Spectroscopy – with logic!

The coherent manipulation of trapped ions enables the precision spectroscopy of previously inaccessible species

Piet O. Schmidt

Optical spectroscopy with the highest resolution is only possible on atoms which have transitions suitable for laser cooling and for detecting the internal state. This posed a significant limitation, e.g. for the development of highly accurate atomic clocks. A new method based on quantum information processing techniques lifts this limitation and makes numerous other atoms and molecules accessible. This opens up fascinating possibilities in the development of optical clocks and tests on fundamental theories.

Precision spectroscopy is a driving force in the development of our understanding of physics. Thus, increasingly higher spectroscopic resolutions have made effects – such as the fine structure and hyperfine structure, as well as the Lamb shift – visible and have led to the development of quantum electrodynamics (QED). QED is one of the cornerstones of the very successful standard model of particle physics, which cannot, however, explain a series of phenomena such as, e.g., dark matter or energy, and the asymmetry in the distribution of matter and antimatter. Furthermore, gravitation is not compatible with QED. For this reason, a common description of all fundamental interactions is sought. There is hope that spectroscopy with increasingly higher resolution will eventually produce further deviations from the predictions of our best models and thus indicate the way towards a refined and possibly unified theory.

Very worthwhile in this respect is the investigation of systems where possible deviations are especially prominent. This includes, in particular, spectroscopic investigations of atoms and molecules, in order to detect possible changes in fundamental constants, to seek a possible dipole moment of the electron, to measure parity violation, as well as generally testing QED. However, there are only a few theoretical predictions about the order of magnitude of the anticipated effects. Since these have not yet been discovered in the laboratory, these deviations must be so tiny that only highest-resolution methods are promising.

The – by far – most accurate measuring method nowadays is laser spectroscopy, with which the frequency ratios of optical clocks can be given accurately to 17 digits [1]. To this end, the reference atoms must be shielded as well as possible from disturbing environmental influences, such as undesirable electromagnetic fields and collisions with other atoms. Paul traps for ions in ultrahigh vacuum are particularly suitable here, since the trapped ions are kept in a nearly field-free location. Due to the strong trap confinement, there is practically no recoil kick (analog to the Mossbauer effect) during spectroscopy, since a single photon does not change the quantized state of motion of the ion in the trap.

For spectroscopy of narrow transitions (long lifetime of the excited state), typically a recurring sequence is used (Fig. 1): Laser cooling minimizes Doppler shifts, the initial state for spectroscopy is initialized with optical pumping, a spectroscopy laser pulse which brings the atom to its excited state with a certain probability, probes the transition. Finally, internal state detection provides information on whether the atom has remained in its ground state. The spectroscopy signal results from the

mean of the excitations over many cycles as a function of the detuning of the laser in terms of the transition.

However, not every interesting species has a suitable transition to laser cooling and detection. In fact, up to now only a small fraction of all neutral and charged atoms have been cooled with lasers. In the case of molecules, the situation is still more dramatic: Due to the numerous rotational and vibrational levels, closed cyclical transitions that are suitable for laser cooling only exist in rare cases. It is precisely molecules, however, which offer a rich pool of transitions with properties that are relevant to the questions referred to at the beginning.

A solution to this problem comes from another, seemingly very different field which has developed at a rapid pace in the past 15 years: Quantum information processing with trapped ions. The objective of this solution is to realize quantum computers and quantum simulators (see the article by D. Leibfried in Physik Journal 12/2009, p. 45). The basic building block thereby is the quantum bit (qubit) consisting of two long-lived levels, where the quantum information is encoded as a superposition of the states. The quantum-mechanical entanglement of several qubits in a quantum register enables certain algorithms to be implemented more efficiently than is possible classically. It is possible to realize such a quantum register, e.g., in the form of chains of ions that are trapped in a linear Paul trap and are strongly coupled via their mutual Coulomb repulsion. The motion of the ions is described in this case via collective motions of all the ions. By means of laser or microwave pulses of suitable frequency and duration, it is possible to change the internal electronic state of the ions as well as their motion state in the trap. In 1995, Ignacio Cirac and Peter Zoller proposed using such laser pulses in order to entangle ions via the mutual motion in the trap and thus implement quantum logic gates [2]. This idea was implemented and further developed in numerous experiments. Impressive quantum algorithms and -simulations were implemented – made possible by efficient decoupling of the internal and external degrees of freedom of environmental influences that cause decoherence, and by means of the efficient preparation, coherent manipulation and detection of internal states with the aid of laser light. The same requirements also apply to laser spectroscopy (Fig. 1).

