Precision spectroscopy of the molecular hydrogen ions: present and future

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Co-funded by the European Union
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Theory

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Swansea University Prifysgol Abertawe
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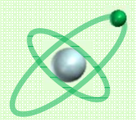
Molecular hydrogen ions: a platform for fundamental physics

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

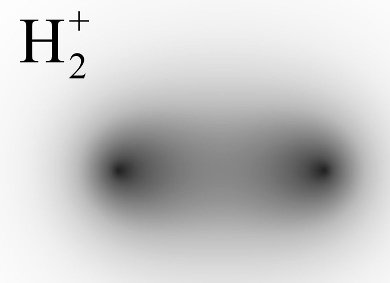
Laser spectroscopy of hydrogen-like atoms and ions



R. Pohl's talk

- Rydberg constant
- Nuclear radii
- QED
- BSM lepton-baryon interaction
- CPT Invariance test

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

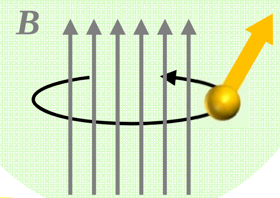


$D_2^+, HD^+, T_2^+, HT^+, DT^+$

- electron-baryon mass ratio
- Rydberg constant
- Nuclear radii
- QED
- BSM lepton-baryon interaction
- BSM baryon-baryon interaction
- CPT invariance test
- Lorentz invariance test

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

Mass spectrometry & magnetic resonance of simple systems



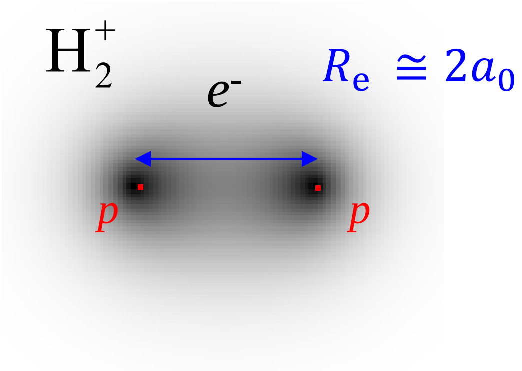
K. Blaum's talk

- Particle masses
- g-factors
- Nuclear radii
- QED
- CPT invariance test
- Lorentz invariance test
- BSM lepton-baryon int.

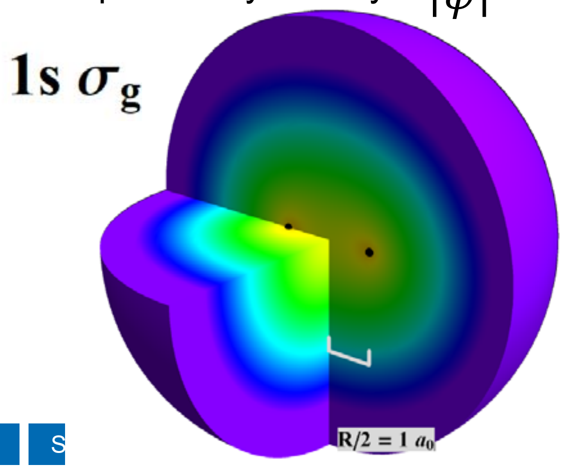
Experiments: Heidelberg, Mainz, Stockholm, CERN, Evanston, Tallahassee, Argonne,…

The simplest molecule

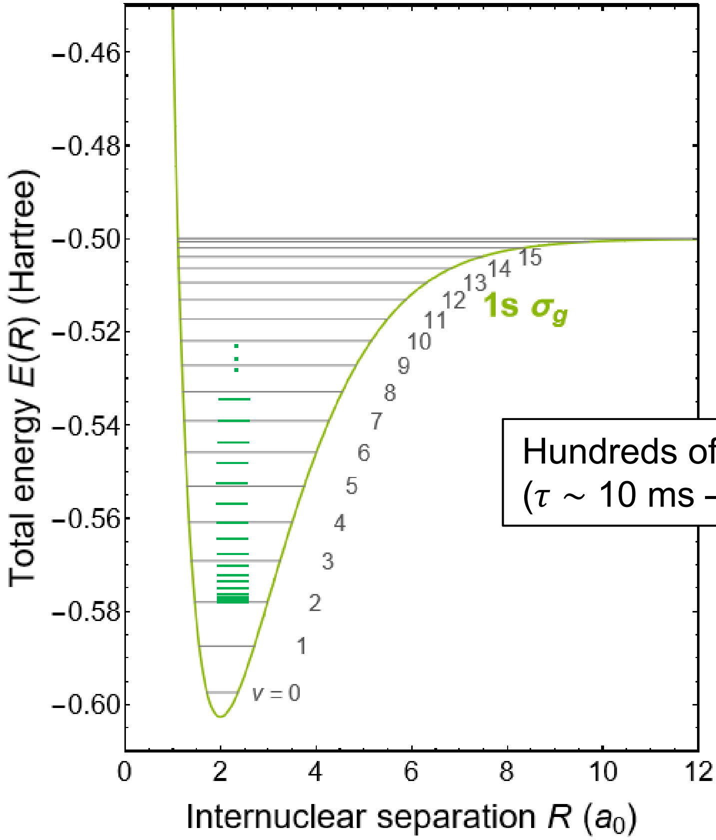
Schiller, *Contemp. Phys.* **63**, 247 (2022)



