Detection of the $5p$ – $4f$ orbital crossing and its optical clock transition in Pr$^{9+}$

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Recent theoretical works have proposed atomic clocks based on narrow optical transitions in highly charged ions. The most interesting candidates for searches of physics beyond the Standard Model are those which occur at rare orbital crossings where the shell structure of the periodic table is reordered. There are only three such crossings expected to be accessible in highly charged ions, and hitherto none have been observed as both experiment and theory have proven difficult. In this work we observe an orbital crossing in a system chosen to be tractable from both sides: Pr$^{9+}$. We present electron beam ion trap measurements of its spectra, including the inter-configuration lines that reveal the sought-after crossing. With state-of-the-art calculations we show that the proposed nHz-wide clock line has a very high sensitivity to variation of the fine-structure constant, $\alpha$, and violation of local Lorentz invariance; and has extremely low sensitivity to external perturbations.
Current single ion clocks reach fractional frequency uncertainties $\delta f / f$ around $10^{-15}$, and enable sensitive tests of relativity and searches for potential variations in fundamental constants$^{1-3}$. These experiments could be improved by exploiting clock transitions with a much reduced sensitivity to frequency shifts caused by external perturbations. Transitions in highly charged ions (HCI) naturally meet this requirement due to their spatially compact wave functions$^{4,5}$. Unfortunately, in most cases this raises the transition frequencies beyond the range of current precision lasers. While some forbidden cases the electronic orbit binding energies along an isoelectronic sequence, interestingly, at configurations have both even parity, strongly mixed levels exist, allowing for relatively strong magnetic-dipole (M1) transitions with rates of order $10^{-12}$ s$^{-1}$. These experiments could be improved by exploiting clock transitions with a much reduced sensitivity to physics beyond the Standard Model. More interestingly, at con-

Results

Measurement and identification of the lines. The Heidelberg electron beam ion trap (HD-EBIT) was employed to produce and trap Pr$^{9+}$ ions$^{15}$. In this setup, a magnetically focused electron beam traverses a tenuous beam of $C_{60}H_{10}O_8$Pr molecules (CAS number 15492-48-5), which are disassociated by electron impact; further impacts sequentially raise the charge state of the ions until the electron beam energy cannot overcome the binding energy of the outermost electron. The combination of negative space-charge potential of the electron beam and voltages applied to the set of hollow electrodes (called drift tubes) trap the HCI inside the central drift tube. By suitably lowering the longitudinal trapping potential caused by the drift tubes, lower ionization states are preferentially evaporated, so that predominantly Pr$^{9+}$ ions remain trapped. Several million of these form a cylindrical cloud with a length of ~5 cm and radius of 200 µm. Electron-impact excitation of the HCI steadily populates states which then decay along many different fluorescent channels. Spectra in the range from 220 to 550 nm were recorded using a 2-m focal length Czerny Turner type spectrometer equipped with a cooled CCD camera$^{16}$. Exploratory searches with a broad entrance slit detected weak lines at reduced resolution. By monitoring the line intensities while scanning the electron beam energy we determined their respective charge state, finding 22 Pr$^{9+}$ lines in total; see Fig. 1c. The charge state identification was made on the basis of a comparison between the estimated electron beam energy at maximum intensity of the lines (135(10) eV), and the predicted

Fig. 1 The $5p - 4f$ orbital crossing and level structures of selected ions along the isoelectronic sequence. a Configuration-averaged binding energies for relevant configurations of the Sn-like (50 electron) isoelectronic sequence, as a function of atomic number Z. b–d Grotrian diagrams for low-lying levels of the $5p^2$, $5p4f$, and $4f^2$ configurations for $Z = 56$, 59, and 62, respectively. Pr$^{9+}$ is situated close to the configuration crossing point, and the corresponding diagram shows that inter-configuration optical transitions are allowed. Fig. 1c shows lines that were measured (blue) in the electron beam ion trap (EBIT). Strongly mixed J = 2 levels are indicated with multiple colors. We identified potential clock transitions (dashed magenta lines), which are not observable in the EBIT.
ionization energy of Pr\(^{9+}\) (147 eV). Here, lines from neighboring charge states appear approximately an order of magnitude weaker compared to their respective maximal intensity. Tentative line identifications were based on wavelengths and line strengths predicted from ab initio calculations. Our Fock-space coupled-cluster\(^{17}\) calculations were found to reproduce the spectra with average difference (theory – experiment) 14 (28) meV, while our AMBIT\(^{18}\) calculations (implementing particle-hole configuration interaction with many-body perturbation theory) were accurate to \(-23\) (29) meV (see Methods for further details). Intensity ratios of the lines were compared to predictions by taking into account the wavelength-dependent efficiency of the spectrometer setup and the Pr\(^{9+}\) population distribution in the EBIT. The latter was determined from collisional radiative modeling using the Flexible Atomic Code (FAC)\(^{19}\).

