Microwave and optical spectroscopy in r.f. traps
Application to atomic clocks
Microwave spectroscopy for hyperfine structure measurements

Energy of a hyperfine state

\[ W_F = \frac{1}{2} \hbar \Delta K + \hbar B \frac{3}{2} K (K + 1) - 2 I (I - 1) J (J + 1) \]
\[ 2 I (2 I - 1) 2 J (2 J - 1) \]

\[ K = F (F + 1) - I (I + 1) - J (J + 1) \]

Hyperfine coupling constants:
A: magnetic dipole interaction
B: Electric quadrupole interaction

\[ A_s = - \frac{1}{\hbar} \frac{16 \pi}{3} \frac{\mu_0}{4 \pi} \frac{\mu_B^2 g_I}{\Psi_s(0)^2} \]

\[ B = \frac{1}{\hbar} \frac{e^2}{4 \pi \varepsilon_0} \frac{2 J - 1}{2 J + 2} \frac{< r^{-3} >_{nl}}{Q} \]
Features of microwave spectroscopy:

- No first order Doppler effect because of Dicke effect (ion oscillation amplitude < wavelength of radiation)
- Stable and accurate radiation sources available
- State preparation by laser or spectral lamp
- Resonance detection by fluorescence light
Example I: Eu+

Optical spectrum of stable Eu+ isotopes 151, 153
Induced hyperfine transitions with Zeeman splitting

Uncertainty of resonances: 20 Hz in 10 GHz
Results for Eu isotopes

<table>
<thead>
<tr>
<th>I</th>
<th>A [MHz]</th>
<th>B [kHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{148}$Eu$^+$</td>
<td>5  $^6 S_4$</td>
<td>517.281 950 (150)</td>
</tr>
<tr>
<td>$^{148}$Eu$^+$</td>
<td>5  $^6 S_3$</td>
<td>-561.647 (100)</td>
</tr>
<tr>
<td>$^{149}$Eu$^+$</td>
<td>5/2 $^6 S_4$</td>
<td>1 585.450 570 (250)</td>
</tr>
<tr>
<td>$^{150}$Eu$^+$</td>
<td>5  $^6 S_4$</td>
<td>599.010 680 (200)</td>
</tr>
<tr>
<td>$^{150}$Eu$^+$</td>
<td>5  $^6 S_3$</td>
<td>-650.334 (2)</td>
</tr>
<tr>
<td>$^{151}$Eu$^+$</td>
<td>5/2 $^6 S_4$</td>
<td>1 540.297 394 (13)</td>
</tr>
<tr>
<td>$^{151}$Eu$^+$</td>
<td>5  $^6 S_3$</td>
<td>-1 672.457 109 (266)</td>
</tr>
<tr>
<td>$^{153}$Eu$^+$</td>
<td>5/2 $^6 S_4$</td>
<td>684.565 993 (9)</td>
</tr>
<tr>
<td>$^{153}$Eu$^+$</td>
<td>5  $^6 S_3$</td>
<td>-743.183 577 (82)</td>
</tr>
</tbody>
</table>

First step towards systematic study of Bohr-Weisskopf effect (distribution of magnetization over nuclear volume)

$$\Delta(1,2) = 1 - (A_1/A_2)(g_{l2}/g_{l1})$$

Need to measure nuclear g factors
Example II: Hg+

Optical pumping of one ground state hyperfine level of 199Hg+ by accidental coincidence of 202Hg+ line with one hyperfine component
Microwave transition between 199Hg+ hyperfine levels monitored by change in fluorescence intensity
Major, Werth (1973)
Principle of Atomic Clocks

Accuracy: How accurately agrees $v_{\text{out}}$ with $v_0$?

Stability: To what extent fluctuates $v_{\text{out}}$ around $v_0$?
Linear ion trap at JPL
for microwave frequency standard

Extended Linear Ion Trap ("LITE")

- Electron gun
- UV interrogation region
- "Shuttle"
- Interaction region
- Inputs:
  - Diagonally opposed molybdenum node are shorted together.
  - Alumina drum for structural support
  - RF trapping potential two phase
  - DC bias for end pin and shuttle
40.9 GHz hyperfine transition in $^{199}\text{Hg}^+$ Ramsey fringes with 11,1 s interrogation time

J. Tjoelker et al., JPL
$^{199}$Hg$^+$ microwave clock
Uncertainty and stability

<table>
<thead>
<tr>
<th>Frequency Offsets</th>
<th>LITS Frequency Offsets &amp; Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC Magnetic (at 0.08G)</td>
<td>Magnitude</td>
</tr>
<tr>
<td>Shielding (24,000)</td>
<td>1 x 10^{-11}</td>
</tr>
<tr>
<td>2nd Order Doppler</td>
<td>&lt;0.002 / mG</td>
</tr>
<tr>
<td>Thermal (300K)</td>
<td>2 x 10^{-13}</td>
</tr>
<tr>
<td>Number Dependent</td>
<td>5 x 10^{-14}</td>
</tr>
<tr>
<td>Collision (pressure)</td>
<td>Magnitude</td>
</tr>
<tr>
<td>Helium (6x10^{-6} Torr)</td>
<td>10^{-13}</td>
</tr>
<tr>
<td>Mercury (10^{-9} Torr)</td>
<td>?</td>
</tr>
<tr>
<td>Other (&lt;2x10^{-9} Torr)</td>
<td>?</td>
</tr>
<tr>
<td>Blackbody</td>
<td>&lt; 10^{-16}</td>
</tr>
<tr>
<td>Gravitational Redshift</td>
<td>10^{-16}/m</td>
</tr>
</tbody>
</table>

