Precision spectroscopy of H_2^+ : present and future

Funded by:

PREMOL

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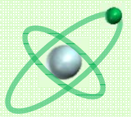
PSAS 2026, Vienna, 18 - 22.5.2026

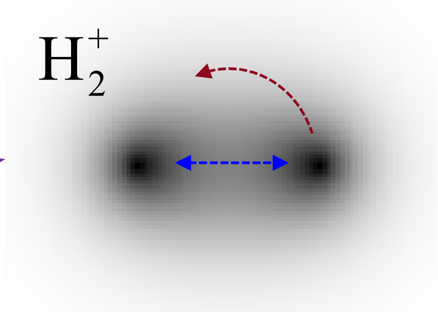
Molecular hydrogen ions: a platform for fundamental physics

The link between *atomic hydrogen spectroscopy* and *magnetic resonance & mass spectroscopy in Penning traps*

Laser spectroscopy of hydrogen-like atoms and ions



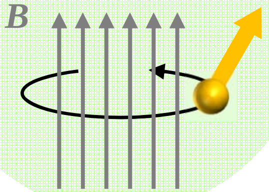
- Rydberg constant
- Nuclear radii
- QED
- BSM lepton-baryon interaction
- (electron-baryon mass ratio)
- CPT



$D_2^+, HD^+, T_2^+, HT^+, DT^+$

- electron-baryon mass ratio
- Rydberg constant
- Nuclear radii
- QED
- BSM lepton-baryon interaction
- BSM baryon-baryon interaction
- CPT
- LLI

Mass spectrometry & magnetic resonance of simple systems



- Particle masses
- g-factors
- Nuclear radii
- QED
- CPT
- LLI
- BSM electron

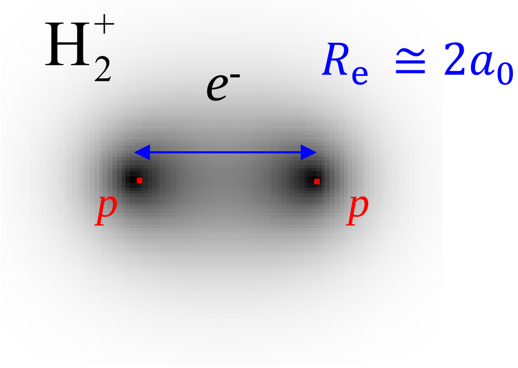
Experiments: München, Paris, Villigen, Toronto, Zürich, Fort Collins, Mainz, CERN, …

Experiments: Düsseldorf, Paris, Amsterdam, Zürich, Heidelberg, Wuhan

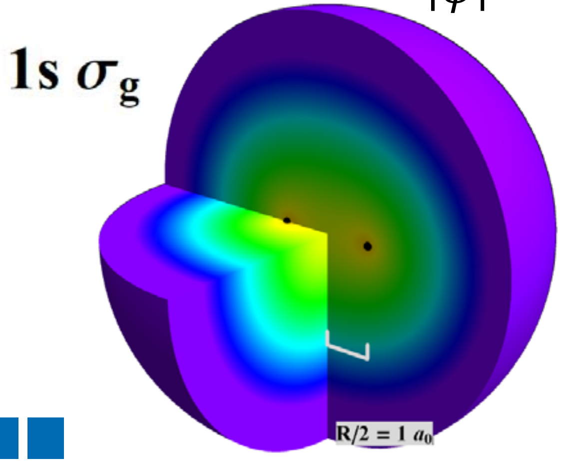
Experiments: Heidelberg, Mainz, Stockholm, CERN, Evanston, Tallahassee, Argonne,…

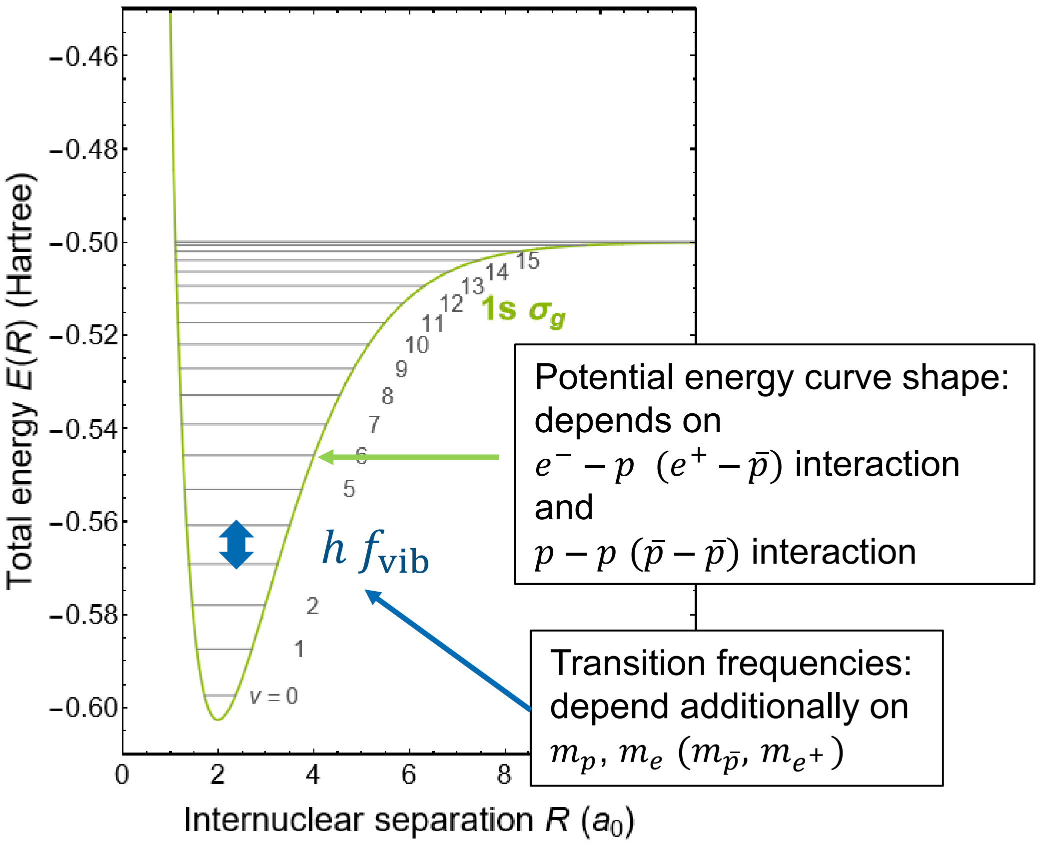
The simplest molecule

Schiller, *Contemp. Phys.* **63**, 247 (2022)



Electronic probability density $|\psi|^2$





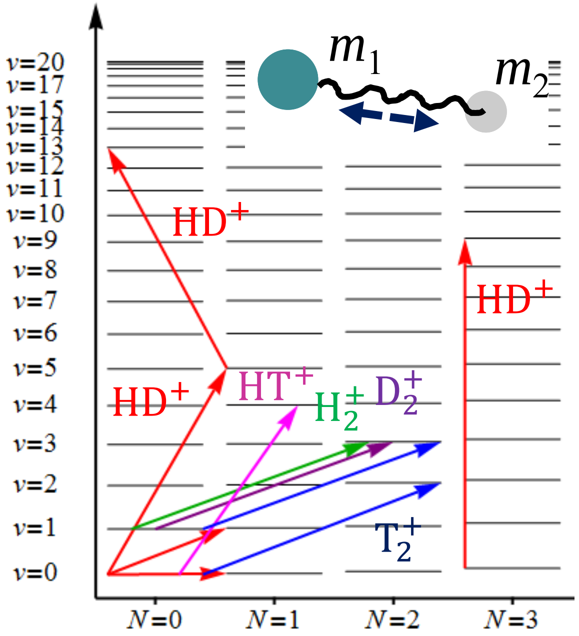
Potential energy curve shape: depends on $e^- - p$ $(e^+ - \bar{p})$ interaction and $p - p$ $(\bar{p} - \bar{p})$ interaction

Transition frequencies: depend additionally on m_p, m_e $(m_{\bar{p}}, m_{e^+})$

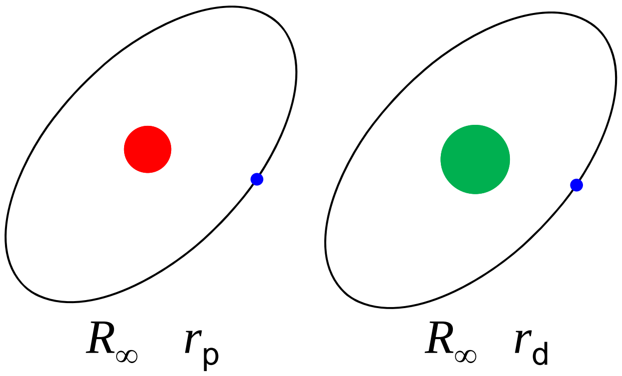
Motivation: Determination of fundamental constants

FUTURE SCENARIO:

- measure 9 MHI transition frequencies with 1 Hz uncertainty
- Improve numerical precision of certain QED quantities



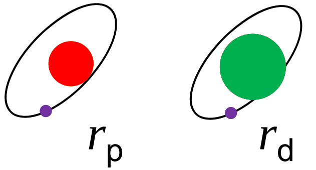
Schiller and Karr, PRA 109, 042825 (2024)
Karr et al. PRA 112, 022809 (2025)



H(1s – 2s), D(1s – 2s)
available data

	$u_r(R_\infty)$	$u_r(m_p/m_e)$	$u_r(m_d/m_e)$	$u_r(m_t/m_e)$	$u(r_p)$	$u(r_d)$	$u(r_t)$
MHI , H , D	0.8×10^{-12}	2.5×10^{-13}	2.7×10^{-13}	2.3×10^{-13}	1.0	0.39	0.46
CODATA2022	1.1×10^{-12}	1.7×10^{-11}	1.7×10^{-11}	3.8×10^{-11}	0.64	0.27	86