For confirmation and determination of level energies at the part-per-million level, high-resolution measurements were carried out. This revealed their characteristic Zeeman splittings in the \(B = 8.000(3)\) T magnetic field at the trap center. Since the only stable Pr isotope (\(A = 141\)) has a rather large nuclear magnetic moment and a nuclear spin of \(I = 5/2\), hyperfine structure (HFS) had to be taken into account to fit the line shapes. We extended the previously employed Zeeman model\(^{12,16}\), to include HFS in the Paschen-Back regime because \(\mu_B B \gg A_{\text{HFS}}\), for the involved states. We performed a global fit of the complete dataset to ensure consistent \(g\) factors extracted from lines connecting to the same fine-structure levels. The good agreement of these with AMBIT predictions conclusively confirmed our line identifications, see Fig. 2, Table 1, and Table 2. Level energies with respect to the \(5p^2 3P_0\) ground state were determined from the wavelengths using theLOPT program\(^{20}\), yielding those necessary to address the \(5p^4f 3F_2\) and \(5p^5 3P_0\) levels: their separation of 19 cm\(^{-1}\) is comparable to Zeeman splitting in the strong magnetic field. This leads to a pronounced quantum interference of the magnetic substates and to an asymmetry of the emission spectra of the above fine-structure levels when decaying to the \(5p^4f 3F_2\) state (see Fig. 2), also seen in e.g. the D lines of alkali metals\(^{21}\). The non-diagonal Zeeman matrix element between the near-degenerate fine-structure states, characterizing the magnitude of interference, was extracted by fitting the experimental line shapes, and was found to be in good agreement with AMBIT predictions. The magnetic field strength acts in this setting as a control parameter of quantum interference. In future laser-based high-precision measurements, a much weaker magnetic field will be used. This will minimize interference and enable a better determination of field-free transition energies, and consequently of the clock lines.

**Properties of the clock transition.** After discovering this orbital crossing and the interesting clock transition, in the following we discuss its properties. Without HFS, the \(5p^4f 3G_3\) state would decay through a hugely suppressed M3 transition with a lifetime of order 10 million years – a 3 fHz linewidth. However, admixture with the \(5p^4f 3F_2\) state by hyperfine coupling induces much faster E2 transitions (lifetime \(\sim\) years) with widths on the order of nHz, see Fig. 3. In state-of-the-art optical clocks such transitions have been probed\(^4\) and become accessible in HCI using well-established quantum-logic spectroscopy techniques\(^{22-24}\). The \(3G_3 F = 11/2\) state is decoupled from the ground state but decays to the \(F = 9/2\) component with a lifetime of 400 years. For comparison, the \(5p^4f 3F_2\) E2 transition to the ground state has a much broader linewidth of 6.4 mHz, similar to that of the Al\(^{1+}\) clock\(^{5,25}\).