Logical access

Meanwhile, a series of techniques from quantum information processing have been developed for improving precision spectroscopy. The prime example is quantum logic spectroscopy, proposed in 2001 by David Wineland at NIST in Boulder. This enables combining the special spectroscopic properties of one ion species (spectroscopic ion) with the well-developed manipulation techniques of another species (logic ion) when these are stored together in a Paul trap. The motion of the ions is coupled so strongly that the spectroscopy ion is also cooled by the laser cooling of the logic ion. With the aid of quantum logic protocols, it is possible after probing the spectroscopy transition to transfer the internal state information of the spectroscopy ion to the logic ion, where it can be detected with close to 100% efficiency (see infobox). In addition, it is possible to prepare the internal state within the possible spectroscopy states deterministically [3]. Thus, all the requirements are fulfilled which are necessary for the laser spectroscopy of ions lacking a cycling transition.

Thus, this technology offers access to the spectroscopy of previously inaccessible atomic and molecular species that possess interesting spectroscopic properties or are particularly suitable for atomic clocks. Some of the following examples illustrate the implementation of quantum logic spectroscopy.

The clock of choice

As early as 1992, Hans Dehmelt and his colleagues proposed using the aluminum ion as a candidate for a clock, whose reference transition lies in the optical spectral range. Already at that time it was

known that the $^1S_0$-$^3P_0$ transition in Al$^+$ is particularly suitable as a reference for a frequency standard: This forbidden transition is only weakly allowed by the hyperfine interaction of the valence electron with the nuclear spin and thus exhibits a narrow linewidth of 8 mHz. Furthermore, the transition is insensitive to electrical field gradients, one of the larger systematic uncertainties in typical single-ion clocks. ^{27}Al, the only naturally occurring isotope, has a nuclear spin of 5/2, which leads to a weak linear and quadratic Zeeman shift of the clock levels, due to the interaction of the nuclear spin with an external magnetic field. Furthermore, the aluminum ion reacts much more weakly to black-body radiation than all other previously investigated clock atoms. Due to the coupling to the thermal radiation of the environment, both clock levels shift slightly. This is currently one of the greatest systematic uncertainties for most clocks. Since Al$^+$ does not have a suitable transition for laser cooling, it took more than ten years – in spite of all of these positive properties – until quantum logic spectroscopy made the first Al$^+$ clock possible with beryllium as the logic ion (see infobox). According to the quantum logic protocol, both ion species are to be trapped and cooled in a linear Paul trap (Fig. 2). After the spectroscopy of the clock transition in Al$^+$, the internal state is transferred from Al$^+$ to Be$^+$ and then detected. The state transfer is achieved via a series of well-controlled laser pulses. The joint motion of the ions acts as the mediator due to the strong Coulomb coupling. Depending on the internal state of the Al$^+$ ion, the first laser pulse puts the ion crystal into motion which, prior to this, has been cooled to the ground state of motion. A second laser pulse can map this excitation of motion into an internal state on the logic ion, where it is detected through another laser pulse. This scheme was implemented for the first time on an auxiliary transition in Al$^+$ (Fig. 3) [3]. This is the basis of the operation of the Al$^+$ clock which, with a relative uncertainty of $8.6 \cdot 10^{-17}$, is currently the most accurate clock in the world [4].

Frequency comparisons between two different clocks with such high accuracies enable the measurement of the tiniest shifts of the atomic energy levels involved. A change in fundamental constants, such as the fine-structure constant α, can produce such shifts. It is possible to calculate very accurately how the energy levels in different atoms would react to a change of α. This allows an upper bound to be established for a variation of α via a frequency comparison. Two comparisons of the Al$^+$ and Hg$^+$ frequency standards separated by a year thus allowed the inference that the relative temporal change of the fine-structure constant is less than $(-2.6\pm2.3)\times10^{-17}$ per year [1]. Together with comparison measurements of other frequency standards, it is possible to limit the temporal change of further fundamental constants, such as the Rydberg constant (Fig. 4). With an accuracy improved by two orders of magnitude, a spatial change of α predicted from astrophysical observations would be measurable with optical clocks.