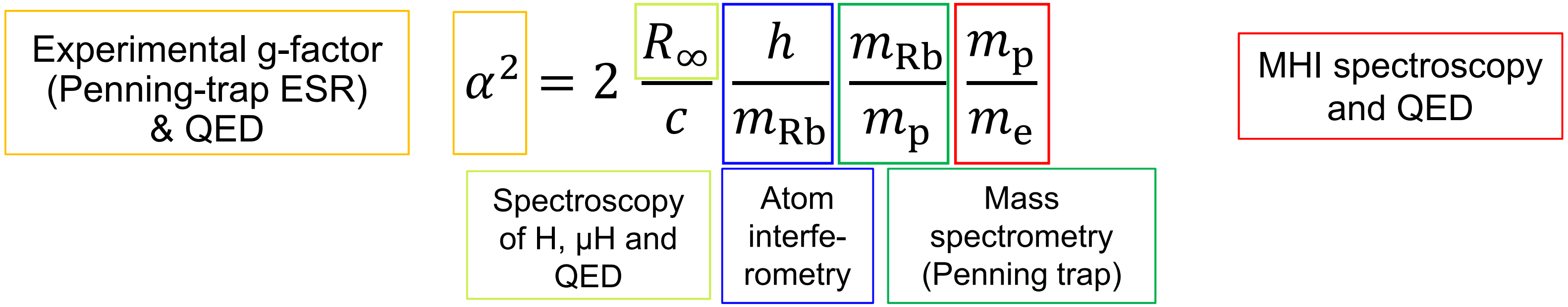
μH μD



Experimental tritium radius r_t can be compared with precise prediction of nuclear EFT

Motivation: Key endeavours in precision atomic physics

g-factor of the free electron



Experimental g-factor (Penning-trap ESR) & QED

$$\alpha^2 = 2\,\frac{R_\infty}{c}\,\frac{h}{m_{\mathrm{Rb}}}\,\frac{m_{\mathrm{Rb}}}{m_{\mathrm{p}}}\,\frac{m_{\mathrm{p}}}{m_{\mathrm{e}}}$$

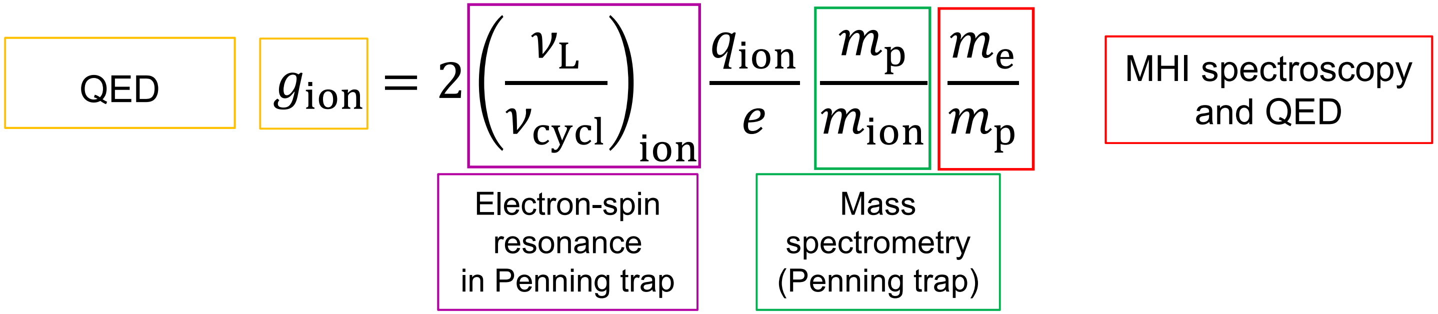
MHI spectroscopy and QED

Spectroscopy of H, μH and QED

Atom interferometry

Mass spectrometry (Penning trap)

g-factor of the bound electron in H-like ions



QED

$$g_{\mathrm{ion}} = 2\left(\frac{\nu_{\mathrm{L}}}{\nu_{\mathrm{cycl}}}\right)_{\mathrm{ion}}\frac{q_{\mathrm{ion}}}{e}\,\frac{m_{\mathrm{p}}}{m_{\mathrm{ion}}}\,\frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}$$

MHI spectroscopy and QED

Electron-spin resonance in Penning trap

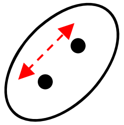
Mass spectrometry (Penning trap)

S. Alighanbari et al, Nature 664, 69 (2025)

Motivation: Future experiments with anti-matter molecules

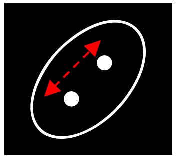
- Experiments on CPTI tests with stable antimatter particles, cooled and trapped, have made great progress in accuracy over the past decade
- Further improvement by orders of magnitude might be hard

H_2^+



2 protons, 1 electron

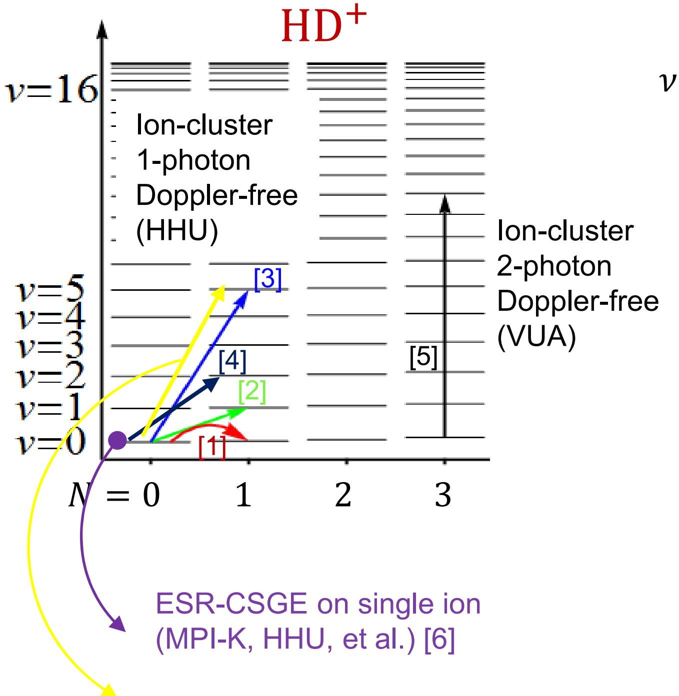
anti-H_2^+



2 antiprotons, 1 positron

[1] Dehmelt, Phy. Scr. T59, 432 (1995)
[2] Myers, PRA 98, 010101(R) (2018)

Overview of high-precision experimental studies



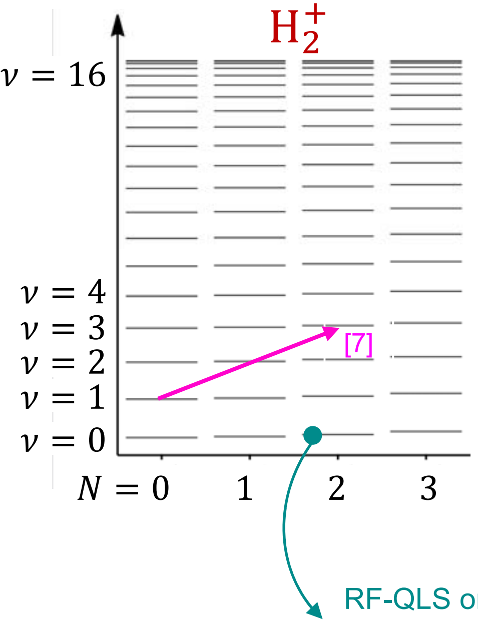
Ion-cluster
1-photon
Doppler-free
(HHU)

Ion-cluster
2-photon
Doppler-free
(VUA)

ESR-CSGE on single ion
(MPI-K, HHU, et al.) [6]

optical-CSGE on single ion
(MPI-K, HHU, et al.)

Talk by M. Bohman (this conference)



Ion-cluster
1-photon E2
Doppler-free
(HHU)

RF-QLS on
single ion (ETHZ) [8]

Talk by F. Schmid (this conference)

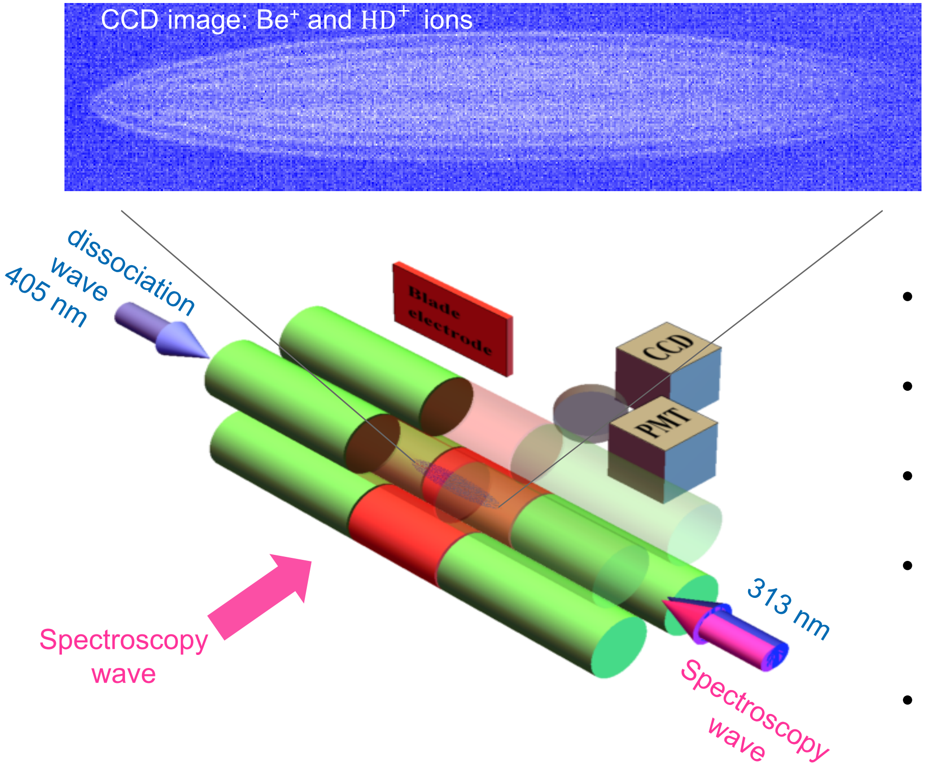
[1] Alighanbari, et al. *Nature* **581**, 152 (2020).
[2] Kortunov, et al. *Nat. Phys.* **17**, 569 (2021).
[3] Alighanbari, et al. *Nat. Phys* **19**, 1263 (2023).
[4] Schenkel, et al. *Nat. Phys.* **20** (2024).
[5] Patra, et al. *Science* **369**, 1238 (2020).
[6] König, et al. *PRL* **136** (2026)
[7] Alighanbari, et al. *Nature* **644**, 69 (2025).
[8] Holzapfel, et al. *PRX* **15**, 031009 (2025).