Blackbody-radiation (BBR) shift is a dominant source of systematic uncertainty in some atomic clocks such as Yb\(^{7+}\). However, the static dipole polarisability \(\alpha_S\) (to which the BBR shift is proportional) is strongly suppressed in HCI by both the reduced size of the valence electron wave functions and the typically large separations between mixed levels of opposite parity. Together, these lead to a scaling \(\alpha_S \sim 1/Z_n^2\) where \(Z_n\) is the effective screened charge that the valence electron experiences\(^8\). Our calculations of the static polarisability for Pr\(^{9+}\) yield for the clock state of \(\alpha_S = 2.4\) a.u. and confirm the expected suppression. Furthermore, the ground state polarisability is rather similar, so the differential polarisability for the clock transition is \(\Delta \alpha_S = 0.05\) a.u., ten times smaller than that of the excellent Al\(^{1+}\) clock transition with \(\Delta \alpha_S = 0.43(6)\) a.u.\(^5\). An atomic clock based on Pr\(^{9+}\), would therefore be extremely resilient to BBR even at room temperature.

Beyond their favourable metrological properties, HCI have been suggested for probing variation of fundamental constants due to their high sensitivity to this\(^{5,7}\). Sensitivity to a variation of a transition with frequency \(\omega\) is usually characterized by the parameter \(q\), defined by the equation

\[
\omega = \omega_0 + qx
\]

where \(\omega_0\) is the frequency at the present-day value of the fine-structure constant \(\alpha_S\) and \(x = (\alpha/\alpha_0)^2 - 1\). Calculated \(q\) values for Pr\(^{9+}\) levels are presented in Table 1, and compared to other proposed transitions in Table 3. The Pr\(^{9+}\) M3 clock transition has a sensitivity similar to that of the 467 nm E3 clock transition in Yb\(^{7+}\), \(4f^{14}6s^2 \text{S}_{1/2} \rightarrow 4f^{13}6s^2 2P_{3/2}^\pm\) \((q = -64000 \text{ cm}^{-1} 26)\), but with opposite sign. The sign change can be understood in the single-particle model: the Yb\(^{7+}\) transition is \(4f^ \rightarrow 6s\), while in Pr\(^{9+}\) it is \(5p \rightarrow 4f\), leading to opposite sign. Comparison of these two clocks would therefore lead to improved limits on a variation and allow control of systematics.

We also investigate the sensitivity of the clock transitions to invariance under local Lorentz transformations. LLI is a fundamental feature of the Standard Model and has been tested
where $c$ is the speed of light, $(\gamma z p z)$ are Dirac matrices, and $p$ is the momentum of a bound electron. We find $\langle J||T^{(2)}||J \rangle = 74.2$

in all sectors of physics. While Michelson-Morley experiments verify the isotropy of the speed of light, recent atomic experiments have placed strong limits on LLI-breaking parameters in the electron-photon sector. The sensitivity of transitions for such studies is given by the reduced matrix element of $T^{(2)}$, defined by

$$T^{(2)} = c y_0 (y \cdot p - 3y_p z)$$

where $c$ is the speed of light, $(y_0, y)$ are Dirac matrices, and $p$ is the momentum of a bound electron. We find $\langle J||T^{(2)}||J \rangle = 74.2$

The rate is calculated using theoretical matrix elements from AMBiT and experimental transition frequencies.
for realistic parameters of laser radiation at 408 nm detuned by 1 MHz from the $^3P_0 - ^5P^4f ^3F_j$ transition. Similarly, motional excitation rates of a few kHz can be achieved by detuning laser radiation at 452 nm by 10 Hz from the nHz-wide $^3P_0 - ^3G_3$ clock transition. Since the ion is long-lived in both states, we distinguish between the two clock states by detuning the beams forming the ODF to additionally change the magnetic substate$^{24}$. State selectivity can be provided by the global detuning of the ODF and the unique $g$-factor of the electronic and hyperfine states. In case the HCI is in one of the excited hyperfine states, the lowest hyperfine state $F=1/2$ can be prepared deterministically by driving appropriate microwave $\pi$-pulses between $F$ states, followed by detection if the target $F$ state has been reached. The $m_f$ substate is then prepared by driving $\Delta m_f = \pm 1$ states using appropriately detuned Raman laser beams on the red sideband, followed by ground state cooling$^{22,24}$.