Spectroscopy at the limit and designer atoms

The entanglement of atoms leads to fascinating applications of quantum logic. In classical Ramsey spectroscopy starting from the ground state, a short laser pulse generates a superposition between the ground state and the excited state with equal amplitudes $(|\downarrow\rangle + \exp(-i\omega t)|\uparrow\rangle)$.[2] The two parts of the wave function develop with a relative phase which corresponds to its energy interval $\hbar\omega$. After a waiting period, a second laser pulse changes the amplitudes of the superposition state, dependent on the relative phase evolution between atom and laser. Thus, the atom is in an excited state after the second pulse, e.g. in the case of an exact resonant excitation and vanishing phase evolution. The measurement of the superposition amplitudes is therefore a measurement of the relative phase evolution between atom and laser. If only a single atom is measured, the signal is very noisy due to projection into one of the two states during the detection (quantum projection noise).

In the classical measurement on N uncorrelated atoms, the signal-to-noise ratio improves with $\sqrt{N}$. By means of entanglement, this scaling can be improved up to the so-called Heisenberg limit, which corresponds to a scaling with N. This can be achieved by generalized Ramsey pulses, which (analogous to the single-atom Ramsey pulses described above) produce and read out a superposition

state which consists of two parts: all atoms in the ground state and all atoms in the excited state ($|\downarrow\downarrow\downarrow\ldots\downarrow\rangle$ + exp($-iN\omega t$)$|\uparrow\uparrow\uparrow\ldots\uparrow\rangle$) **(Fig. 5)**. The difference in energy between both parts of the wave function is given by the sum of all single-atom energy differences and, thus, $N\hbar\omega$, which leads directly to the desired scaling behavior and was demonstrated experimentally with beryllium ions [6] and calcium ions [7]. This scheme is difficult to use in atomic clocks, however, because the increased signal-to-noise ratio only improves the stability when the spectroscopy laser is sufficiently stable in frequency – currently the limiting factor.

Exciting possibilities open up with the entanglement of different states of the same species. A clever combination of states results in both parts of the wave function experiencing the same linear Zeeman shift. Since the phase development between the entangled states is only sensitive to the relative energy shift, the linear magnetic field shift of the transition frequency vanishes **(Fig. 6)**. However, shifts due to the second-order Zeeman effect still have to be taken into account. The entanglement of several atoms, however, enables the design of "super atoms" with properties which a single atom does not exhibit, as, e.g., an immunity to magnetic fields. In this way, it has become possible to measure the electric quadrupole moment of a calcium ion with unprecedented accuracy [8].

State preparation and "Photon Billiards"

The state transfer described for the aluminum clock requires some experimental effort, since it is necessary to cool the ions to the ground state and to implement complex laser pulse sequences. However, again a development from quantum information processing came in convenient: Operations (quantum gates) employed for calculations are based on a state-dependent light force which affects the ions. By modulating this intensity at the frequency of a motional mode, the ion crystal heats up in a state-dependent manner. This effect can become so strong that it detectably modulates the fluorescence signal of the logic ion, as was successfully demonstrated in an experiment with an Al^+/Mg^+ ion crystal [5]. A temporally modulated standing wave field of two opposing laser beams whose light frequency differs exactly by the frequency of a motional mode can implement the necessary light force. The laser beams are detuned with respect to a transition in the atom in order to ensure a sufficiently large force while avoiding an excitation of the transition. This ensures that the internal state does not change during detection.

This method is particularly well suited to prepare the states of atoms and molecules with complex level structures where the usual optical pumping may not be used. The objective is to accumulate the population distributed over many levels in a single state by means of suitable couplings. If one now combines a weak coupling between the occupied states with the state detection described above, the ion will be projected into the target state sooner or later. A possible application is the preparation and spectroscopy of selected rotation-vibration states in molecular ions [9]. The applications which thus open up for precision spectroscopy are diverse and range from QED tests and a more accurate determination of the fine-structure constant to measurements of a possible dipole moment of the electron and a possible change of the mass ratio from electron to proton.