Electronic probability density $|\psi|^2$



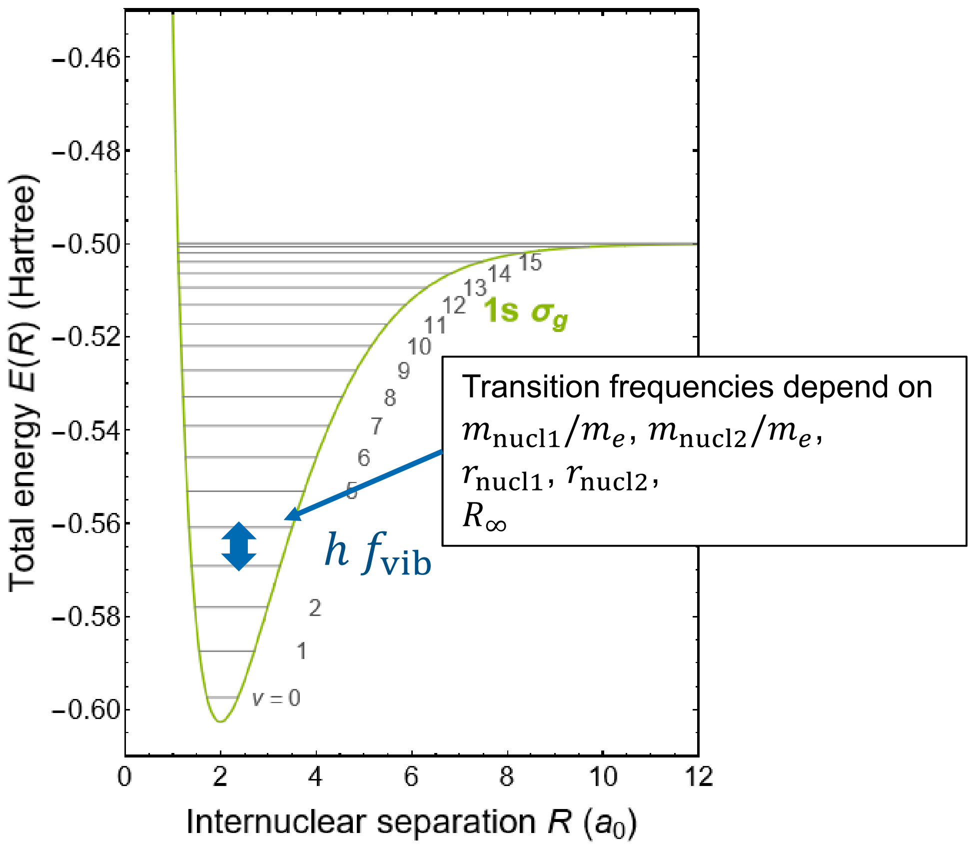
- A rich rovibrational level spectrum



Hundreds of metastable levels
($\tau \sim$ 10 ms – days)

I. Ab initio theory

- Accurate computation of f_{vib}
  - Numerical solution of the three-body Schrödinger equation
  - QED corrections
  - Corrections from finite size of nuclei: $\frac{\delta f}{f} \approx 2 \times 10^{-9}$
- Input parameters are:
  - mass ratios m_{nucl}/m_e
  - R_∞
  - nuclear charge radii r_{nucl}



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Experimental determinations of f_{vib} challenge QED calculations

Trust QED calculations →
Fit $\boldsymbol{m_{\mathrm{nucl}}/m_e}$, R_∞, r_{nucl}
to reproduce experimental f_{vib}

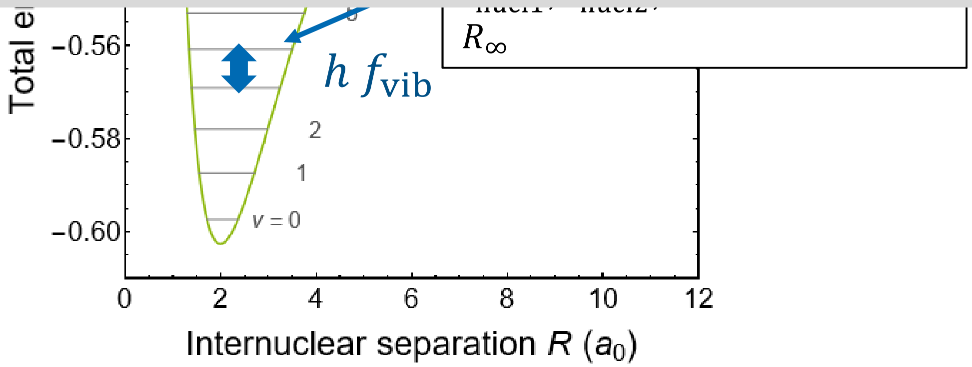
Theory development:
V. Korobov et al., J.-Ph. Karr et al., Z.-X. Zhong et al.

H_2^+ vibrational transition $v = 1 \rightarrow v' = 3$

Order	Value (kHz)	
α^2	124 485 554 550.71	Eigenenergy of 3-body Schrödinger equation
α^4	2 002 698.73	Relativistic correct. in Breit-Pauli approx.; finite-size nuclei
α^5	−521 345.53	Leading-order radiative corrections (e.g. leading-order Lamb shift, anomalous magnetic moment of electron)
α^6	−3 689.05	1-loop, 2-loop radiative corrections, more relativ. correct.
α^7	228.67	Radiative corrections up to 3-loop diagrams, Wichmann-Kroll contrib.
α^8	−1.62	Higher-order radiative corrections (1-loop self-energy, 2-loop radiative)
other	0.54	Muon and hadron vacuum polarization

Total: 124 487 032 442.5 kHz

uncertainty: 1.0 kHz [8×10^{-12}]



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		Radiative corrections up to 3-loop diagrams

g-factor of the free electron

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

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

Spectroscopy of H, μH and QED | Atom interfe-rometry | Mass spectrometry (Penning trap) | MHI spectroscopy and QED

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

QED

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

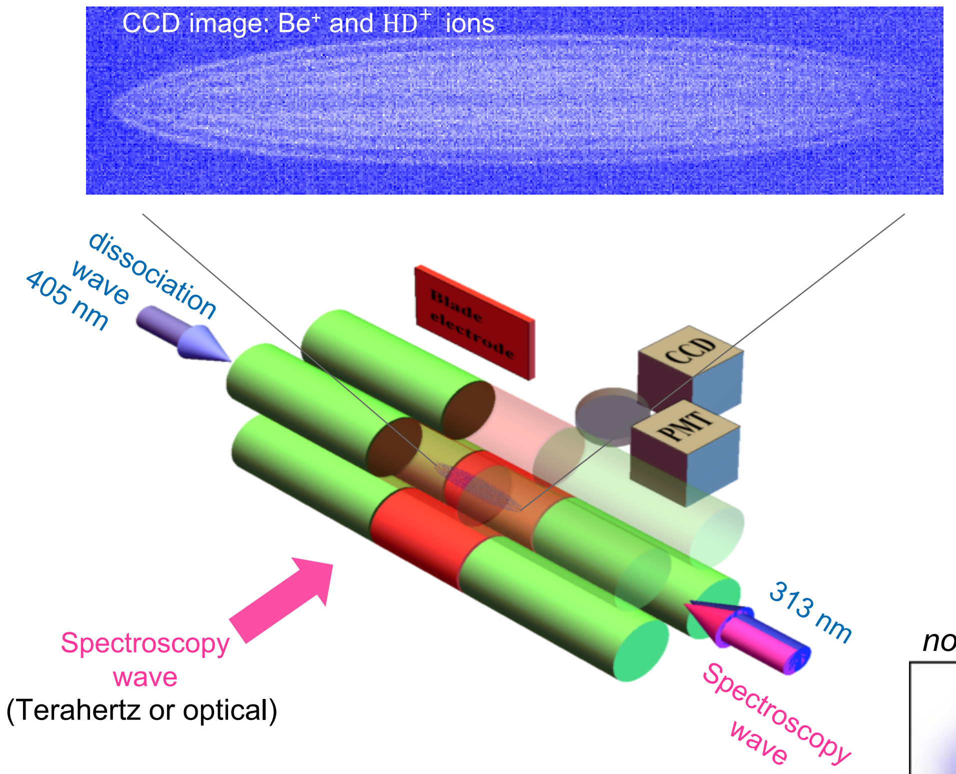
Electron-spin resonance in Penning trap | Mass spectrometry (Penning trap) | MHI spectroscopy and QED