Despite the high resolution of the measured lines, the $^3P_0 - ^3G_3$ clock transition with expected nHz linewidth is only known to within 1.5 GHz. We can improve this by measuring the $^3P_0 - ^5P^4f ^3F_j$ and $^3G_3 - ^5P^4f ^3F_j$ transitions and performing a Ritz combination. The transitions can be found by employing again counter-propagating Raman beams that excite motion inversely proportional to the detuning of the Raman resonance to the electronic transition$^{23}$. Using realistic laser parameters similar to above, tuned near the electronic resonance, we estimate that a scan with 10 MHz steps using 10 ms probe pulses can be performed without missing the transition. Assuming that each scan point requires 100 repetitions we can scan the $\pm 2\sigma$ range in $\sim 10$ min. By reducing the Raman laser power while extending the probe time, the resolution can be enhanced to the sub-MHz level. Once identified, quantum-logic spectroscopy following$^{11,22}$ on the clock transition can commence. Since the linewidth of the transition is significantly narrower compared to the currently best available lasers$^{35}$, we expect laser-induced ac Stark shifts that need mitigation using hyper-Ramsey spectroscopy or a variant thereof$^{36-45}$.

### Discussion

We have measured optical inter-conﬁguration lines of $^3P_{0,1,2}$, finding the $5p - 4f$ orbital crossing, and thereby determined the frequency of the proposed $^3P_0 - ^3G_3$ clock transition with an accuracy sufﬁcient for quantum-logic spectroscopy at ultra-high-resolution. Our state-of-the art calculations agree well with the measurements, thus we used the obtained wave functions to predict the polarizabilities of the levels and their sensitivities physics beyond the Standard Model. These are crucial steps towards future precision laser spectroscopy of the clock transition, for which we have also proposed a detailed experimental scheme.

### Methods

#### Line-shape model.

In the hyperfine Paschen-Back regime, the energy shift of a fine-structure state’s magnetic sublevel in an external magnetic ﬁeld is given by

$$
E_{B0} = g_I m_I \mu_B B + A_{IJ} m_I m_J.
$$

(3)

Hence, a transition between two ﬁne-structure states has multiple components with energies $E_i = E_0 + \Delta E_{B0} + \Delta E_{B0}$, where $E_0$ the transition energy without an external ﬁeld, and $\Delta E_{B0} = E_{B0} - E_{B0}$. Here, and in the following, primed symbols differentiate upper states from lower states. Taking into account the Gaussian shape of individual components, the line-shape function is deﬁned as

$$
\mathcal{F}(E) = \sum_{i} \frac{M_i}{\Delta \omega_i} \exp \left( -\frac{(E - E_i)^2}{2 \Delta \omega_i^2} \right),
$$

(4)

where the sum is taken over all combinations of upper and lower magnetic sublevels. The factors $\Delta \omega_i$ take into account the known efﬁciencies of the setup for the two perpendicular linear polarizations of the light, and $w$ is the common linewidth, which is determined by the apparatus response and Doppler broadening. The magnetic-dipole matrix elements $M$ are given by

$$
M = (|J, m_J, I, m_I|' |J', m_J', m_I'|) \approx \frac{1}{\sqrt{2}} \sum_{\mu} <\mu | J' m'_{J'} | J m_J m_I > \langle \mu | m_{J'} | m_J m_I >,
$$

(5)

The large parentheses denotes a Wigner 3j-symbol. It follows that $\Delta m_I = m_I - m'_I = 0, \pm 1$. In case of the asymmetric lines, the above $|J, m_J|$ initial ﬁne-structure states were transformed to the eigenstates of the Zeeman Hamiltonian also taking into account non-diagonal coupling.

Equation (4) was ﬁtted to each measured line with the following free parameters: $E_i, w$, a constant baseline (noise ﬂoor), and overall amplitude. The results for the extracted transition energies are presented in Table 2. The $g_I$ values of all involved states were kept as global ﬁt parameters for the whole dataset of 22 lines. Shot noise and read-out noise were taken into account for the weighting of the data points. The ﬁnal uncertainties on the transition energies for each line were taken as the square root of its ﬁt uncertainty and calibration uncertainty added in quadrature.

