Improving the hyperfine structure theory in hydrogen molecular ions

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International Conference on Precision Physics and Fundamental Physical Constants (FFK-2019)
Tihany, 10 June 2019

1. Motivations

Rovibrational spectroscopy of hydrogen molecular ions

LKB

- Sensitivity to fundamental constants

$$\nu = c R_\infty \left[\varepsilon_{nr}(\mu_{ne}) + \alpha^2 F_{QED}(\alpha) + \sum_n A_n^{fs} (r_n / a_0)^2 \right]$$

Schrödinger

Relativistic and QED corrections

Nuclear finite size correction

$$\nu_{vibr} \propto R_\infty \sqrt{m_e / m_r} \qquad \nu_{rot} \propto R_\infty m_e / m_r$$

H_2^+ $R_\infty, r_p, m_e / m_p$

HD^+ $R_\infty, r_p^2 + r_d^2, m_e / m_r^{(pd)}$

Brand new CODATA 2018 recommended values

$r_p = 0.8414(19)$ fm ***(shifted by 4%)*** R_∞ : **1.9 10^{-12}** ***(shifted by 3 10^{-11})***

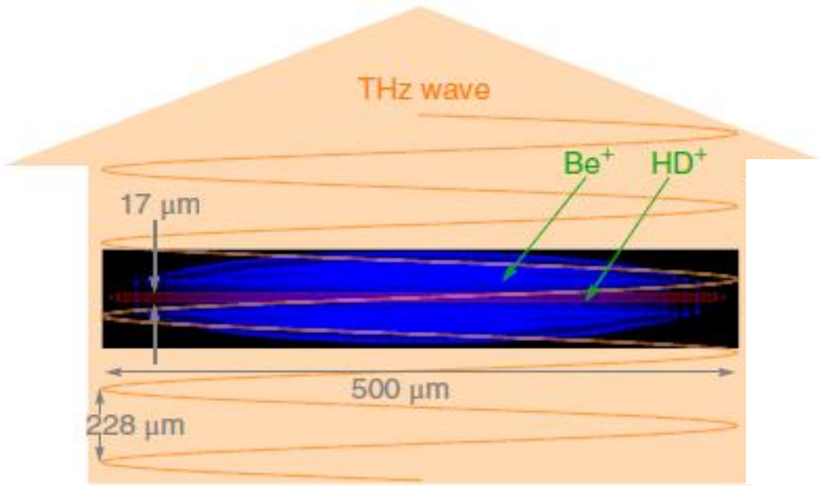
m_e / m_p : **6.0 10^{-11}** m_e / m_d : **3.5 10^{-11}**

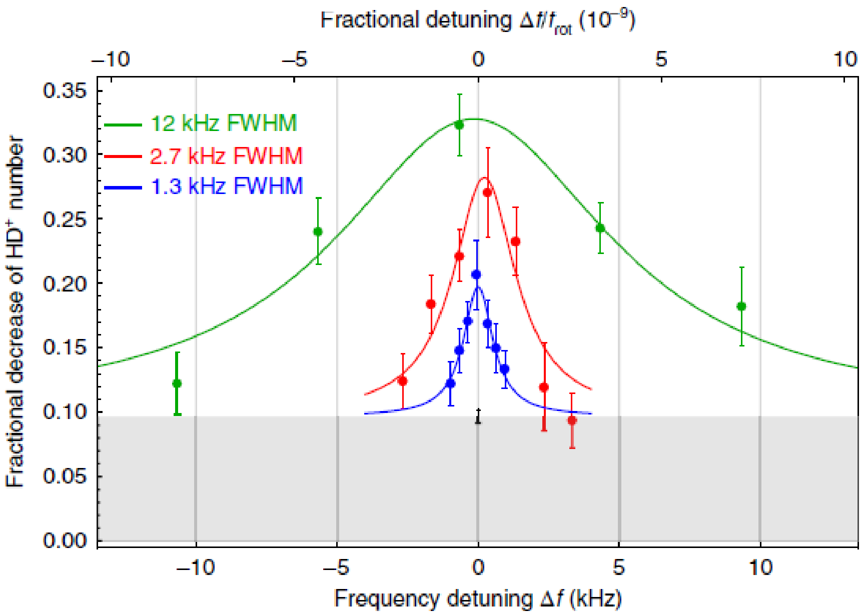
- Theoretical accuracy for vibrational transitions = **7.5 10^{-12}**
  rotational transitions = **1.35 10^{-11}**