Essential theory development:
V. Korobov et al.
J.-Ph. Karr et al.
Z.-X. Zhong et al.

Earlier expt. work:
Jefferts,
Menasian & Dehmelt
McNab et al, Loch et al
Related work: Doran et al.

Our technique: Trapped and sympathetically cooled MHI

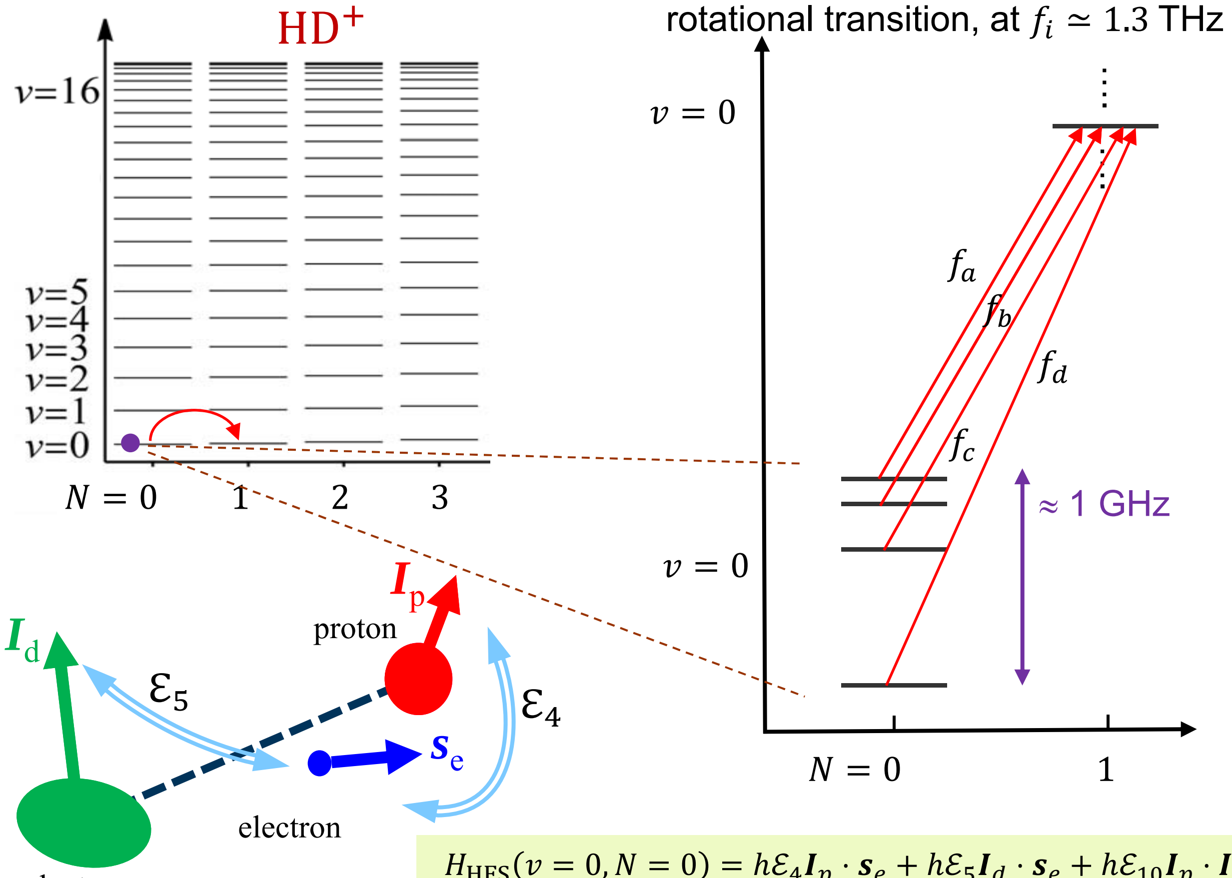
Roth et al. *PRA* 74, 040501 (2006)



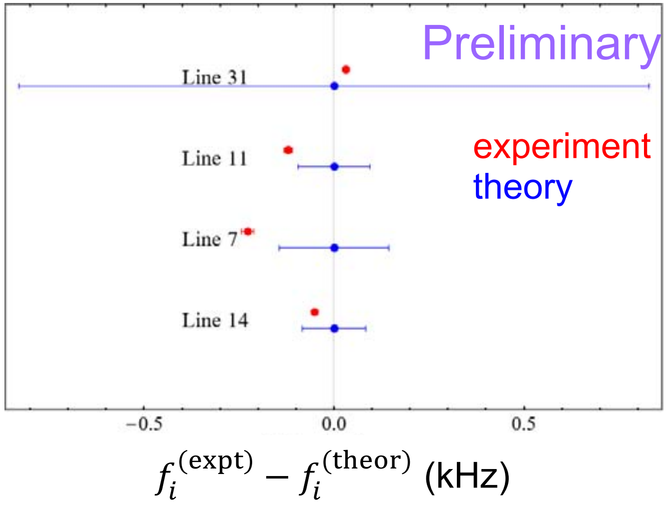
- A Coulomb cluster of few-10^3 laser-cooled Be$^+$ ions
- Simultaneous trapping of few 100 MHI
- MHI cluster temperature: few mK
- Destructive spectroscopy:
  dissociation of MHI from excited spectroscopy level
- Measure MHI number reduction by axial-motion excitation
  → spectroscopy signal

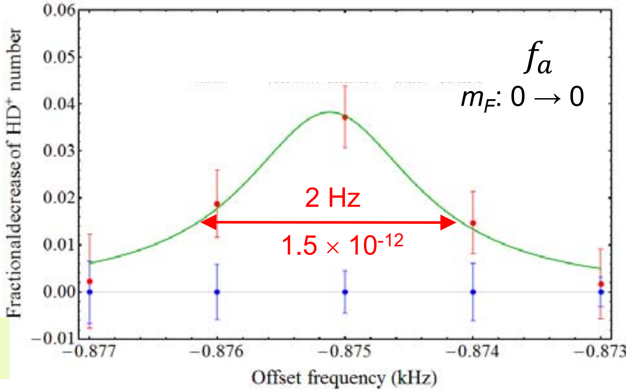
Hyperfine structure: a direct measurement

Measure 4 components of the rotational transition, at $f_i \simeq 1.3$ THz



$$H_{\mathrm{HFS}}(v=0, N=0) = h\mathcal{E}_4 \boldsymbol{I}_p \cdot \boldsymbol{s}_e + h\mathcal{E}_5 \boldsymbol{I}_d \cdot \boldsymbol{s}_e + h\mathcal{E}_{10} \boldsymbol{I}_p \cdot \boldsymbol{I}_d$$





$$H_{\mathrm{HFS}}(v=0,N=0) = h\mathcal{E}_4\boldsymbol{I}_p\cdot\boldsymbol{s}_e + h\mathcal{E}_5\boldsymbol{I}_d\cdot\boldsymbol{s}_e + \underbrace{h\mathcal{E}_{10}}_{\substack{\text{from theory}\\ (\approx 20\ \text{Hz})}}\boldsymbol{I}_p\cdot\boldsymbol{I}_d$$

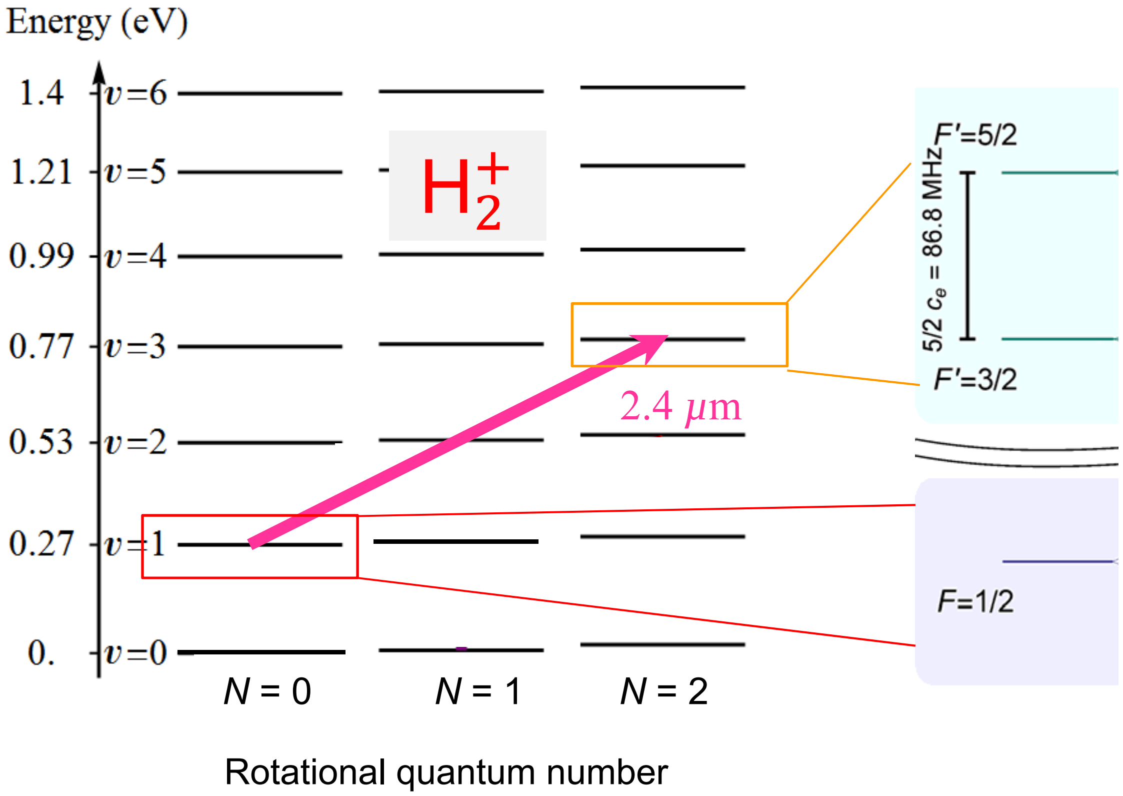
	$\mathcal{E}_4$ (kHz)	$\mathcal{E}_5$ (kHz)	
Expt., this work (B = 0)	925 394.347(12)	142 287.654(6)	Preliminary
Theory*	925 394.16(86)	142 287.556(84)	
Difference	+ 0.2 σ	+ 1.2 σ	Preliminary

cf. König et al, PRL 136, 143002 (2026) : measurement in B = 4 T

*J.-P. Karr et al., Phys. Rev. A 102, 052827 (2020).