#### Fock-space coupled-cluster calculations.

The Fock-space coupled-cluster (FSCC) calculations of the transition energies were performed within the framework of the projected Dirac-Coulomb-Breit Hamiltonian$^{46}$. In atomic units ($\hbar = m_e = c = 1$),

$$
H_{DCB} = \sum \xi_{ij} (1 + \gamma_{ij}) + \sum \frac{1}{r_{ij}} + B_0.
$$

(5)

Here, $\xi_{ij}$ is the one-electron Dirac Hamiltonian,

$$
\xi_{ij} = c \alpha_i \cdot \alpha_j + (\beta_i - 1) c^2 + V_{ne}(i),
$$

(6)

$\alpha$ and $\beta$ are the four-dimensional Dirac matrices and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The nuclear potential $V_{ne}(i)$ takes into account the finite size of the nucleus, modeled by a uniformly charged sphere$^{47}$. The two-electron term includes the nonrelativistic electron repulsion and the frequency-independent Breit operator,

$$
B_0 = -\frac{1}{2 \gamma} \left[ \sum_{ij} \alpha_i \cdot \alpha_j + (\alpha_i \cdot \gamma_j) (\alpha_j \cdot \gamma_i) / r_{ij}^3 \right],
$$

(7)

and is correct to second order in the ﬁne-structure constant $\alpha$.

The calculations started from the closed-shell reference $[\text{Kr}]4d^85s^2$ configuration of $\text{Pr}^{2+}$. In the ﬁrst stage the relativistic Hartree-Fock equations were solved for this closed-shell reference state, which was subsequently correlated by solving the coupled-cluster equations. We then proceeded to add two electrons, one at at time, reevaluating at each stage, to reach the desired valence state of $\text{Pr}^{3+}$. We were primarily interested in the $5p^4$ and $5s5p$ conﬁgurations of $\text{Pr}^{3+}$; however, to achieve optimal accuracy we used a large model space, comprised of 4 s, 5 p, 4 d, 5 f, 3 g, 2 h, and 1 i orbitals. The intermediate Hamiltonian method$^{48}$ was employed to facilitate convergence.

The uncontracted universal basis set$^{49}$ was used, composed of even-tempered Gaussian type orbitals, with exponents given by

$$
\xi_n = y \delta_n^{\alpha-1}, \quad y = 106 111 395.371 615
$$

(8)

The basis set consisted of 37 s, 31 p, 26 d, 21 f, 16 g, 11 h, and 6 i functions; the convergence of the obtained transition energies with respect to the size of the basis set was veriﬁed. All the electrons were correlated.

The energy calculations were performed using the Tel-Aviv Relativistic Atomic Fock-Space-coupled-cluster-cluster (TRAFS-3C), written by E. Elav, U. Kaldor and Y. Ishikawa. The final FSCC transition energies were also corrected for the QED contribution, calculated using the AMBPT program.
Polarizabilities. The polarizabilities were also calculated using the Fock-space coupled-cluster method within the finite-field approach. We used the DIRAC17 program package, as the Tel-Aviv program does not allow for addition of external fields. The v32 basis set of Dyll was used; 20 electrons were correlated and the model space consisted of 5p and 4f orbitals. These calculations were carried out in the framework of the Dirac-Coulomb Hamiltonian, as the Breit term is not yet implemented in the DIRAC program.

CI - MBPT calculations. Further calculations of energies and transition properties were obtained using the atomic code AMBIT8. This code implements the particle-hole CI+MBPT formalism24, which builds on the combination of configuration interaction and many-body perturbation theory described in ref. 25 (see also ref. 36). This method also seeks to solve Eqs. (5)–(7), but treats electron correlations in a very different way. Full details may be found in ref. 25; below we present salient points for the case of Pr4+.

For the current calculations, we start from relativistic Hartree-Fock using the same closed-shell reference configuration used in the FSSC calculations: [Kr]4d105s2. We then create a B-spline basis set in this V⁵N–2 potential, including virtual orbitals up to n = 30 and l = 7. In the particle-hole CI+MBPT formalism the orbitals are divided into filled shells belonging to a frozen core, valence shells both below and above the Fermi level, and virtual orbitals. The CI space includes single and double excitations from the 5p, 5sα, and 4fα ("leading configurations") up to 8spd5, including allowing for particle-hole excitations from the 4d and 5s shells. This gives an extremely large number of configuration state functions (CSFs) for each symmetry, for example the J = 4 matrix block has N = 798134. To make this problem tractable we use the emu CI method37 where the interactions between highly-excited configurations with holes are ignored.