see also Klaus Blaum's talk

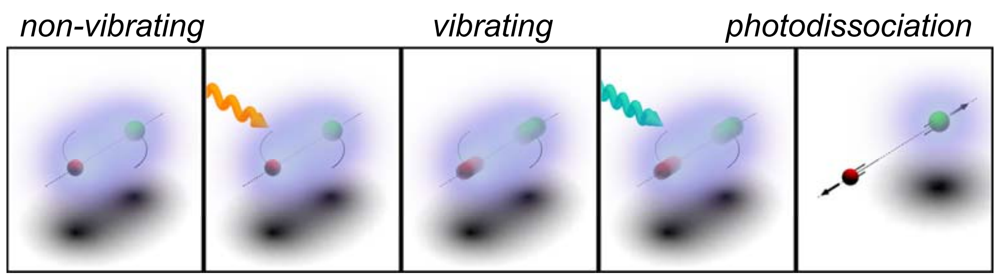
S. Alighanbari et al, Nature 664, 69 (2025)

Method I: trapped and sympathetically cooled MHI ensembles

Roth et al. PRA 74, 040501 (2006)



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



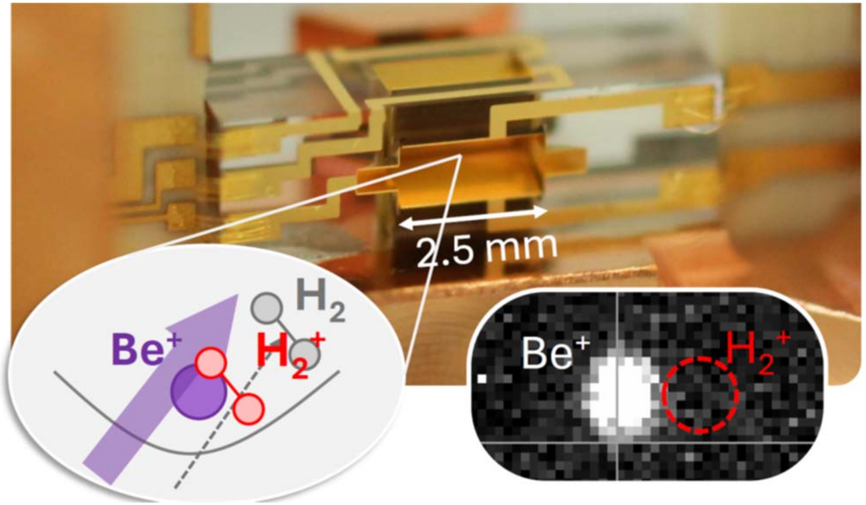
Method also employed in:
Amsterdam (HD^+), Paris (H_2^+), Wuhan (HD^+)

Method II: trapped and sympathetically cooled *single* MHI

see poster Mon-027, He et al.

ETH Zürich:

- Quantum-logic spectroscopy
- Cryogenic trap

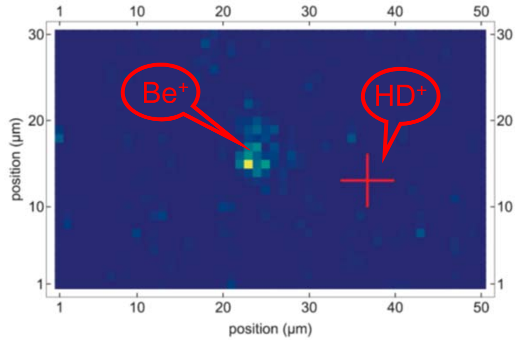


- Raman and r.f. transitions between hyperfine states observed
- Narrow linewidths (4 kHz, ~ 1 Hz)

N. Schwegler et al., PRL 131, 133003 (2023)
D. Holzapfel et al., PRX 15, 031009 (2025)

Own work:

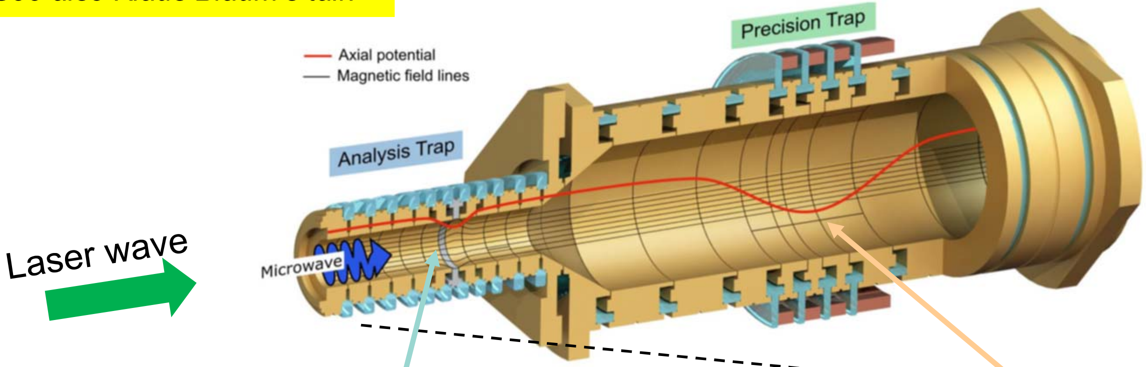
Wellers, C. et al. *Mol. Phys.* e2001599 (2021)