Laser spectroscopy of H_2^+ in a RF trap

Spectroscopy of H_2^+



Spin-rotation interaction

$$H_{\mathrm{spin}} = c_e(\boldsymbol{N} \cdot \boldsymbol{s}_e)$$

Non-negligible Zeeman shifts

Result

S. Alighanbari et al, Nature 664, 69 (2025)

Experiment and theory comparison

	$f_{\text{spin-avg}}$ (kHz)	c_e (kHz)
Experiment	124 487 032 442.69 (0.95)	34 730.18 (10)
Theory [1,2]	124 487 032 442.5 $(0.9)_{\text{QED}}(0.96)_{\text{CODATA22}}$	34 730.25 (12)
Exp. - theory	0.19 (1.6)	−0.07 (15)

$$H_{\text{spin}} = c_e(\boldsymbol{N} \cdot \boldsymbol{s}_e)$$

→ **Agreement!**

- QED contributions „measured“ to 3×10^{-6}
- proton charge radius „measured“ to 1%

Proton-electron mass ratio

	m_p/m_e
This work: experiment and theory of H_2^+	1836.152 673 416 (44)
CODATA 2018: incl. g-factor, experiment and theory	1836.152 673 43 (11)
CODATA 2022: incl. g-factor & HD^+ spectroscopy	1836.152 673 426 (32)

Agreement!

[1] Korobov and Karr, *PRA* 104, 032806 (2021)

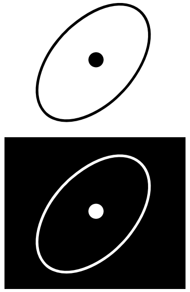
[2] Haidar, et al. *PRA* 106, 022816 (2022)

Towards a future test of CPT invariance by spectroscopy of H_2^+ and anti-H_2^+

Suggestion:	Dehmelt, Physica Scripta **T59**, 423 (1995)
Analysis:	Myers, Phys. Rev. A **98**, 010101(R) (2018)
Impact within SME:	Shore, PRD 112, 056015, 056016 (2025); arXiv:2604.15518 Vargas, arxiv:2503.06306v1
Feasibility analysis:	Schiller et al., arxiv:2605.16585

Motivation

- H vs. $\bar{\mathrm{H}}$ 1s – 2s comparison (ALPHA @ CERN):

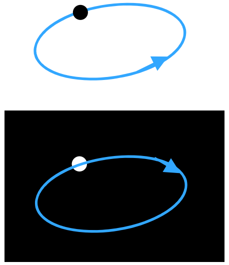


$$\frac{E_h(\mathrm{H})}{E_h(\bar{\mathrm{H}})} \propto \frac{(q_e)^2(q_p)^2\, m_e}{(q_{e^+})^2(q_{\bar{p}})^2\, m_{\bar{e}}} = 1\,?$$

$$+ \text{ weak dependence on } \frac{m_e/m_p}{m_{e^+}/m_{\bar{p}}}$$

Currently: u ~ 10^{-12} level

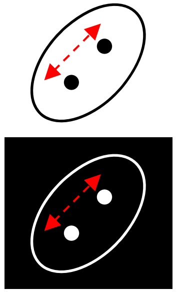
- p vs. $\bar{\mathrm{p}}$ charge-mass & g-factor comparison (BASE @ CERN):



$$\frac{q_p\, m_{\bar{p}}}{q_{\bar{p}}\, m_p} = 1\,?$$

Currently: u ~ 10^{-11} level

- H_2^+ vs. anti-H_2^+ vibrational frequency comparisons would test:*

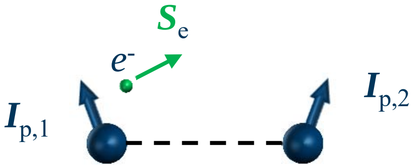


$$\frac{f_{\mathrm{vib}}(\mathrm{H}_2^+)}{f_{\mathrm{vib}}(\bar{\mathrm{H}}_2^-)} \propto \frac{(m_e)^{3/2}(m_p)^{-1/2}(q_e)^{4+\kappa}(q_p)^{-\kappa}}{(m_{e^+})^{3/2}(m_{\bar{p}})^{-1/2}(q_{e^+})^{4+\kappa}(q_{\bar{p}})^{-\kappa}} = 1\,?$$

(assuming Coulomb interactions have usual character; $\kappa \approx 0.02$)

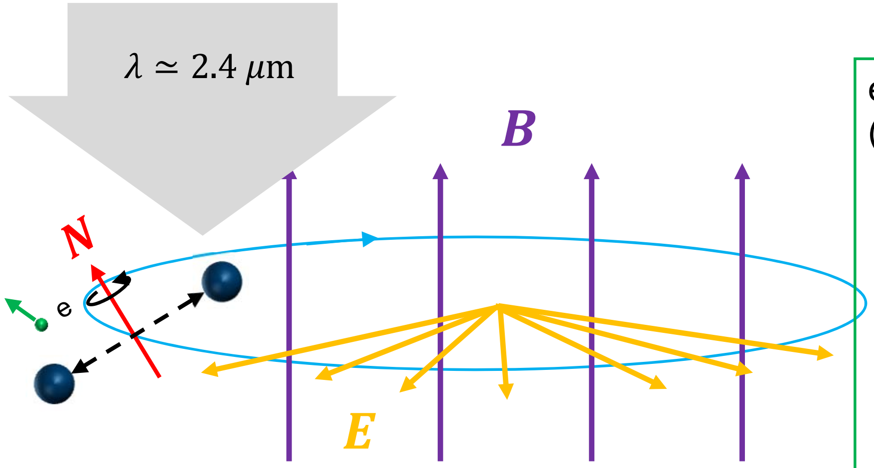
Future uncertainty ??

- Comparison of e^-/e^+ g-factor comparison of $p/\bar{p}$ g-factor



* Schiller, Contemp. Phys. 63, 247 (2022)

Para-H_2^+ and external-field shifts in a Penning trap



electron-Zeeman effect
(*isotropic, anisotropic*)

$$H_{\mathrm{Z}}(v,N) = -\mu_B\, g_e(v,N)\, \mathbf{s}_e \cdot \mathbf{B}$$

$$H_{\mathrm{Z}}^{a}(v,N) \propto -\mu_B\, g_t(v,N)\left(N_Z^2 - \tfrac{1}{3}\mathbf{N}^2\right) \mathbf{s}_e \cdot \mathbf{B}$$

rotational Zeeman effect

$$H_{\mathrm{Z-rot}}(v,N) = -\mu_{\mathrm{n}} g_r(v,N)\, \mathbf{N} \cdot \mathbf{B}$$

Diamagnetic effect (*1st-order, 2nd-order*)*

$$H_{\mathrm{dia}}(v,N) = -\frac{\alpha^2}{2}\tilde{B}^2(\chi_s^{(d)}(v,N) + \chi_t^{(d)}(v,N)(N_z^2 - \tfrac{1}{3}\mathbf{N}^2))$$

$$H_{\mathrm{para}}(v,N) = -\frac{\alpha^2}{2}\tilde{B}^2(\chi_s^{(p)}(v,N) + \chi_t^{(p)}(v,N)(N_z^2 - \tfrac{1}{3}\mathbf{N}^2))$$

- Static trap B-field
- Static trap E-field
- Motionally induced E-field
- Spectroscopy wave´s E-field
- Black-body radiation
- Residual motion

  → Relativistic Doppler effect

$$\begin{aligned} H_{\mathrm{dc-Stark}}(v,N) = & -\tfrac{1}{2}\alpha_s(v,N)(E_x^2 + E_y^2 + E_z^2) \\ & -\tfrac{1}{2}\alpha_t(v,N)(E_z^2 - \tfrac{1}{2}(E_x^2 + E_y^2))(2N_z^2 - \tfrac{2}{3}\mathbf{N}^2) \end{aligned}$$

$$H_{\mathrm{ac-Stark}}(v,N,\omega) = -\frac{F^2}{2}(\alpha_s(v,N,\omega) + \alpha_t(v,N,\omega)(2\,N_z^2 - \tfrac{2}{3}\,\mathbf{N}^2))$$

$$H_{\mathrm{EQ}}(v,N) = (3/2)^{3/2}E_{14}(v,N)\,V_{zz}(N_z^2 - \tfrac{1}{3}\mathbf{N}^2)$$

*S.S., A. Aucar, V.I. Korobov, D. Bakalov (unpubl.)