Quantum logic spectroscopy requires a sufficiently long-lived excited state, so that no decay occurs during the state transfer sequence. In a variation of this method, fast dipole-allowed transitions can be investigated stray-light-free and with a significantly improved efficiency with respect to the direct detection of scattered photons. To this end, the spectroscopy ion is cooled with the aid of a logic ion to the motional ground state of a mode in the trap. If the spectroscopy laser is applied close to a resonance in the spectroscopy ion along the direction of motion of this mode, it scatters photons from the laser. For each absorption/emission cycle, the ion is subjected to a recoil kick along the mode direction during absorption and another recoil kick along directions that are in accordance with the dipole scattering characteristics during emission. Due to the strong confinement of the ions in the trap, the recoil kick energy of one single optical photon is not sufficient to excite a phonon in

the mode. On average, several tens to hundreds of scattering cycles are necessary until excitation of the motion from the ground state occurs. This motion can be detected on the logic ion with the help of a laser pulse, which changes the internal state of the logic ion depending on the motion state, and thus provides the spectroscopy signal **(Fig. 7)**.

Since this method is only suitable for relatively broad transitions, effects such as asymmetries in the line shape due to the motion of the ion play only a minor role. In this way, it is possible to detect the signal of only some tens to hundreds of scattered photons. This enables spectroscopy of systems with only partially closed cycling transitions, as they occur in the case of some molecule ions. Furthermore, scattered light plays practically no role, since the detection of the photons is only carried out via their kinematic effect on the ion. That opens up new perspectives, e.g. in direct frequency comb spectroscopy, where the stabilized spectrum of a frequency comb interacts directly with the atoms or molecules. Excitation occurs predominantly through the interaction of only a few "teeth" of the comb spectrum with the atom; the light of the entire remaining comb provides scattered light which is difficult to filter. Photon recoil spectroscopy could thus enable the detection of the weak signal of a single ion in direct frequency comb spectroscopy.

The emerging field of quantum logic spectroscopy has already been able to demonstrate impressive results and makes a whole series of new spectroscopy species accessible. This promises an exciting future development of the field, with the prospect of further increasing spectroscopic accuracy in order to discover previously unknown phenomena.

Literature

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THE AUTHOR

Piet O. Schmidt studied physics in Konstanz (Germany) and Oregon (USA) and received a doctorate degree at the University of Stuttgart. As a Feodor Lynen Fellow of the Humboldt Foundation he built, together with his colleagues at NIST in Boulder (USA), the first aluminum quantum logic clock. He was able to build on this experience at the University of Innsbruck with his research work on quantum information processing and cavity QED with trapped ions. Since 2009, he has been a professor at Leibniz University Hannover and at the National Metrology Institute of Germany (PTB) in Braunschweig.

COMPACT:

- Quantum logic spectroscopy enables combining the special spectroscopic properties of an ion species (spectroscopy ion) with the well-developed manipulation techniques of another species (logic ion) if these are stored in a Paul trap.
- Since both ions are strongly coupled due to Coulomb interaction, it is possible, with the aid of suitable protocols, to transfer the internal state of the spectroscopy ion to the logic ion and to read it out there.
- In this way, it was possible to build the currently most accurate clock in the world, although the aluminum ion used allows direct manipulation only to a limited extent.
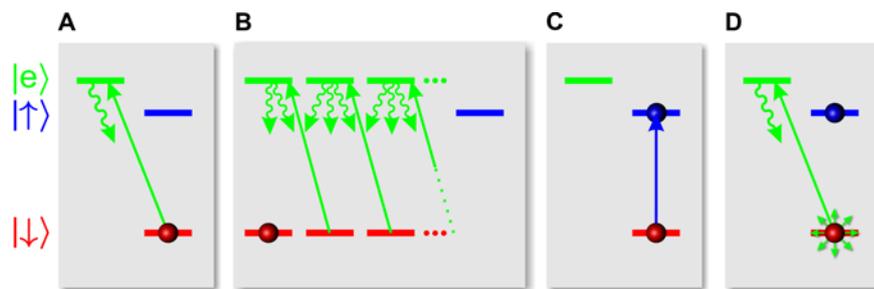