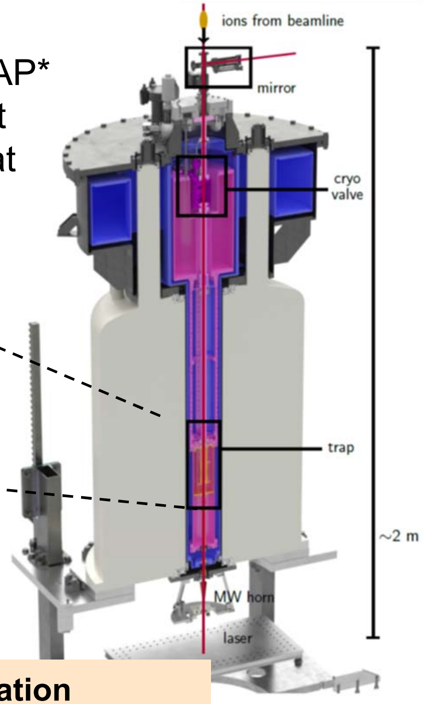
Method III: trapped and resistively cooled MHI

König et al, PRL 134, 163001 (2025)

See also Klaus Blaum's talk



ALPHATRAP*
4 T magnet
4 K cryostat



- ion temperature (axial mode) ~ 6 K

1. Nondestructive detection of electron spin state *(Continuous Stern-Gerlach effect)*:

Magnetic „bottle“: $E_{\text{Zeeman}}(z) = -\mu_B g_{e,bound} M_s (B_0 + B_2 z^2)$

$$E_{\text{ion}}(z) = \frac{1}{2} q \left(\frac{\partial^2 V}{\partial z^2}\right) z^2 + E_{\text{Zeeman}}(z)$$

Axial oscillation frequency:
- depends on spin orientation M_s
- is measured without disturbing the internal state

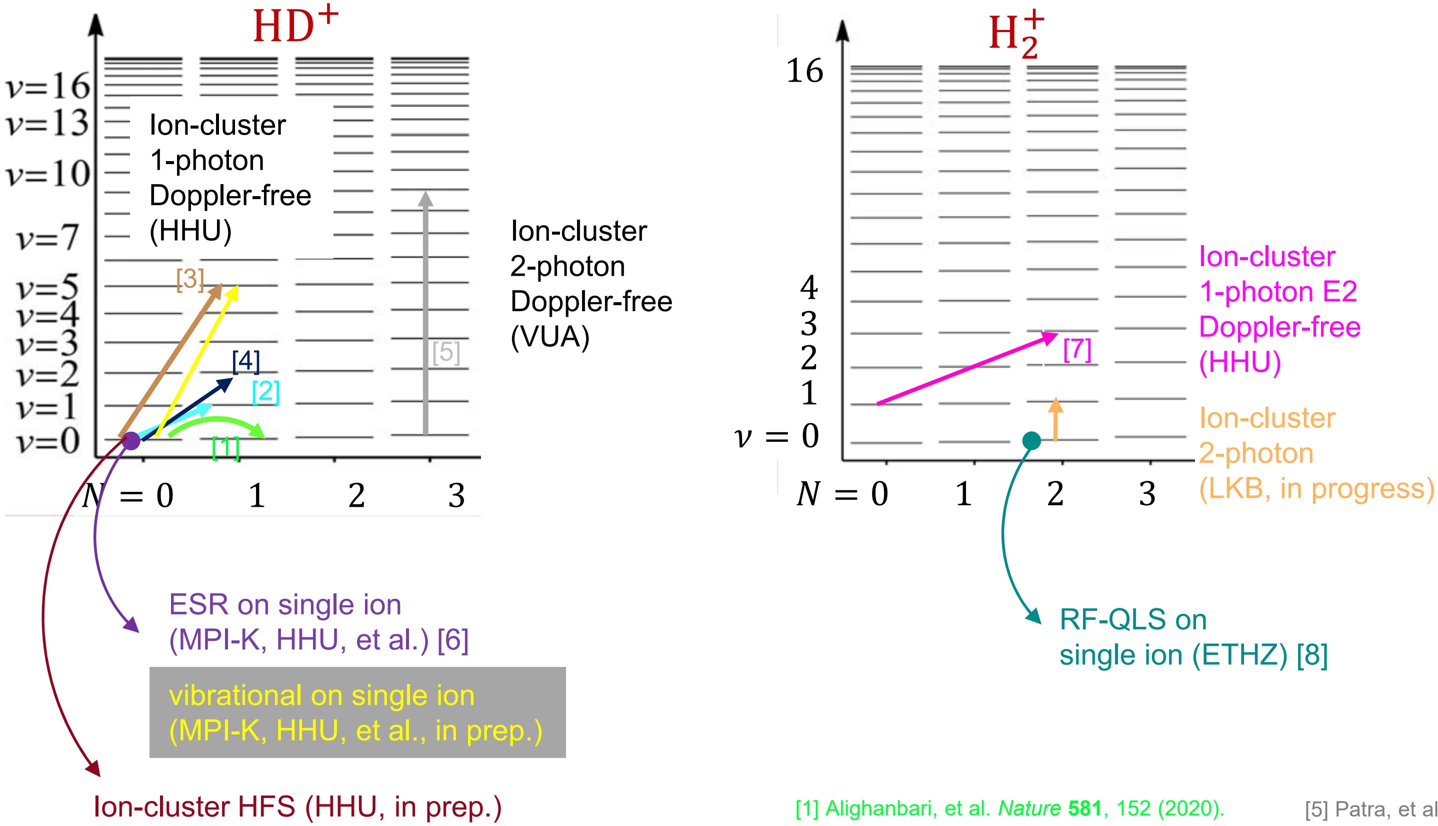
2. State identification/preparation

Electron-spin flip frequency is state-specific:
- $g_{e,bound} = g_{e,bound}(v, N)$
- HFS = HFS$(v, N, M_{I_1}, M_{I_2}, M_s)$

**Sturm et al. EPJ Spec. Top. 227, 1425 (2019)*

- Single ion with well-defined axial mode → **optical spectroscopy with resolved carrier**

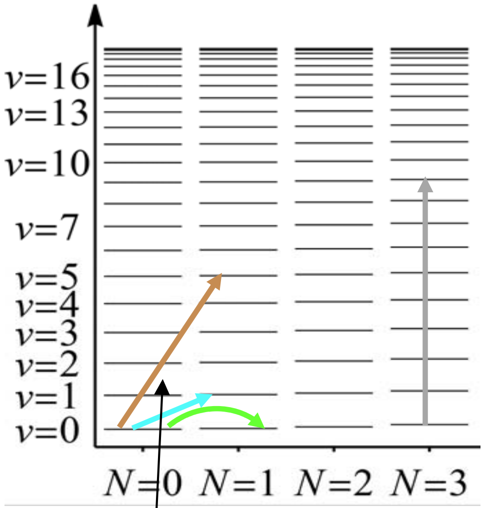
Overview of high-precision experimental studies