- Experiments may soon reach a few **10^{-12}** using Doppler-free schemes

Current experiments: HD^+

Rotational transition in the Lamb-Dicke regime

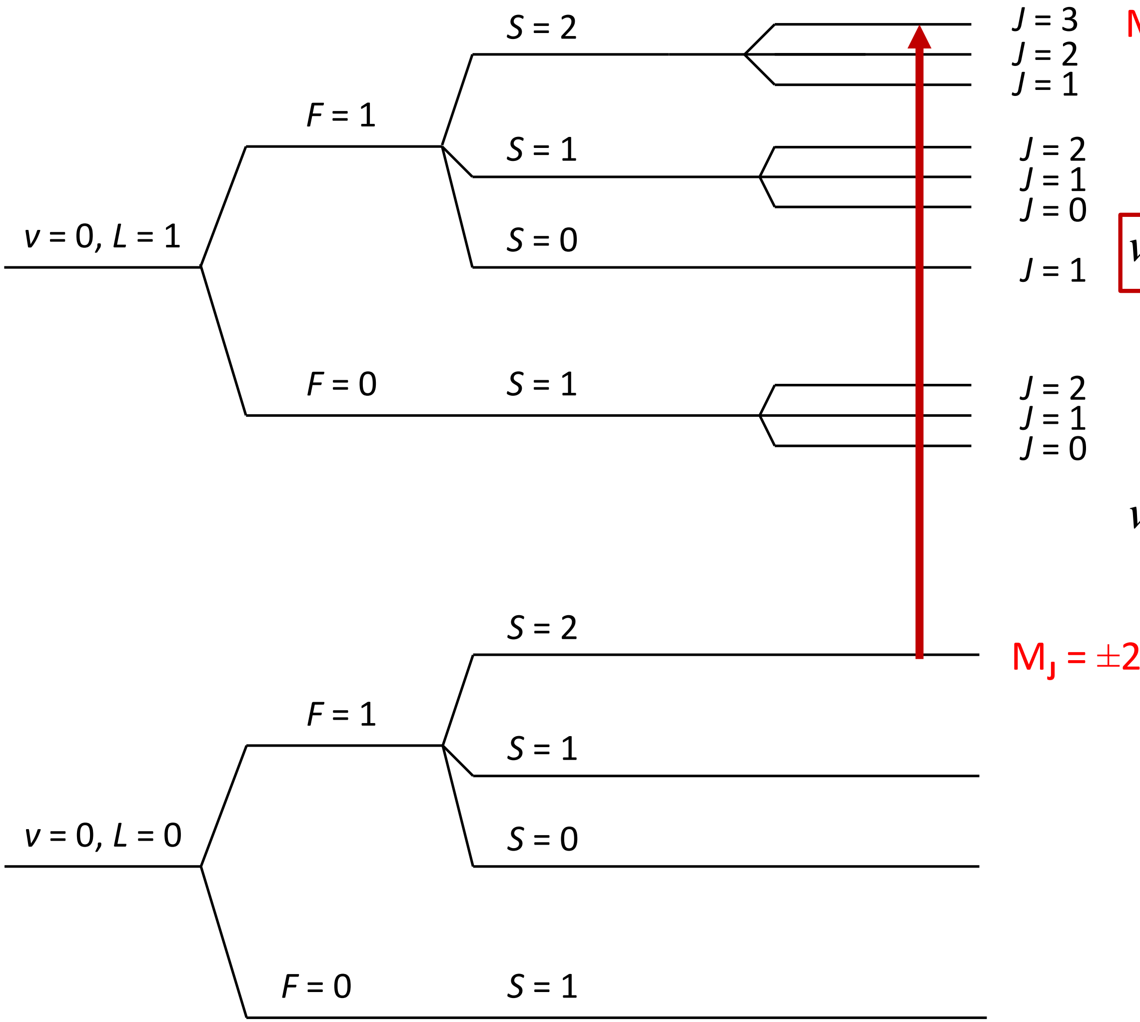




S. Alighanbari et al., Nature Phys. **14**, 555 (2018)

Current experiments: HD^+

Rotational transition in the Lamb-Dicke regime



$$\nu_{\text{exp}} = 1\,314\,935\,828.0(5)\ \text{kHz}$$ 3.8 10^{-10}

$$\nu_{\text{theor}} = \nu_{\text{spin-avg}} + \nu_{\text{hfs}}\ ,$$ 7.6 10^{-10}