Fig. 1 A cycle of laser spectroscopy of narrow transitions begins with laser cooling on a closed transition, where the atom after excitation can decay via a slightly detuned laser from state $|e\rangle$ only back to the ground state $|\downarrow\rangle$, (A). The atomic levels split up in a magnetic field into their magnetic components (symbolized by the red and green bars, B). For the experiment it is necessary to specifically prepare one of these states. This is done by optical pumping with polarized light on the transition $|\downarrow\rangle \leftrightarrow |e\rangle$, where the atoms absorb angular momentum from the light until they arrive at the extreme substate with a maximum angular momentum component (B). A laser pulse excites the spectroscopy transition $|\downarrow\rangle \leftrightarrow |\uparrow\rangle$ (C). The internal state can be detected via state-dependent laser fluorescence (D). This is typically implemented on the laser cooling transition.
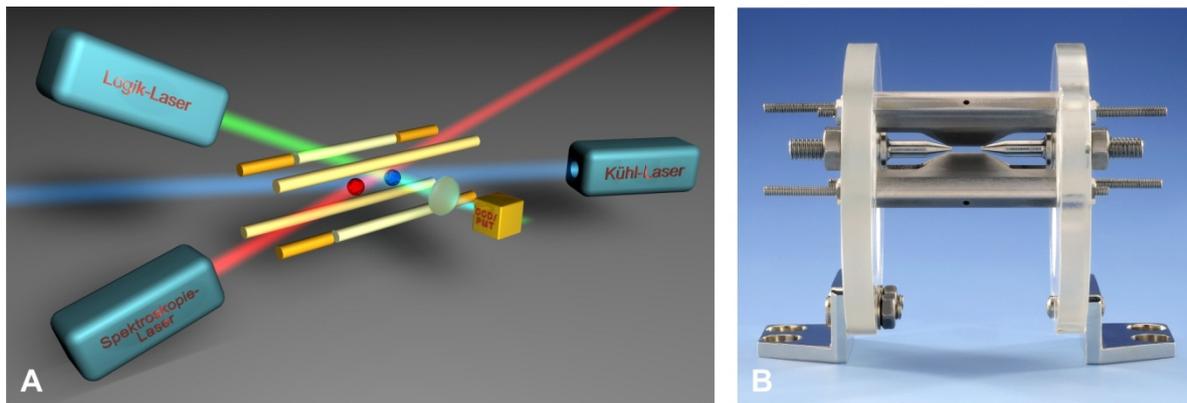
Fig. 2 (A) In the case of quantum logic spectroscopy, the spectroscopy ion (red) and the logic ion (blue) are trapped together in a linear Paul trap. (B) A Paul trap, made of precision-machined titanium electrodes and a sapphire mount, is the core element of the Al$^+$ quantum logic clock being set up at PTB.
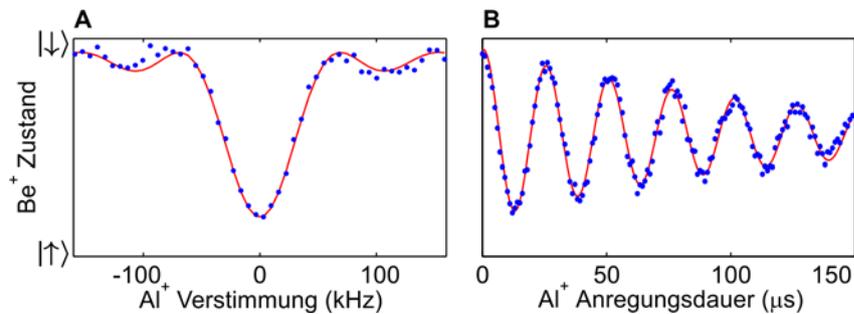