Relativistic Doppler effect

$$\frac{\Delta f_{\mathrm{RDE}}}{f_0} = -\frac{\langle v(t)^2 \rangle}{2\,c^2} \simeq 1 \times 10^{-13} \quad @\, T = 4.2\ \mathrm{K} \qquad \text{(1 mode)}$$

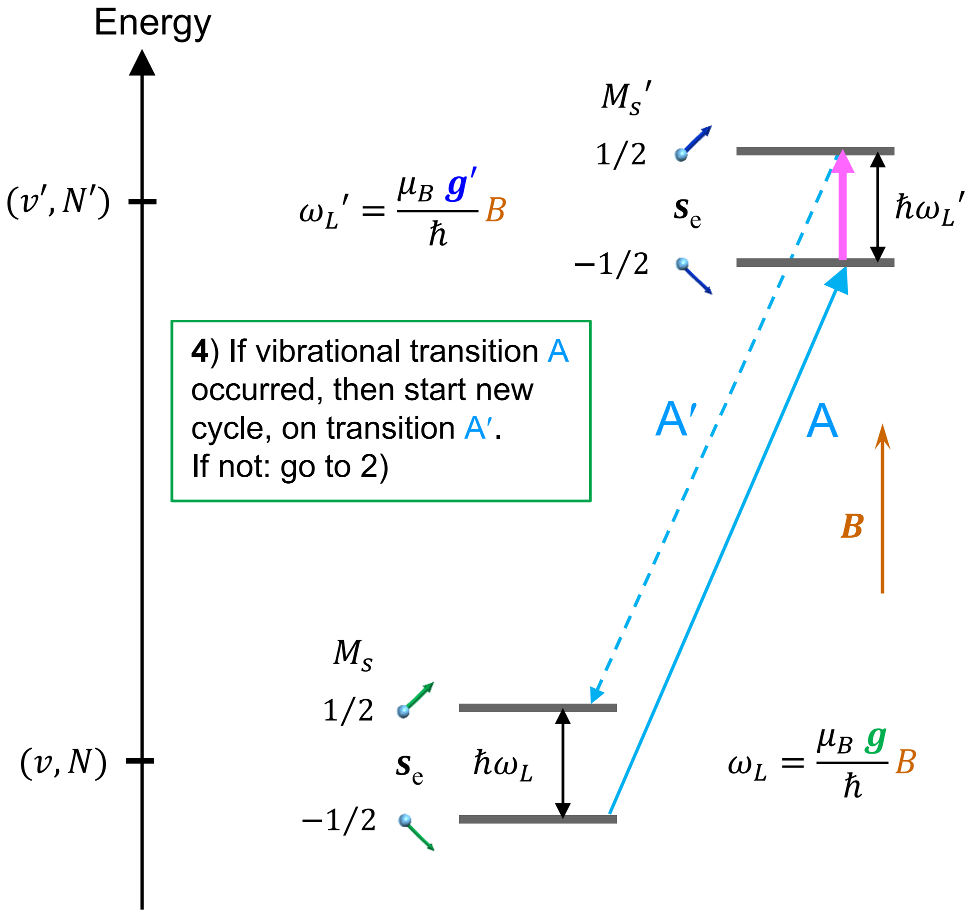
➡ Reduce ion temperature

➡ Monitor ion temperature precisely

Approach I: Penning trap with CSGE detection

Proposed by E. Myers (2018)

earlier: Quint et al.
demos: Mooser et al., Egl. et al.,
König et al.,
MPIK – HHU collaboration



1) Determine nondestructively which spin state the particle is in

2) Attempt to drive optical transition A

3) Drive ESR (spin flip) transition. (ESR frequency in excited state differs from that of ground state!) Detect spin state nondestructively.

CSGE method

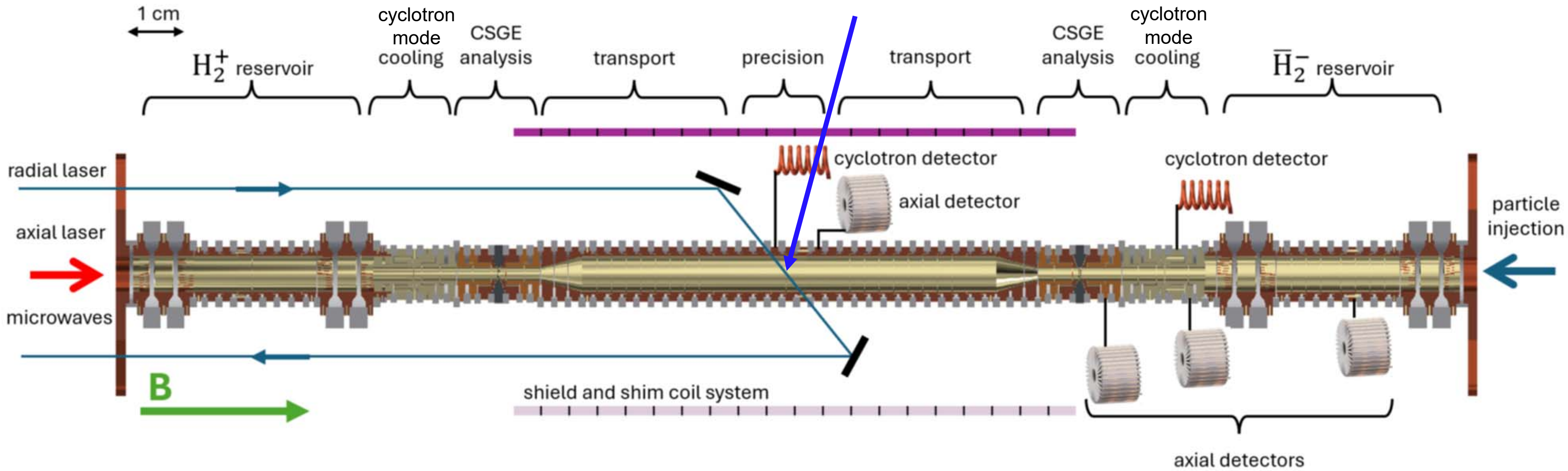
4) If vibrational transition A occurred, then start new cycle, on transition A′. If not: go to 2)

Approach I: Proposed apparatus using CSGE detection

- Evolution of design from BASE collaboration
- 7 individual traps connected by transport sections
- 4 K cryostat
- Sub-thermal cooling of ion‘s radial modes to ≤ 0.2 K

See talk by J. Morgner (this conference)

H_2^+ and $\overline{\mathrm{H}}_2^-$ alternatingly spectroscopied here



Particle A in cooling/analysis traps:
cooling of radial modes (1 – 10 min)
analysis of radial motional state
spin-state identification

Alternate

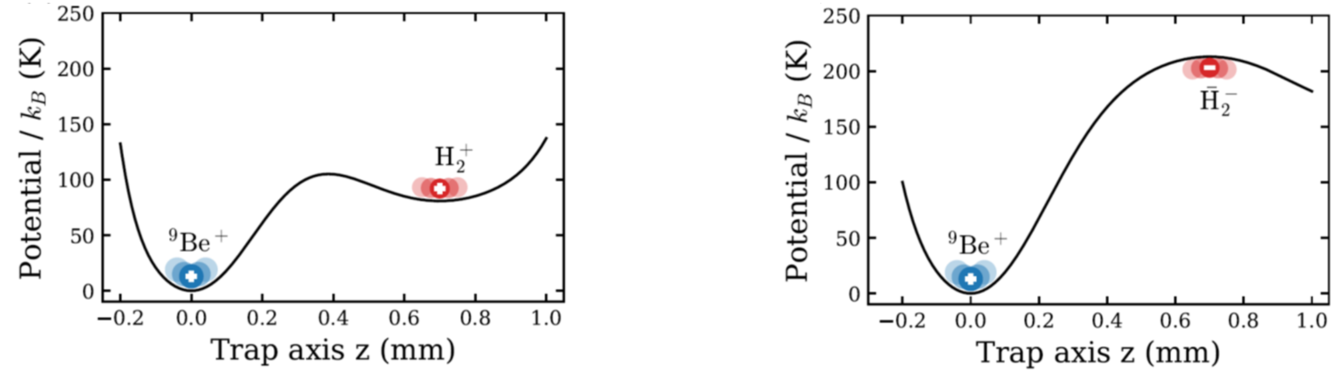
⇔

Particle B in precision trap:
magnetic field measurement;
spectroscopic excitation;
axial temperature measurement

✓ Tracking of particle temperatures (5 mK-level @ few min), tracking of magnetic field (10-pT level)

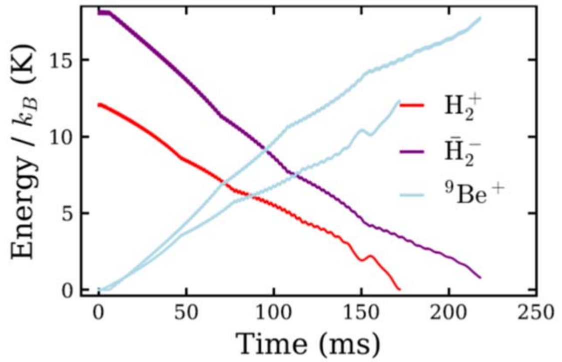
Approach II: Sympathetic cooling in a Penning trap

Trapping in separate axial potential wells



First, Be^+ is laser-cooled to mK temperature
Then, H_2^+ /anti-H_2^+ is cooled by energy **exchange**.

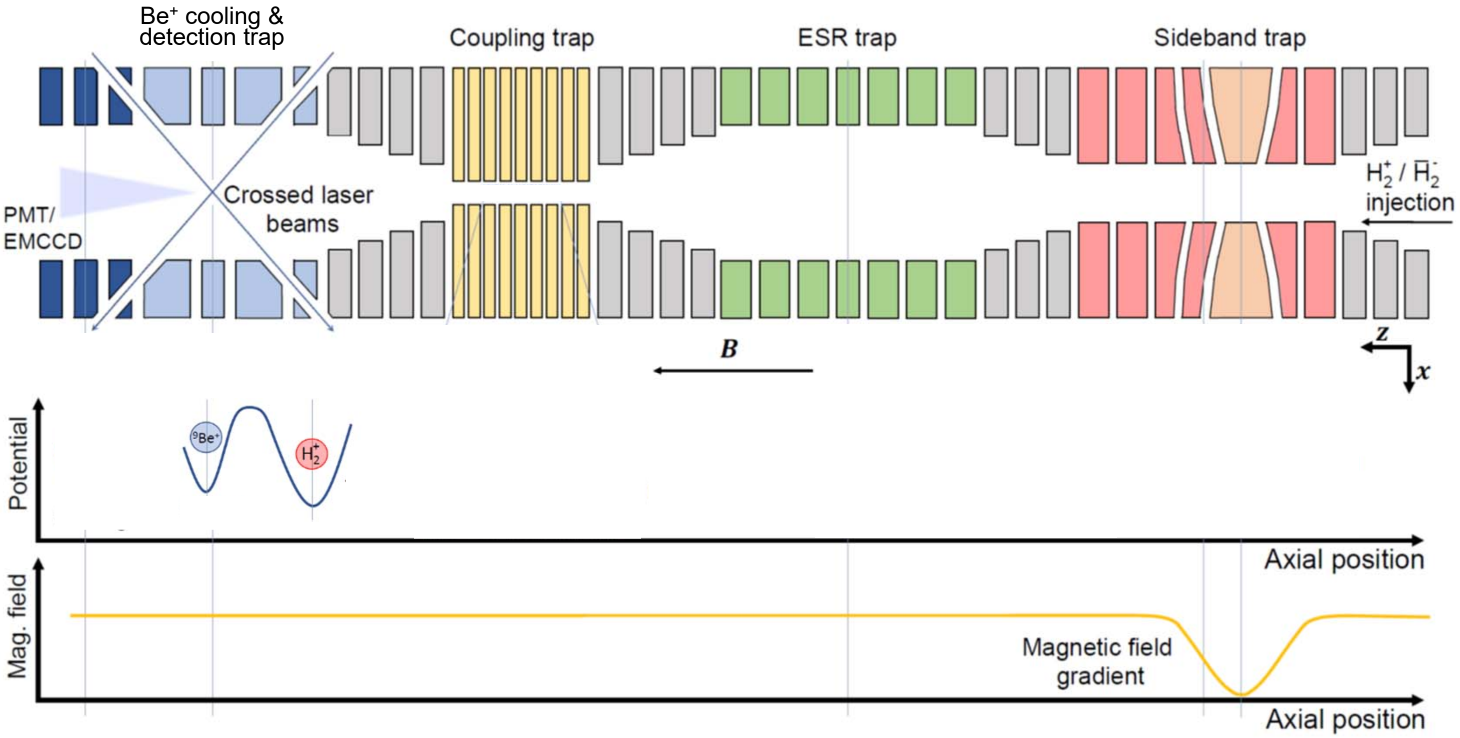
Classical simulation:



Molecular ion: T ~ 1 mK

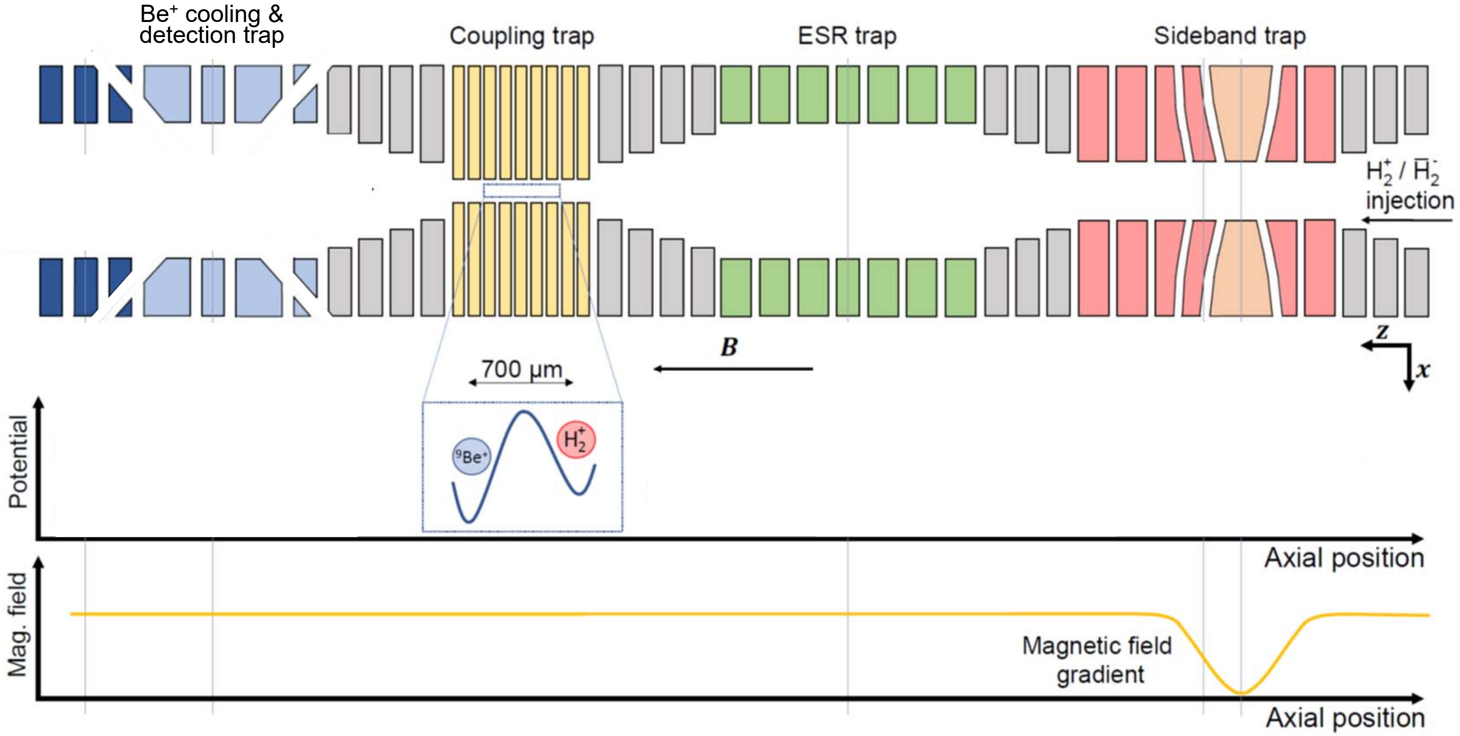
Approach II: Quantum logic spectroscopy in a Penning trap

- ✓ Laser cooling and initialization of Be^+



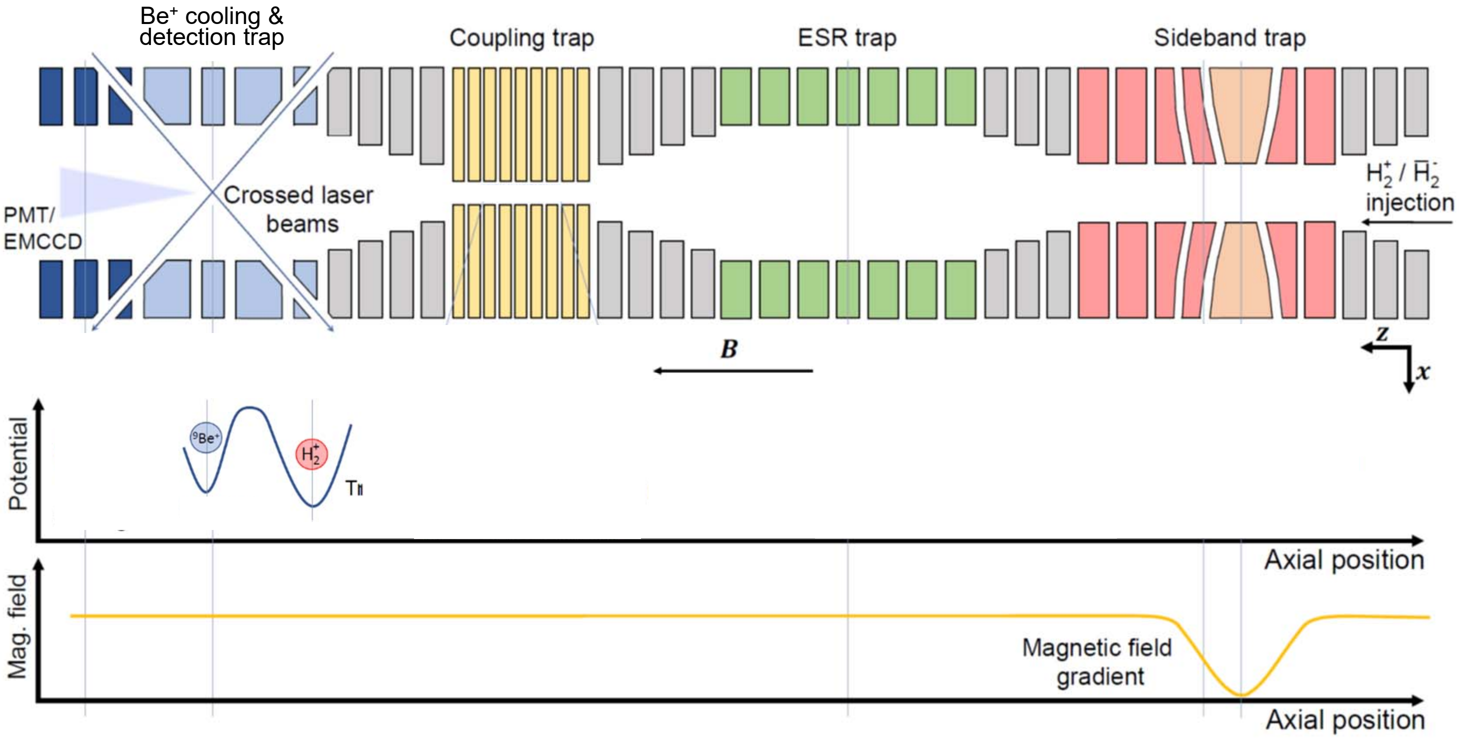
Approach II: Quantum logic spectroscopy in a Penning trap

- ✓ Adiabatic transport to coupling trap
- ✓ There, kinetic energy of H_2^+ is transferred to Be^+