Correlations with the frozen core orbitals (including 4s, 4p, 3d shells and those below) as well as the remaining virtual orbitals (n > 8 or l > 3) are treated using second-order MBPT by modifying the one and two-body radial matrix elements25. The effective three-body operator 26 is applied to each matrix element separately; to reduce computational cost it is included only when at least one of the configurations involved is a leading configuration24. Finally, for the energy calculations we include an extrapolation to higher l in the MBPT basis28 and Lamb shift (QED) corrections29.

Diagonalisation of the CI matrix gives energies and many-body wave functions for the low-lying levels in Pr4+. Using these wave functions we have calculated electromagnetic transition matrix elements (and hence transition rates), hyperfine structure, and matrix elements of f J (Eq. (2)). For all of these we have included the effects of core polarisation using the relativistic random-phase approximation (see ref. 36 for relevant formulas). By contrast q values (Eq. (1)) were obtained in the finite-field approach by directly varying α in the code and repeating the energy calculation. In Table 3, the predicted matrix elements and sensitivities are compared to those of other proposed systems and those already under investigation in relevant high-precision experiments.

Lifetimes calculations. Direct decay of the 5p⁴7/2 G1 clock state to the ground state proceeds as an M3 transition, which is hugely suppressed and would indicate a lifetime of order 10 million years. However, the hyperfine components of the 1⁵P₁ clock state have a small admixture of J = 2 levels, allowing for decay via a much faster E2 transition. The rate of the hyperfine-interaction-induced decay can be expressed as a generalized E2 transition

\[ R_{\text{IFS}} = \frac{1}{15} \frac{A_{\text{IFS}}^{2}}{2F + 1} \]

where F is the quantum number of total angular momentum of the upper state (F = 1 +) and the amplitude can be expressed as

\[ A_{\text{IFS}}^{2}(a \rightarrow 0) = \sum_{n} \left[ \frac{(a_{\text{IFS}}/\eta_{n})^{(n)(2)}(b)}{B_{n}-B_{n}} + \frac{(b_{\text{IFS}}/\eta_{n})^{(n)(2)}(a)}{B_{n}-B_{n}} \right] \]

Here \( \eta_{\text{IFS}} \) and \( (n)(2) \) are the operators of the hyperfine dipole interaction and the electric quadrupole amplitude, respectively. For the clock transition the sum over intermediate states n in Eq. 10 is dominated by the lowest states with J = 2: 5p⁴7/2 9Σ₁ and 5p⁴9/2 9Π₂.

MCDF calculations. Transition energies, hyperfine structure coefficients, and g factors were also evaluated in the framework of the MCDF and relativistic CI methods, as implemented in the GRASP2K atomic structure package32, and were found to be in reasonable agreement with the experiment on the level of the CI + MBPT results. As a first step, an MCDF calculation was performed, with the active space formed by one- and two-electron interactions ranging from the 5s, 5p, and 4f spectral orbitals up to 8f. In the second step, the active space was extended to also include the 4d orbitals for a better account of core polarisation effects, and CI calculations were performed with the optimized orbitals obtained in the first step. The extension of the active space in the second step has led to 9466 g-coupled configurations. For a more detailed model of the spectral line shapes, the non-diagonal matrix elements of the hyperfine and Zeeman interactions33 and mixing coefficients for sublevels of equal magnetic quantum numbers were also evaluated.

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Code availability
The AMBIT code is available at https://github.com/djula/AMBIT18, the LOPT program at http://cpc.cs.qub.ac.uk/summaries/AEHN_v1_0.html, the DIRAC17 package at http://www.dircaprogram.org, and the GRASP2K code at https://www-amdis.iaea.org/GRASP2K/34. The TRAFS-3C code is available upon reasonable request.

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