Fig. 3 For the demonstration of quantum logic spectroscopy, the Al$^+$ ion was excited on the auxiliary transition $^1S_0 - ^3P_1$ with the specified frequency detuning from resonance (A). On resonance, the ion performs so-called Rabi oscillations as a function of the excitation period. (B) After each excitation, the internal state was transferred to the Be$^+$ logic ion and was detected there, according to the protocol described in the info box.
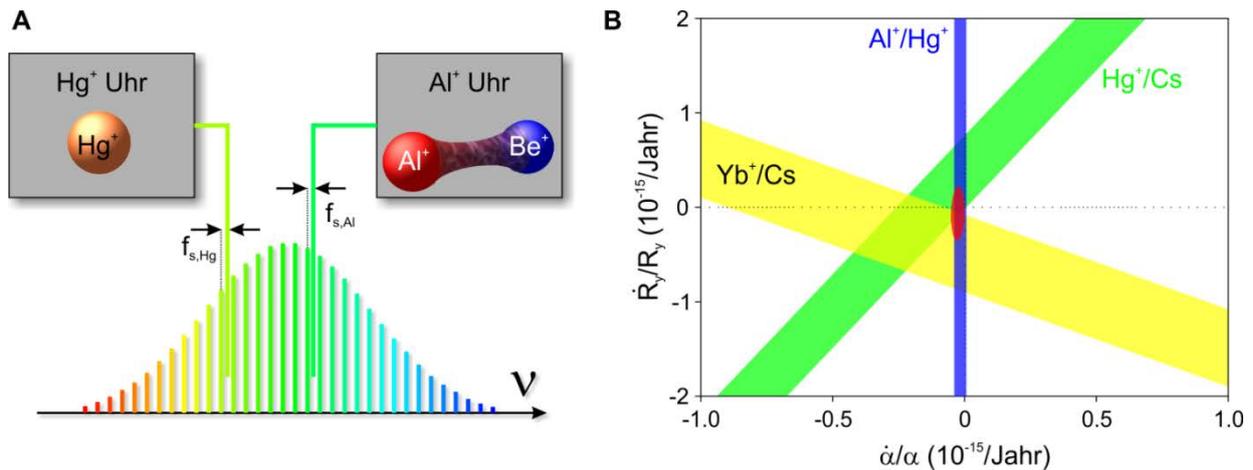
Fig. 4 The comparison between the mercury- and the aluminum-ion clocks results in an upper limit for a change in the fine-structure constant. To this end, optical clocks are compared with the aid of a frequency comb having a comb line spacing f_{rep} and an offset frequency f_{CEO} (A). The comb teeth have an optical frequency of $m \cdot f_{rep} + f_{CEO}$, where m is an integer. It is possible to determine the frequency ratio of both clocks from the beat frequencies $f_{s, Al}$ and $f_{s, Hg}$ of the optical clocks with the nearest comb teeth. The constancy of the frequency ratios of different clocks over long periods of time limits the temporal change of the Rydberg constant Ry and of α within the bounds of the measurement accuracy (B).
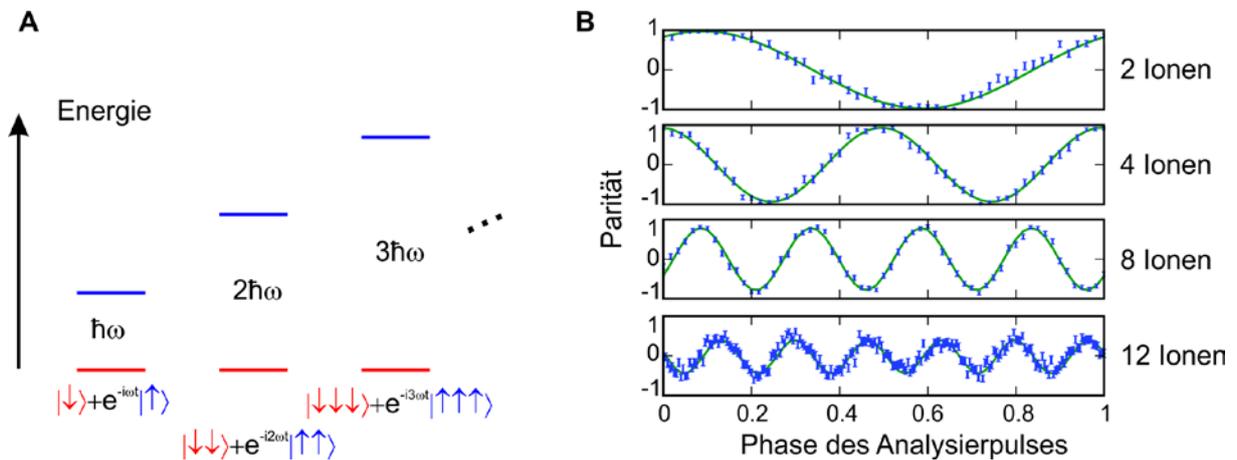