$^{199}\text{Hg}^+$ hyperfine frequency shifts with He buffer gas pressure
Frequency stability of $^{199}\text{Hg}^+$ microwave standard
H-maser as reference

Red line: H-maser drift
Optical spectroscopy

High resolution requires:

- Cooling into Dicke regime
- Long lived metastable states
- Lasers of high spectral purity

Optical clocks:
Laser stabilization on narrow transition to long lived metastable state,
Measurement of laser frequency
Required level diagram

Requirement to level scheme:
Fast E1 cooling transition
Narrow „clock“ transition

Candidate ions: $\text{Hg}^+$, $\text{Yb}^+$, $\text{Sr}^+$, $\text{Ca}^+$, $\text{In}^+$
State detection using electron shelving

detection

Clock transition

observe quantum jumps online

fluorescence intensity

time (s)
Example: $^{199}$Hg$^+$

$^{199}$Hg$^+$ Energy Levels

$^2P_{\frac{1}{2}}$ \[ \rightarrow \] $^2S_{\frac{1}{2}}$

$^2P_{\frac{1}{2}}$ \[ \rightarrow \] $^2D_{\frac{5}{2}}$

194 nm
Wide, fast transition
Laser cooling, detection

282 nm
Clock reference;
Narrow ("forbidden") transition

Metastable state
$T_d \approx 86$ ms
Linear ion trap at NIST for Hg$^+$ optical clock
Quantum-jump absorption spectra of the $^2S_{1/2}(F=0) - ^2D_{5/2}(F=2)$ transition in $^{199}\text{Hg}^+$

J. Bergquist et al. (2002)
Work at NRC Canada: single Sr+ optical clock
Sources of uncertainty in single ion Sr+ clock

<table>
<thead>
<tr>
<th>Source</th>
<th>Shift of line center</th>
<th>Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second order Doppler effect</td>
<td>0.13 Hz</td>
<td>$3 \times 10^{-16}$</td>
</tr>
<tr>
<td>Quadratic Stark shift</td>
<td>0.2 Hz</td>
<td>$5 \times 10^{-16}$</td>
</tr>
<tr>
<td>Electric quadrupole shift</td>
<td>&lt;0.5 Hz</td>
<td>$&lt;1 \times 10^{-15}$</td>
</tr>
<tr>
<td>of $4d^2 D_{5/2}$ level</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blackbody ac Stark shift</td>
<td>0.16 Hz</td>
<td>$4 \times 10^{-16}$</td>
</tr>
<tr>
<td>ac magnetic fields</td>
<td>&lt;0.2 Hz</td>
<td>$&lt;5 \times 10^{-16}$</td>
</tr>
<tr>
<td>Quadratic Zeeman shift</td>
<td>15 mHz</td>
<td>$3 \times 10^{-17}$</td>
</tr>
<tr>
<td>(static field)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collisions</td>
<td>&lt;10 mHz</td>
<td>$&lt;2 \times 10^{-17}$</td>
</tr>
</tbody>
</table>
Measured stability of a single Hg$^+$ optical standard Cs standard (solid line) for comparison

S. Diddams et al., Science 293, 825 (2001)
Frequency stability of Hg$^+$ optical standard vs. Ca standard

\[ \sigma(\tau) = 6.4 \times 10^{-14} \tau^{-1/2} \]
Al\(^+\)/Hg\(^+\) Stability

29096 seconds of data

- Green line: \(7 \times 10^{-15} \tau^{-1/2}\)
- Blue line: Hg vs Maser (AVAR)
- Black line: Hg vs Al (AVAR)
- Red line: Hg vs Al (THEO1)

Recently: \(4 \times 10^{-15} \tau^{-1/2}\)

\(4 \times 10^{-17}\)
Systematic Frequency Shifts

The immediate future:
Begin averaging over quadrupole shift

Error budget:
Estimated partial error budget for the near future

<table>
<thead>
<tr>
<th>Effect</th>
<th>Correction (Hz) (at 1.06 PHz)</th>
<th>Fractional uncertainty $\Delta f/f_0 \times 10^{-15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second-order Zeeman</td>
<td>1.19</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>(B field uncertainty)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2D_3$ quadrupole shift</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Gravitational redshift</td>
<td>0.55</td>
<td>0.01</td>
</tr>
<tr>
<td>Micromotion shifts</td>
<td>0</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Expected fractional systematic uncertainty: $\sim 2 \times 10^{-17}$
Measuring the frequency of optical transitions