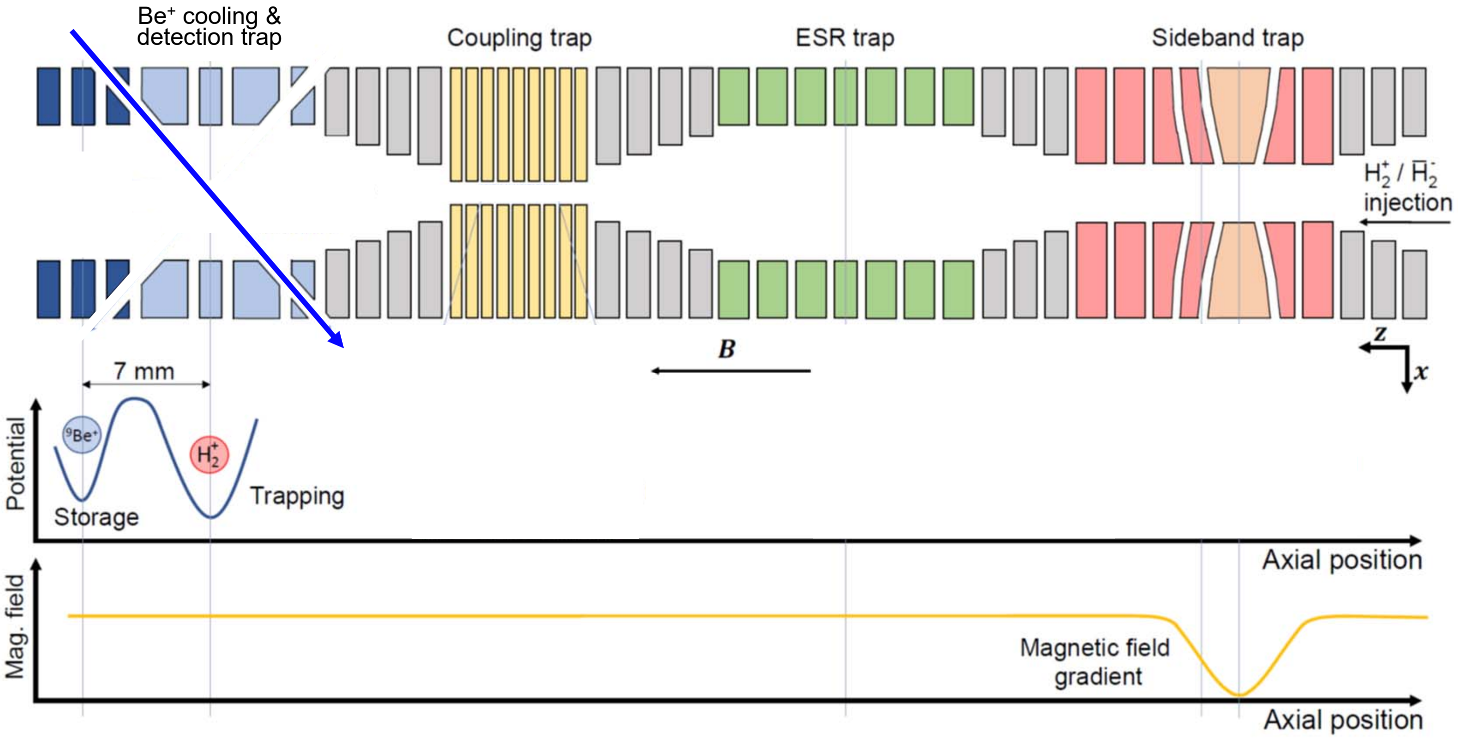
Approach II: Quantum logic spectroscopy in a Penning trap

- ✓ Re-cooling and re-initialization of Be$^+$



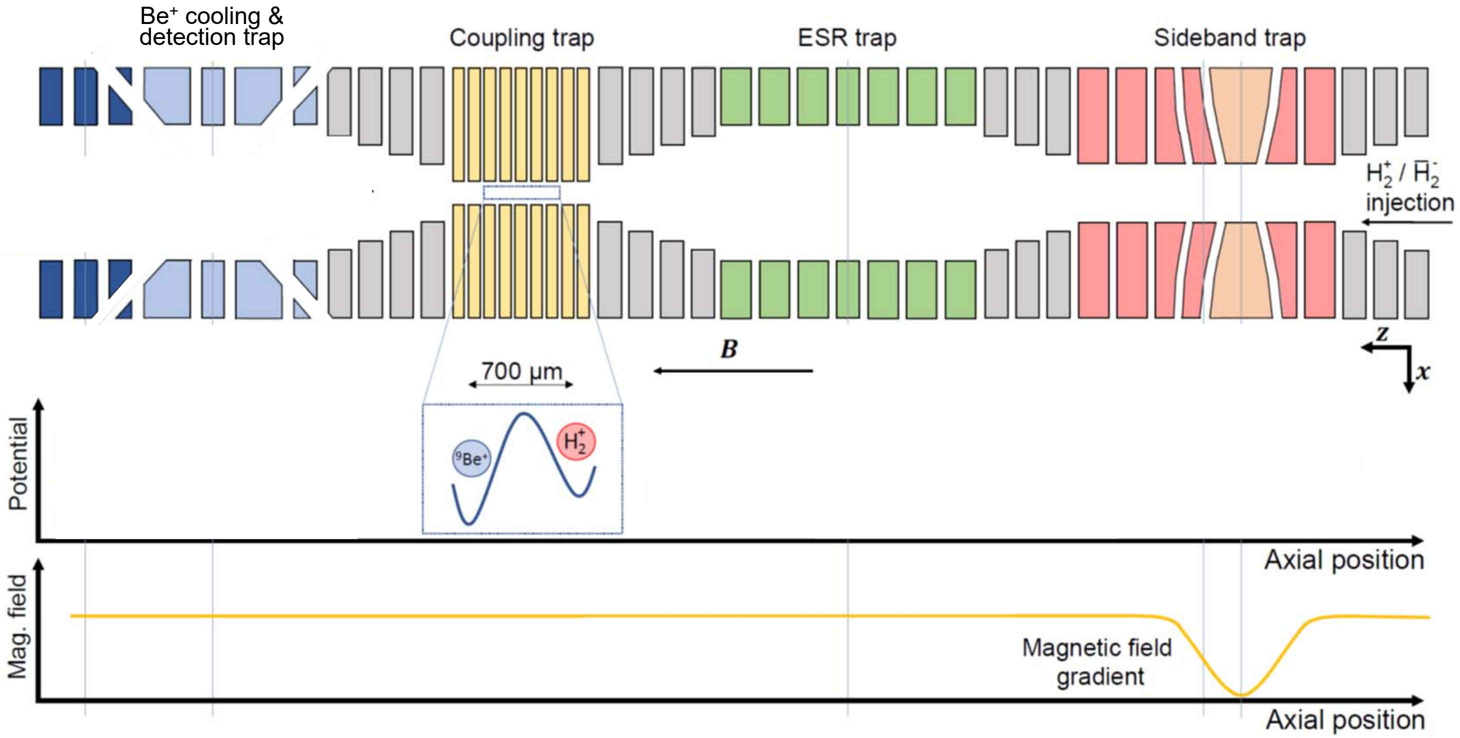
Approach II: Quantum logic spectroscopy in a Penning trap

✓ Blue-sideband, 1-photon or Raman vibrational (or Raman spin-flip) excitation attempt of H_2^+.
An axial oscillation quantum of H_2^+ is generated if excitation takes place



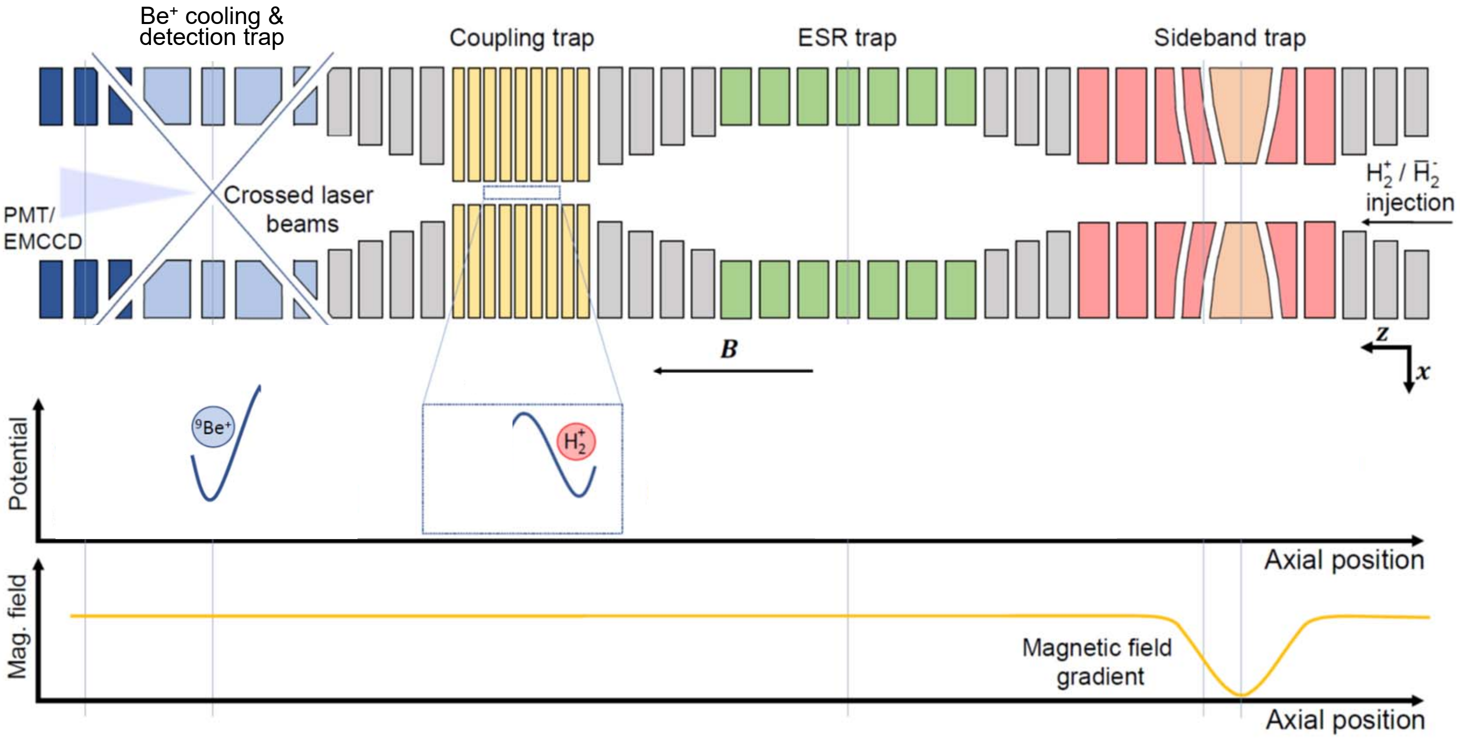
Approach II: Quantum logic spectroscopy in a Penning trap

- ✓ Adiabatic transport to coupling trap
- ✓ If H_2^+ internal excitation was successful, then the H_2^+ axial oscillation energy quantum is transferred to Be^+