Fig. 5

Heisenberg-limited spectroscopy uses entangled atoms whose energy levels and phase evolution are shown for one, two and three entangled atoms in (A). For the experimental realization with Ca$^+$ ions (B), the parity signal shown is proportional to the phase evolution of the entangled state [7].
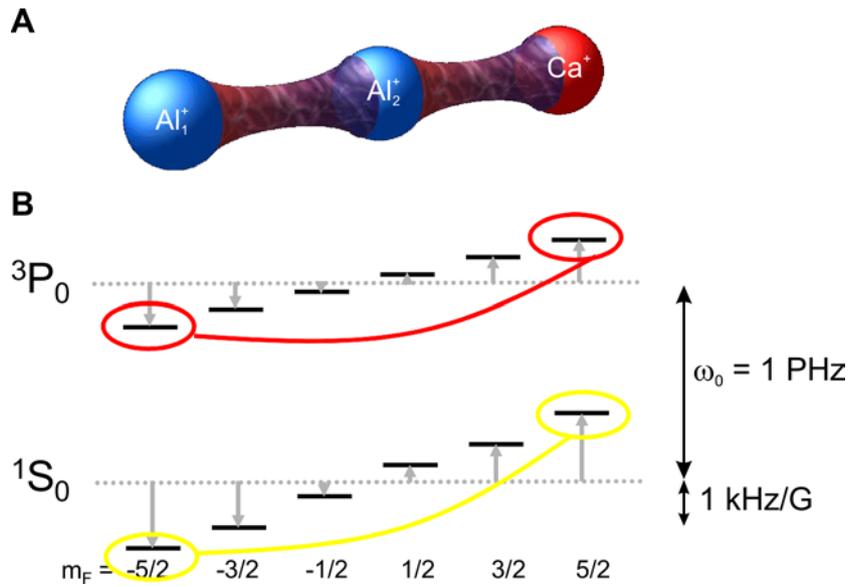
Fig. 6 Two Al$^+$ ions (Indices 1 and 2) are trapped together with a Ca$^+$ logic ion in a Paul trap (A). Via two suitable laser pulses, different internal states of the two Al$^+$ ions are entangled (B). Both parts of the wave function contain both positively and negatively shifted states. Therefore, the total wave function does not depend on the linear Zeeman effect. Furthermore, the relative phase evolution of the two partial wave functions oscillates with $2\omega_0$, and thus, $\sqrt{2}$ faster than uncorrelated atoms.
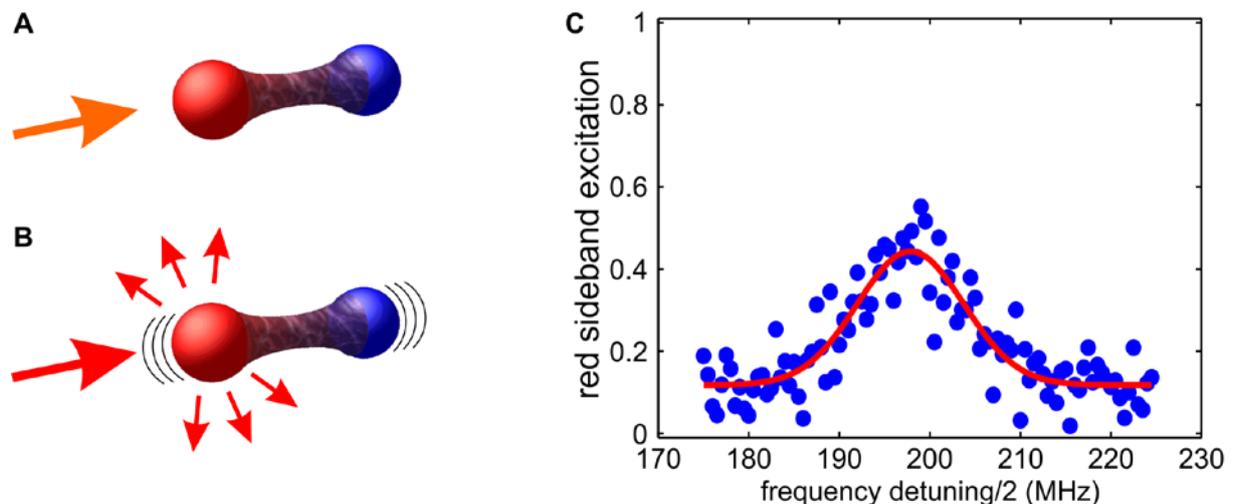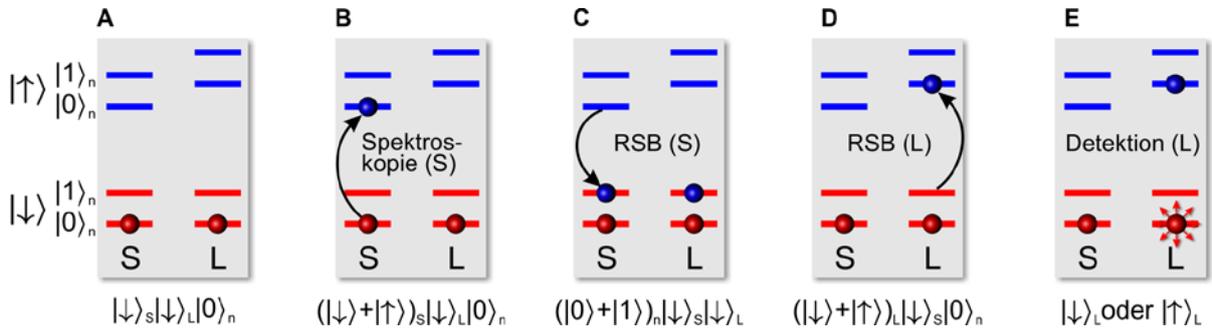

