implies a four order of magnitude gain in statistical uncertainty according to Eq. (9) for the same probe time. One may ask if a similar jump can be envisioned by again going higher in photon energy, say into the vacuum-ultraviolet (VUV) or soft x-ray range. The main obstacle for this in the realm of atoms and singly charged ions (Rosenband et al., 2008; Wolf et al., 2009; Wübbena et al., 2012) as x-ray clocks, is the ionization of such systems under irradiation. Ions in higher charge states overcome this limitation and offer both allowed and forbidden transitions, the latter with suitably long lifetimes. Recent developments of VUV frequency combs based on high-harmonic sources (Gohle et al., 2005; Jones et al., 2005; Yost et al., 2008) have paved the way for the extension of the current photon-metrology methods by at least one order of magnitude. In view of the very rapid developments in this field, one can expect that within few years the same quality of combs becomes available at wavelengths of a few nm. By then, the methods of trapping and cooling of HCI have to be sufficiently improved to take full advantage of the exquisite frequency control at the 10\(^{18}\) Hz range.

The main advantage of x-ray clocks would be their improved statistical uncertainty according to Eq. (9) for the same probe times. However, this will put stringent requirements to the phase coherence of the probe laser and its delivery all the way to the ion. To take full advantage of the improved statistical uncertainty, systematic shifts need to be suppressed using advanced schemes developed in the context of quantum-information processing. Examples are decoherence-free subspaces (Pruttivarasin et al., 2015; Roos et al., 2006) or other correlation-based measurement schemes (Chwalla et al., 2007). A long term perspective for the development of the field can be drawn along the following lines: The development of VUV and soft x-ray frequency combs will enable HCI frequency standards as well as HCI probes for fundamental physics in this wavelength regime, supported by quantum-computing based control schemes for systematic shift suppression and advanced sensing schemes.

### IX. CONCLUSION

Stimulating the further development of ideas for new applications of highly charged ions, enabled by rapidly improving control of these systems is the central aim of this work. We hope that this review will assist in promoting further rapid experimental progress, and that it will also serve to bring together the HCI and laser-cooled trapped ion communities, which have been previously somewhat disjoint due to very distinct experimental approaches. On the background of earlier theoretical and experimental work, we discuss novel developments and their implications for the future. Based on recent developments, exciting new avenues of research are opened by the use of cold HCI in such diverse applications as tests of fundamental physics, metrology, development of frequency combs, and quantum information.

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