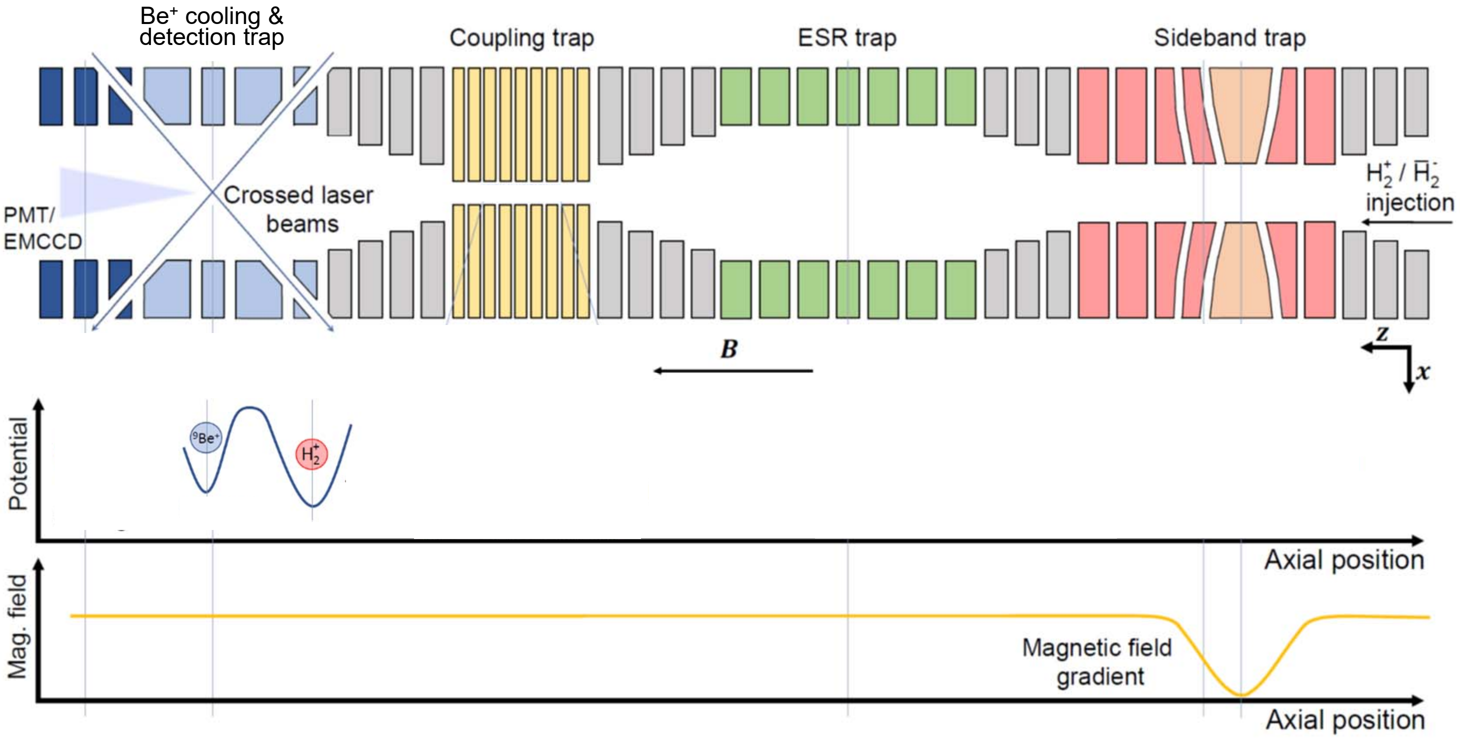
Approach II: Quantum logic spectroscopy in a Penning trap

✓ Read-out of Be^+ motional state: yields a signal that indicates whether molecular spectroscopy was successful



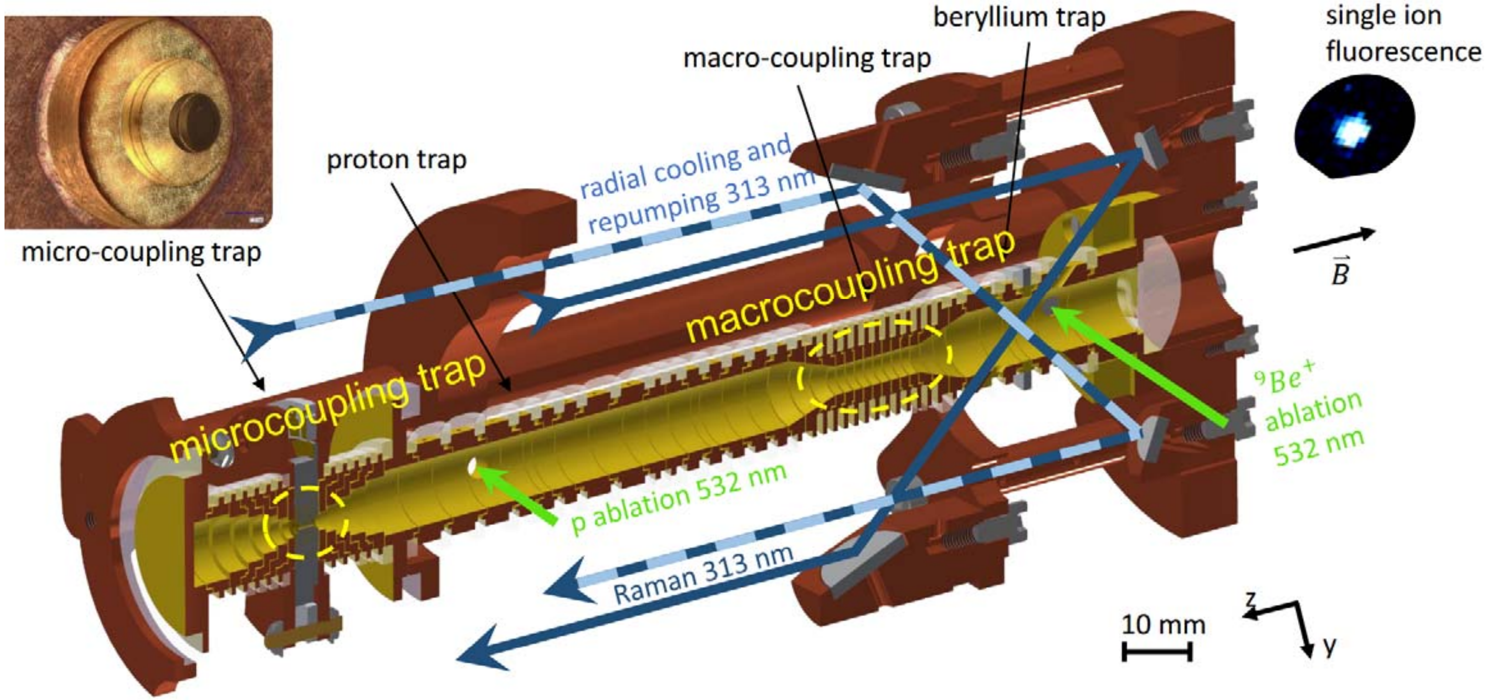
Approach II: Quantum logic spectroscopy in a Penning trap

- ✓ **Next cycle**: Re-cooling and re-initialization of Be$^+$



Approach II: Apparatus

Similar to apparatus of BASE-QLEDS:



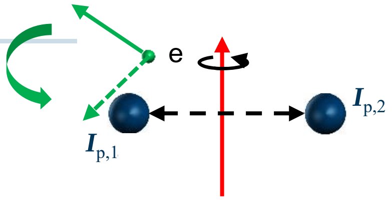
Poljakov et al., Proc. of Science **480**, 102 (2025)
Cornejo et al. Phys. Rev. Res. **6**, 033233 (2024)

Note: the macrocoupling trap is used for studying Be^+ - Be^+ coupling and motional heating as a function of electrode distance

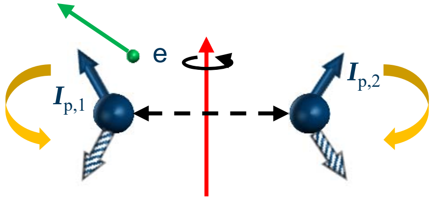
Comparison of approach I and II

	Approach I (CSGE)	**Approach II (Quantum logic)**
Cryostat	4 K	
Spectroscopy laser	ultra-narrow-linewidth (10^{-15})	
Ion temperature	200 mK (radial), 4 K (axial)	< 1 mK
Rotational Zeeman shift unc.	$\simeq 3\times10^{-18}$	
Stark shift unc.	2×10^{-18}	$< 1\times10^{-18}$
Light shift unc.	$< 1\times10^{-18}$	
Relativistic Doppler unc.	2×10^{-16}	3×10^{-18}
Cycle time	minutes	10 s
Statistical unc.	5×10^{-17} after weeks	1×10^{-17} after 1 d
$u\left(f_{\mathrm{vib}}(\mathrm{H}_2^+) - f_{\mathrm{vib}}(\overline{\mathrm{H}}_2^-)\right)$	$\boldsymbol{\simeq 2\times10^{-16}}$ (1 month)	$\boldsymbol{\simeq 1\times10^{-17}}$ (2 days)

Additional CPTI tests



- Comparison of g factors of bound e^- in *para*-H_2^+ and bound e^+ in *para*-$\overline{\mathrm{H}}_2^-$:
  - Via comparison of electron-spin-resonance frequencies $\mu_{e^-}B$ vs. $\mu_{e^+}B$ (~ 100 GHz)
  - Proposal: extend trap stack to have **two, adjacent precision traps; simultaneous interrogation** of H_2^+ and $\overline{\mathrm{H}}_2^-$
  - → B-field fluctuations cancel, no need to accurately determine the magnetic field
  - → test at $\mathbf{10^{-13}}$ **level** in a CSGE Penning trap (weeks-long integration times)
  - cf. $u_r(e^- \text{ vs. } e^+) = 2 \times 10^{-12}$ Van Dyck et al (1987)



- Comparison of g factors of bound p in *ortho*-H_2^+ and bound $\bar{p}$ in *ortho*-$\overline{\mathrm{H}}_2^-$
  - Proposal: measure pure proton/antiproton spin-flip transitions in both $M_s = +1/2$ and $M_s = -1/2$
  - The sum of transition frequencies is nearly independent of B-field value; probes the HFS ($b_F \approx$ 1 GHz).
    Advantage #1: **no need to accurately determine the magnetic field**
  - In a QLS-Penning trap: test at $\mathbf{10^{-12}}$ **level** (very long integration time); [cf. $u_r = 1.5 \times 10^{-9}$ @ BASE]
  - Advantage #2 compared to planned $p/\bar{p}$ comparisons: higher resolution due to high HFS frequency

cf. Myers (2018)

Summary:

Novel approach to hyperfine structure measurement in HD^+

Precision vibrational spectroscopy of H_2^+ is feasible

Probably, accuracy can be pushed to the 10^{-17} level in a Penning trap

Suitable trapping and spectroscopy technology is in principle available; needs to be applied

Exciting possibilities to test CPTI for baryons and leptons bound in H_2^+ and $\overline{\mathrm{H}}_2^+$