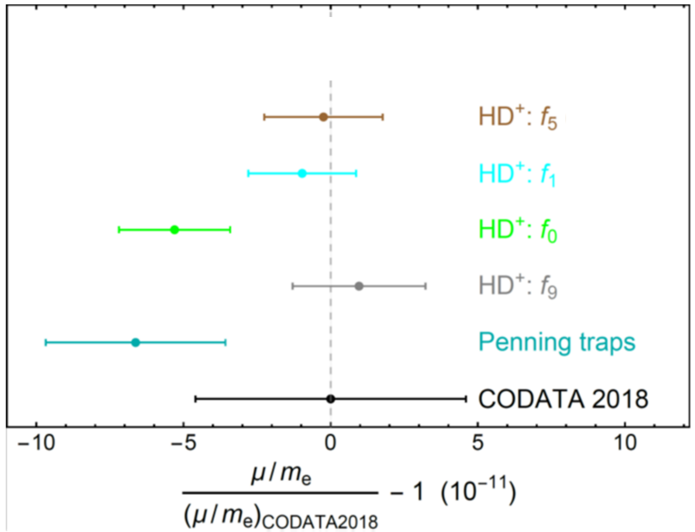


[1] Alighanbari, et al. *Nature* **581**, 152 (2020).
[2] Kortunov, et al. *Nat. Phys.* **17**, 569 (2021).
[3] Alighanbari, et al. *Nat. Phys* **19**, 1263 (2023).
[4] Schenkel, et al. *Nat. Phys.* **20** (2024).
[5] Patra, et al. *Science* **369**, 1238 (2020).
[6] König, et al. *PRL* **136** (2026)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

HD$^+$ rovibrational spectroscopy: determination of μ_{pd}/m_e

Determination of a combination of two fundamental constants: $m_e/\mu_{pd} = \frac{m_e}{m_p} + \frac{m_e}{m_d}$





Results included in CODATA 2022 compilation

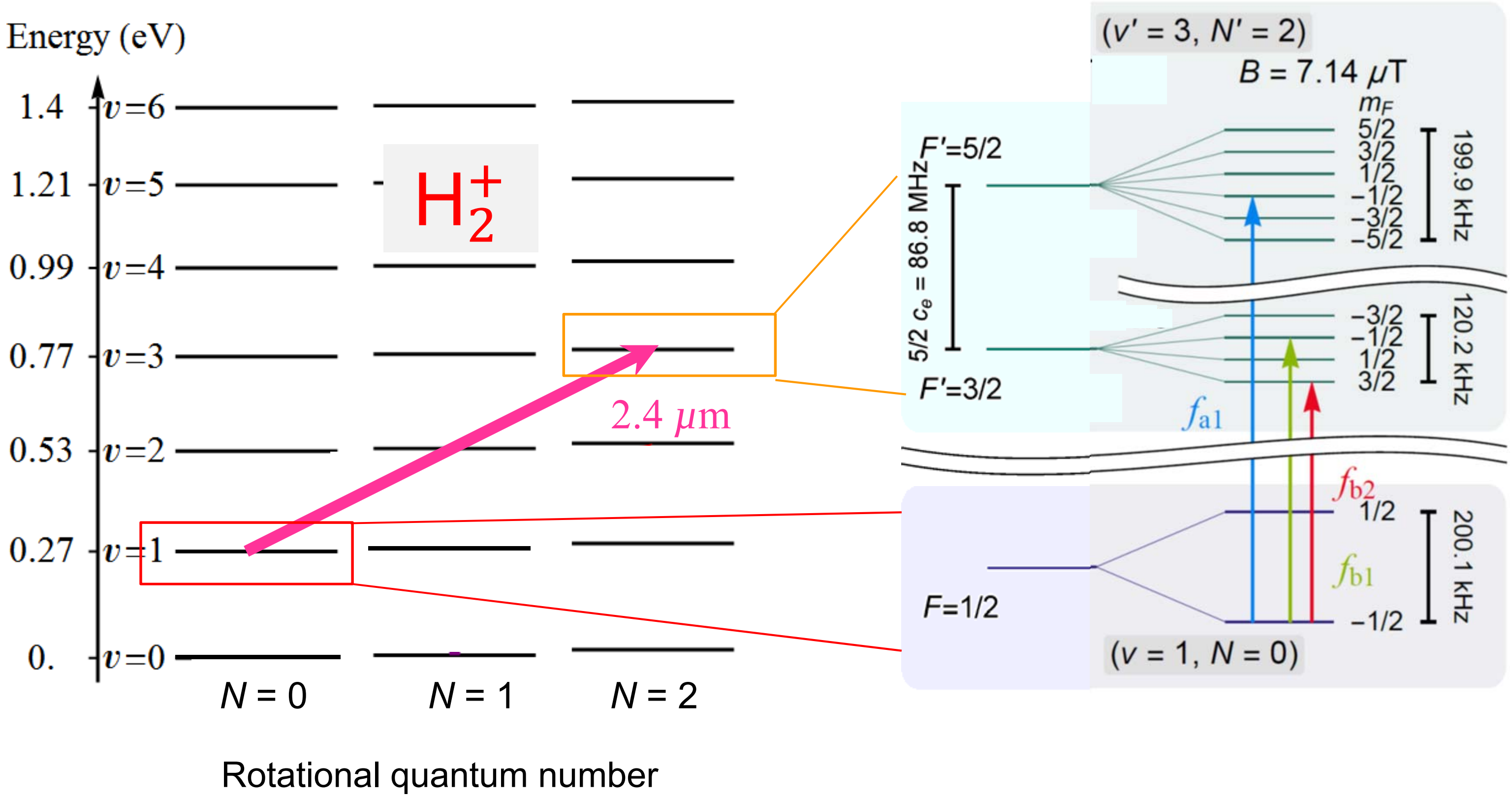
See Klaus Blaum's talk

- Linewidths of rovibr. transition: as low as 2×10^{-12}
- Systematic shifts are determined
- Experimental uncertainty 2.3×10^{-12}
- HFS theory invoked to find $f_{vib}^{(expt)}$

Spectroscopy of H_2^+

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

- Choose para-H_2^+ $\rightarrow$ very simple HFS



Spin-rotation interaction

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

Non-negligible Zeeman shifts

Result

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

Experiment and theory comparison

	f_{vib} (kHz)	c_e (kHz)
Experiment	124 487 032 442.73 $(0.95)_{\text{expt}}$	34 730.18 (10)
Theory*	124 487 032 442.5 $(1.0)_{\text{QED}}(0.96)_{\text{CODATA22}}$	34 730.25 (12)
Expt. - theory	0.19 $(1.6)_{\text{tot}}$	−0.07 (15)

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

Agreement!