Fig. 7 The starting point for photon recoil spectroscopy is a 2-ion crystal cooled to the ground state and composed of a spectroscopy ion (red) and a logic ion (blue, A). From a non-resonant spectroscopy laser (orange), no photons are scattered; the ions remain in the ground state. Near the resonance, the spectroscopy laser (red) scatters photons off the spectroscopy ion (B). The photon recoil kick excites the ions to common oscillations which can be detected with high efficiency. This is shown in (C) for a Ca$^+$ spectroscopy ion and a Mg$^+$ logic ion.

QUANTUM LOGIC TRANSFER

$$|\uparrow\rangle \; {|1\rangle_n \atop |0\rangle_n}$$

$$|\downarrow\rangle \; {|1\rangle_n \atop |0\rangle_n}$$

A — S, L — $|\downarrow\rangle_S|\downarrow\rangle_L|0\rangle_n$

B — Spektros-kopie (S) — S, L — $(|\downarrow\rangle+|\uparrow\rangle)_S|\downarrow\rangle_L|0\rangle_n$

C — RSB (S) — S, L — $(|0\rangle+|1\rangle)_n|\downarrow\rangle_S|\downarrow\rangle_L$

D — RSB (L) — S, L — $(|\downarrow\rangle+|\uparrow\rangle)_L|\downarrow\rangle_S|0\rangle_n$

E — Detektion (L) — S, L — $|\downarrow\rangle_L$ oder $|\uparrow\rangle_L$

For the implementation of quantum logic spectroscopy, several laser pulses transfer the internal state from the spectroscopy ion (S) to the logic ion (L). Relevant here are the two clock states ($|\downarrow\rangle_S$ and $|\uparrow\rangle_S$), two long-lived states in the logic ion ($|\downarrow\rangle_L$ and $|\uparrow\rangle_L$), and a motional mode in the ground state ($|0\rangle_n$) and the first excited state ($|1\rangle_n$). The starting point is the ground state of the system, which is initialized by optical pumping and ground state cooling of the mode (A). The spectroscopy pulse creates a superposition state between the ground and the excited clock states (B). Here, we assume equal amplitudes of the two states and neglect the normalization factors. Via a so-called red sideband pulse (RSB), the electronic superposition state is mapped into a superposition state of motion (C). This laser pulse can, e.g., be implemented with the spectroscopy laser, and addresses only the electronically excited part of the wave function ($|\uparrow\rangle_S$), since there is no state to which the $|\downarrow\rangle_S$ could couple resonantly. A similar laser pulse maps the superposition from motion states into an electronic superposition on the logic ion (D). There, it is possible by irradiation with the cooling laser to discriminate between the two states $|\downarrow\rangle_L$ and $|\uparrow\rangle_L$, since only the ground state scatters photons via coupling to a third electronic level, while the excited state remains dark (E).