Frequency comb technique
Hänsch, Hall: Nobelprize 2005

Femtosecond Laser into photonic fiber

Honeycomb Microstructure Optical Fiber
CLEO, May, 1999
Output of optical fiber:
Discrete wavelength pulses
at interval of laser repetition frequency
The frequency of the $^{88}\text{Sr}^+$ S-D transition measured in two different traps (NPL, 2003)

**Systematic frequency shifts [Hz]**

<table>
<thead>
<tr>
<th>Source</th>
<th>Trap 1</th>
<th>Trap 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Correction</td>
<td>Uncertainty</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>152</td>
<td>104</td>
</tr>
<tr>
<td>422 nm ac Stark shift</td>
<td>-48</td>
<td>60</td>
</tr>
<tr>
<td>1092 nm ac Stark shift</td>
<td>0</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Servo errors</td>
<td>-3</td>
<td>3</td>
</tr>
<tr>
<td>Other frequency shifts</td>
<td>0</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Maser frequency</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Total uncertainty for each trap</td>
<td>164</td>
<td>105</td>
</tr>
</tbody>
</table>
Potential future nuclear clock with $^{229}$Th

\[
\begin{align*}
\frac{3}{2}^+ [631] & \quad {^{229}\text{m} \text{Th Isomer}} \\
& \quad \mu = -0.08 \mu_N \\
& \quad Q \approx 2 \cdot 10^{-28} \text{ e}\cdot\text{m}^2 \\
\Delta E &= 7.8 \text{ eV} \\
& \quad \text{M1 transition} \\
& \quad \tau \approx 1000 \text{ s} \\
\frac{5}{2}^+ [633] & \quad {^{229}\text{Th Ground State}} \\
& \quad \mu = 0.4 \mu_N \\
& \quad Q = 3.1 \cdot 10^{-28} \text{ e}\cdot\text{m}^2
\end{align*}
\]
The only known isomer with an excitation energy in the optical range and in the range of outer shell electronic transitions.

- Studied by C.W. Reich et al. at INL since the 1970s, established the low energy isomer from $\gamma$-spectroscopy: $3.5 \pm 1.0$ eV, published in 1994

- Theoretical work by E.V. Tkalya, F.F. Karpeshin, and others, isomer lifetime, coupling to electronic excitations ($\tau \sim$ few 1000 s)

- False detections of optical emission in the U-233 decay chain in 1997/98

- Proposal of nuclear laser spectroscopy and nuclear clock E. Peik and Chr. Tamm, published in 2003

- Unsuccessful search for optical nuclear excitation or decay

- More precise energy measurement from $\gamma$-spectroscopy at LLNL: $7.6 \pm 0.5$ eV, published in 2007

- 2011: still no direct detection of the optical transition; experimental efforts in several groups worldwide

Possible realizations of Th-229 nuclear clocks:
- Laser-cooled Th$^{3+}$ in an ion trap
- Th ions as dopant in a transparent crystal (like CaF$_2$, LiCAF etc.)

Experimental problem:
Transition energy known only to $\approx 10\%$ uncertainty, not a system for high resolution spectroscopy yet
Nuclear clock with laser cooled $^{229}\text{Th}^{3+}$

- $\text{Th}^{3+}$ possesses a much more simple level scheme (single valence e⁻)
- can be laser-cooled using diode lasers & detected via resonance fluorescence in the red or NIR
- electronic and nuclear resonances are separated in energy

Estimates for long term frequency stability: $10^{-19}$
Experiment at PTB Braunschweig

- Loading via laser ablation with ns pulsed Nd:YAG (tripled)
- Trap L = 188 mm r = 3.3 mm, tailored for efficient loading of ablation plume
- Trapping and cooling $10^3 - 10^4$ Th$^{3+}$ ions (Th-229 & Th-233: enhanced loading efficiency with initial buffer gas cooling)

Low lying energy levels in $^{220}$Th$^{3+}$:

- cooling on 1088 nm line to tens of K
- cooling to tens of mK on lambda scheme
- sympathetic cooling on even isotope (no HF!) for lowest temperatures

Laser cooled ion crystals:

- $^{229}$Th$^{3+}$
- $^{232}$Th$^{3+}$

Clock transition from ground state \((5F_{5/2})\):

With laser cooled and trapped fractional frequency inaccuracy as low as \(10^{-19}\) should be possible!
Search for variation of the finestructure constant $\alpha$ in time by clock comparison.

\[
\frac{\partial \ln \alpha}{\partial t} = (-2.4 \pm 2.7) \cdot 10^{-17} \text{ yr}^{-1}
\]

\[
\frac{\partial \ln Ry}{\partial t} = (0.0 \pm 3.2) \cdot 10^{-16} \text{ yr}^{-1}
\]

Present status:
Ion trap frequency standards operate in the microwave domain and optical domain.

Stabilities below the $10^{-15}$ level have been reached in both cases.

Optical frequency measurements have reached high precision.

Further progress is expected with potential nuclear clock.