- QED contributions „measured" to 2×10^{-6}
- proton charge radius „measured" to 1%

Proton-electron mass ratio

	m_p/m_e
This work: experiment and theory of H_2^+	1836.152 673 414 (47)
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)

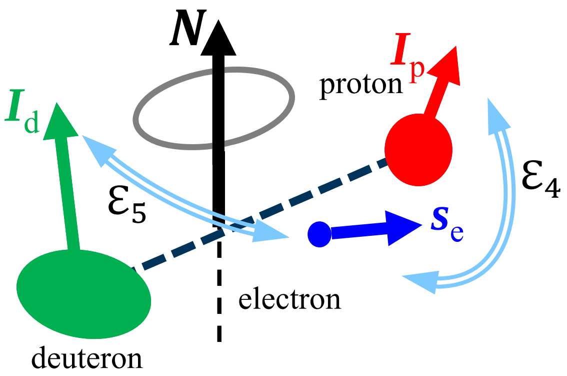
[2.6×10^{-11}]

Agreement!

*Korobov and Karr, PRA 104, 032806 (2021)
Haidar, et al. PRA 106, 022816 (2022)

Hyperfine structure in HD$^+$

- HFS is more complex that in hydrogen atom



- Ab initio calculation is possible*

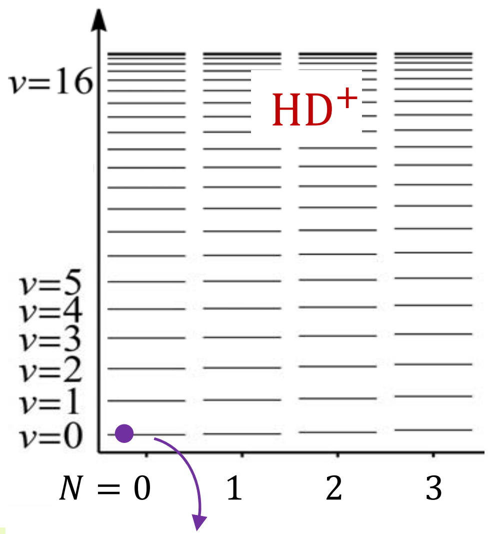
→ HFS theory input is (sometimes) essential for allowing to extract $f_{vib}^{(expt)}$

- Opportunity to search for spin-dependent BSM forces

*Bakalov et al PRL 97, 243001 (2006)
Korobov et al PRA 74, 040502(R) (2006)
Korobov and Karr, PRA 104, 032806 (2021)
Haidar, et al. PRA 106, 022816 (2022)

- In rovibrational transitions studied so far, HFS of lower and upper level are probed simultaneously

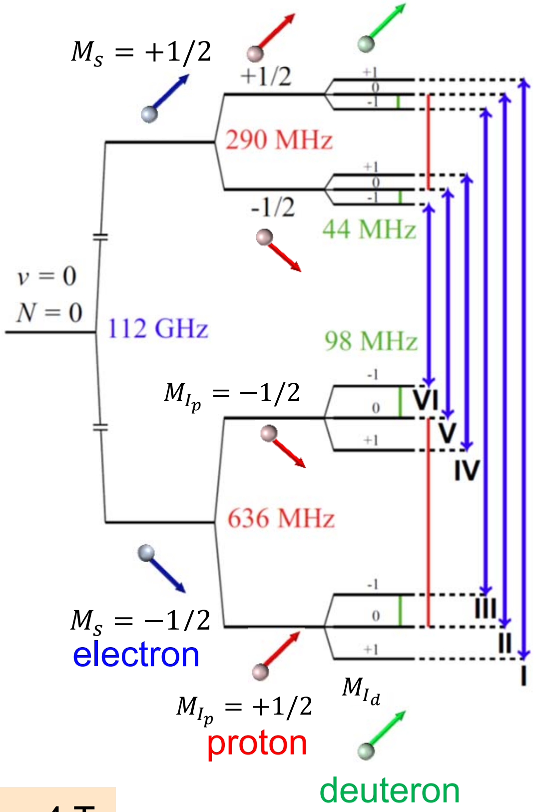
- → Study HFS in a single level;
  Choose $N = 0$ as simplest case



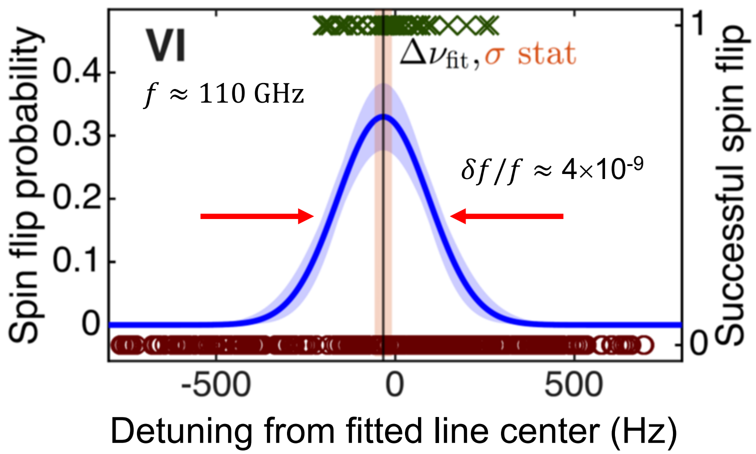
$$H_{\mathrm{HFS}}(v=0,N=0) = h\mathcal{E}_4(0,0)\boldsymbol{I}_p\cdot\boldsymbol{s}_e + h\mathcal{E}_5(0,0)\boldsymbol{I}_d\cdot\boldsymbol{s}_e + h\mathcal{E}_{10}(0,0)\boldsymbol{I}_p\cdot\boldsymbol{I}_d$$

Hyperfine and magnetic structure via ESR in a Penning trap

König et al, PRL 136, 143002 (2026)



B = 4 T



- Whole measurement campaign used only 8 ions

not accessible to us

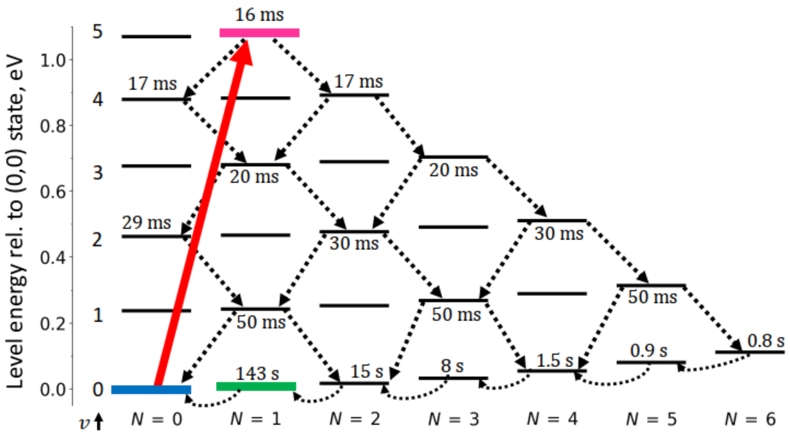
$$H_{\rm HFS}(v=0, N=0) = h\mathcal{E}_4 \boldsymbol{I}_p \cdot \boldsymbol{s}_e + h\mathcal{E}_5 \boldsymbol{I}_d \cdot \boldsymbol{s}_e + h\mathcal{E}_{10} \boldsymbol{I}_p \cdot \boldsymbol{I}_d$$

	$\mathcal{E}_4$ (0,0) (kHz)	$\mathcal{E}_5$(0,0) (kHz)	$g_{e,bound}$(0,0)
Expt.	$925\,395.758(39)_{\rm stat}(11)_{\rm sys}$	$142\,287.821(20)_{\rm stat}(8)_{\rm sys}$	$-2.002\,278\,540\,96(18)_{\rm stat}(35)_{\rm sys}$ [2.0×10^{-10}]
Theory	$925\,394.16(86)$	$142\,287.556(84)$	$-2.002\,278\,540\,70(10)$ [5.0×10^{-11}]
Difference	+ 1.9 σ	+ 3.1 σ	+ 0.5 σ

To be compared with upcoming results from RF traps

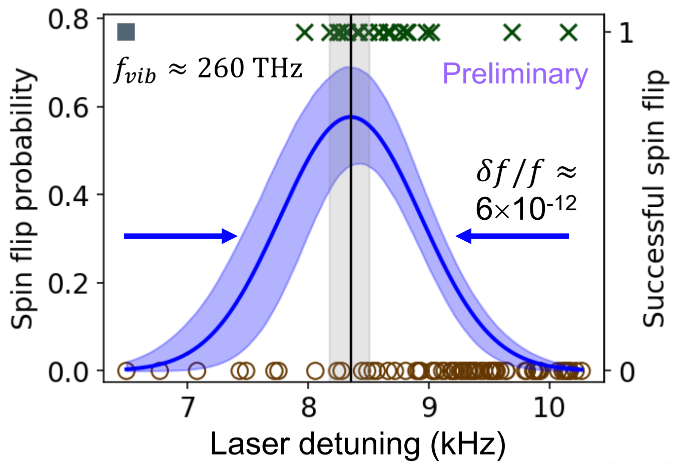
Laser vibrational spectroscopy of HD⁺ in a Penning trap

Principle:



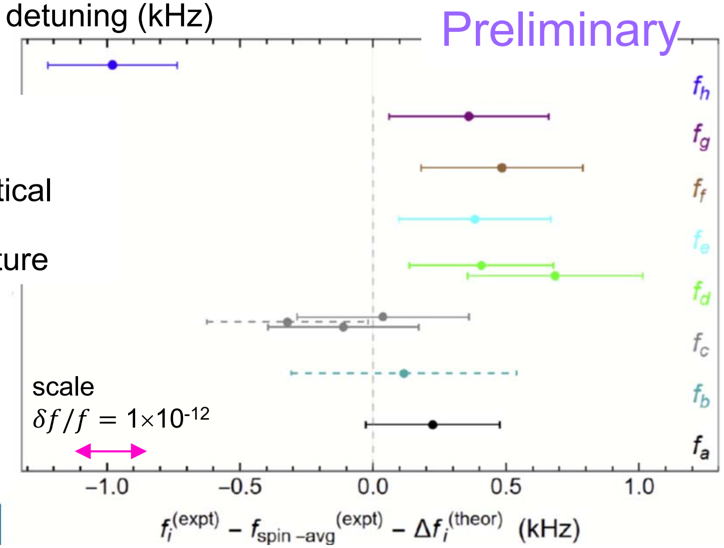
1. After long irradiation, molecule may end up in the bottleneck level $(v = 0, N = 1)$
2. Electron-spin flip pulse is applied for this level
3. Molecule decays back to initial level $(v = 0, N = 0)$
4. Electron-spin state is measured

- First ultra-high-resolution optical spectroscopy of a non-laser-coolable ion in a Penning trap
- General method



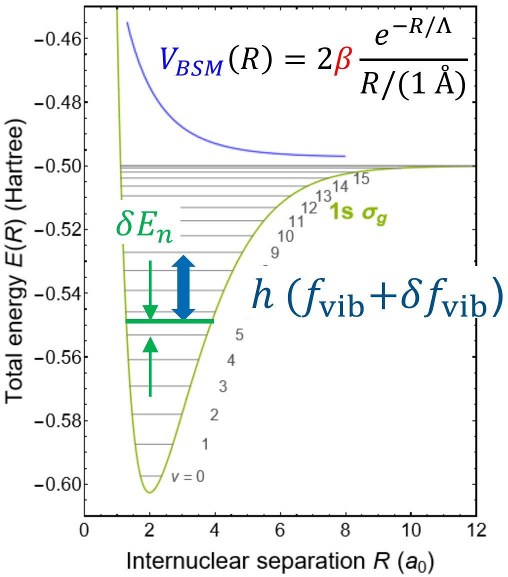
- Measured 8 non-particle-spin-flip optical transitions
- Systematic unc. $u_r < 1 \times 10^{-13}$
- Whole campaign used 1 (!) ion

- Comparison of exptl. and ab initio theoretical hyperfine + magnetic structure



Bounds on nuclear BSM interaction from HD$^+$ spectroscopy

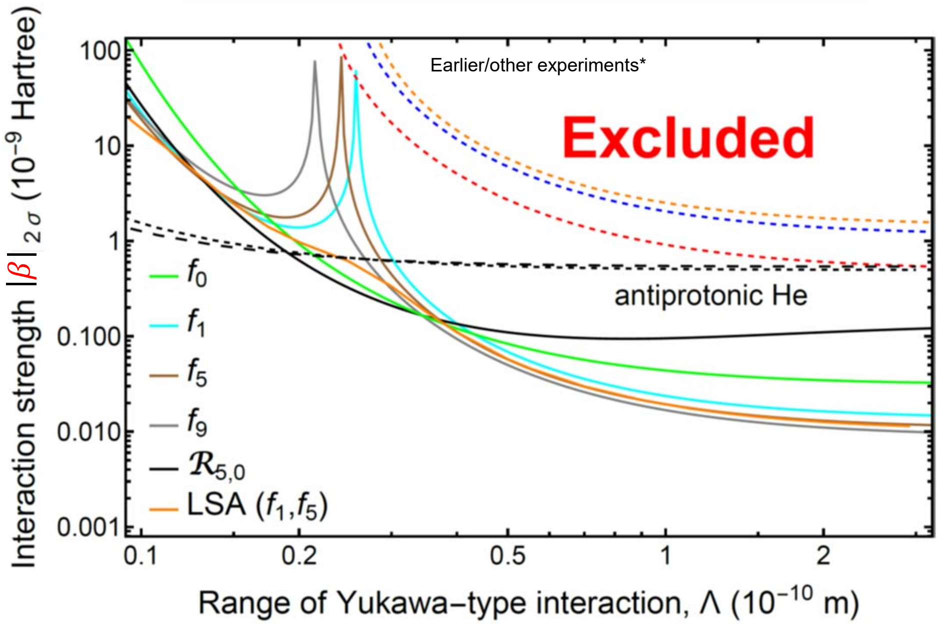
- Transition frequencies are a function of the interparticle interactions
- Hypothetical interaction between *nuclei*



$$\delta E_n = \langle \psi_{X,n}(R) | V_{BSM}(R) | \psi_{X,n}(R) \rangle$$

If expt. and theory prediction match
→ bounds on strength β

Bounds to strength of a BSM interaction between **proton** and **deuteron**



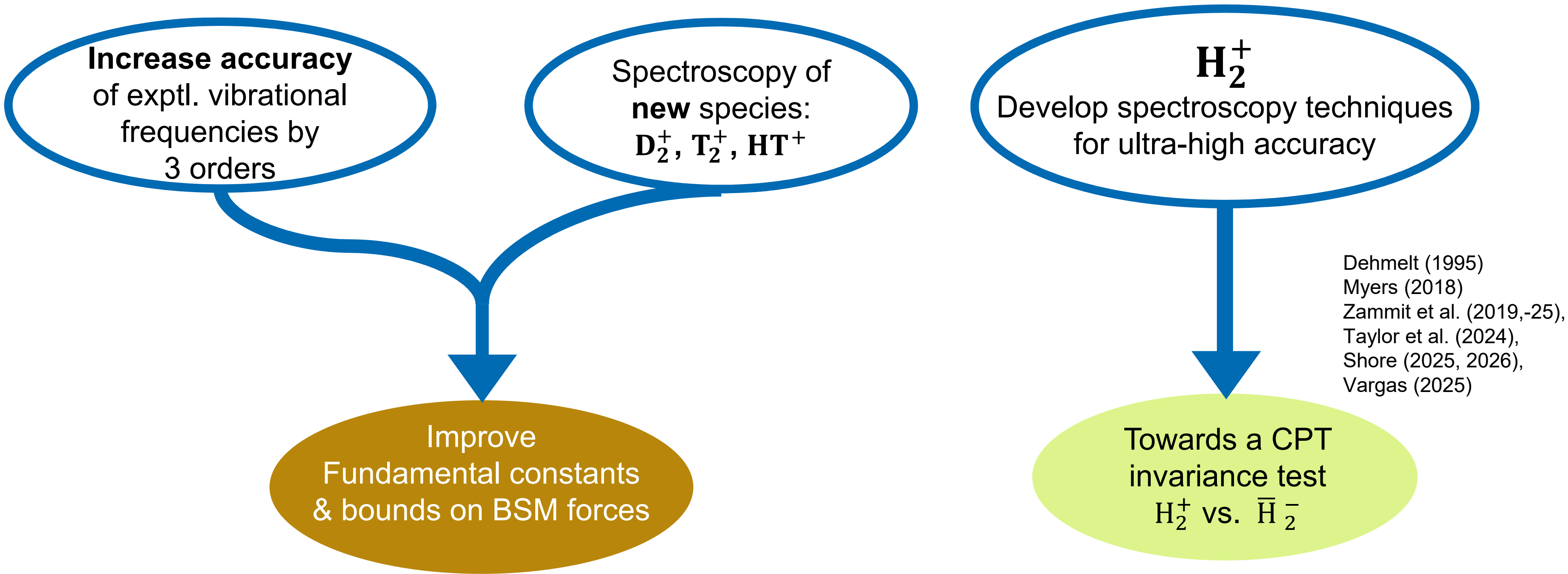
- Other BSM forces?
  Must apply framework for bounding BSM forces in a consistent way

  Delaunay et al. Phys. Rev. Lett. 130, 121801 (2023)

Weak bounds @ 25 pm: spurious cancellation of sensitivity $\delta E_n - \delta E_{n'} \approx 0$

*Koelemeij et al, PRL 98, 173002 (2007)
Bressel et al, PRL 108, 183003 (2012)
Biesheuvel et al., Nat. Comm. 7, 10385 (2016)
Hori et al., Nature 475, 484 (2011)

Perspectives



- Reduce m_e/m_p, m_e/m_d, m_e/m_t uncertainties by 100 ×
- Obtain r_p, r_d from electronic systems only
  → lepton universality test
- Reduce uncertainty of r_t by 200 × → Test of nuclear theory

Karr et al., PRA 112, 022809 (2025)

- Penning trap: $\frac{u\left(f(H_2^+)-f(\bar{H}_2^-)\right)}{f} \simeq 10^{-17}$ realistic
- Complete test of CPTI:
  baryon properties, lepton properties
  baryon-baryon & baryon-lepton interaction

Schiller et al., arXiv:2605.16585