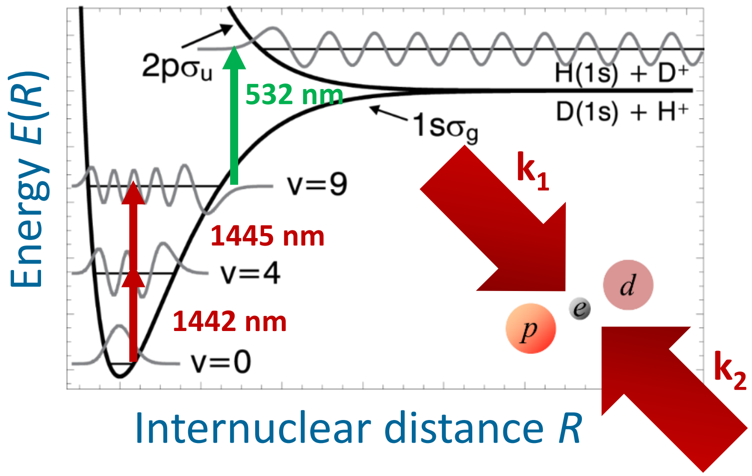
$$\nu_{\text{spin-avg}} = 1\,314\,925\,752.627(18)\ \text{kHz}$$ 1.35 10^{-11}

$$\nu_{\text{hfs}} = 10\,074.7(10)\ \text{kHz}$$

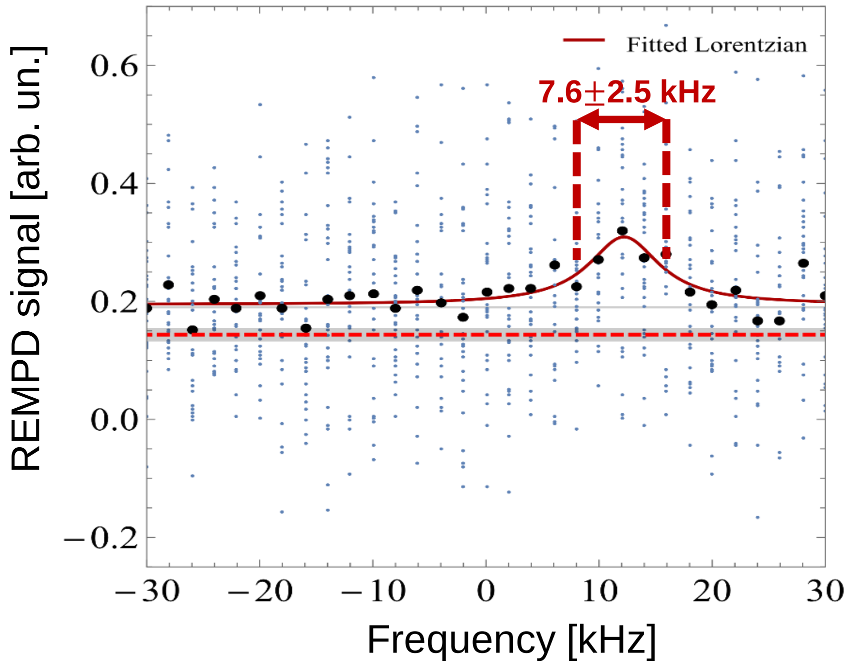
S. Alighanbari et al., Nature Phys. **14**, 555 (2018)

Current experiments: HD^+

Quasi-degenerate two-photon transition in the Lamb-Dicke regime



$$\lambda_{\text{eff}} = \frac{2\pi}{\|\mathbf{k}_1 + \mathbf{k}_2\|} = \left|\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right|^{-1} \approx 730\,\mu\text{m}$$

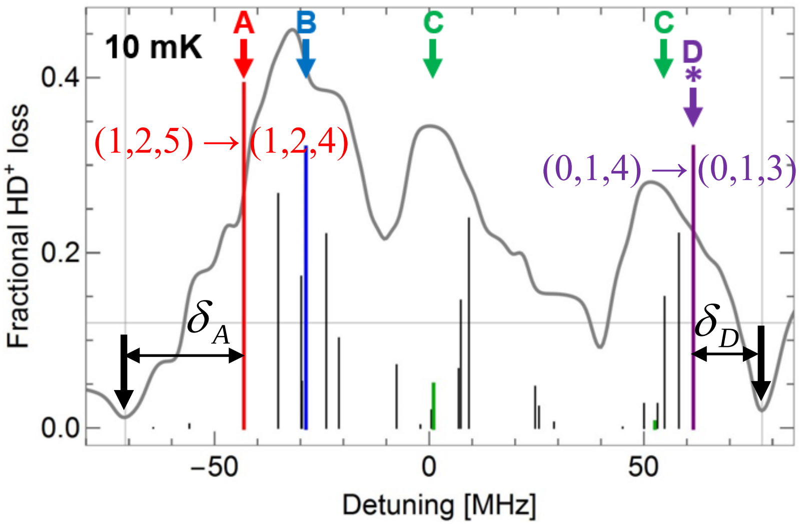


S. Patra, PhD thesis (2019)

Current experiments: HD$^+$

Quasi-degenerate two-photon transition in the Lamb-Dicke regime

Simulated Doppler-broadened single-photon spectrum of the (v,L) : (0,3) → (4,2) transition at 1442 nm

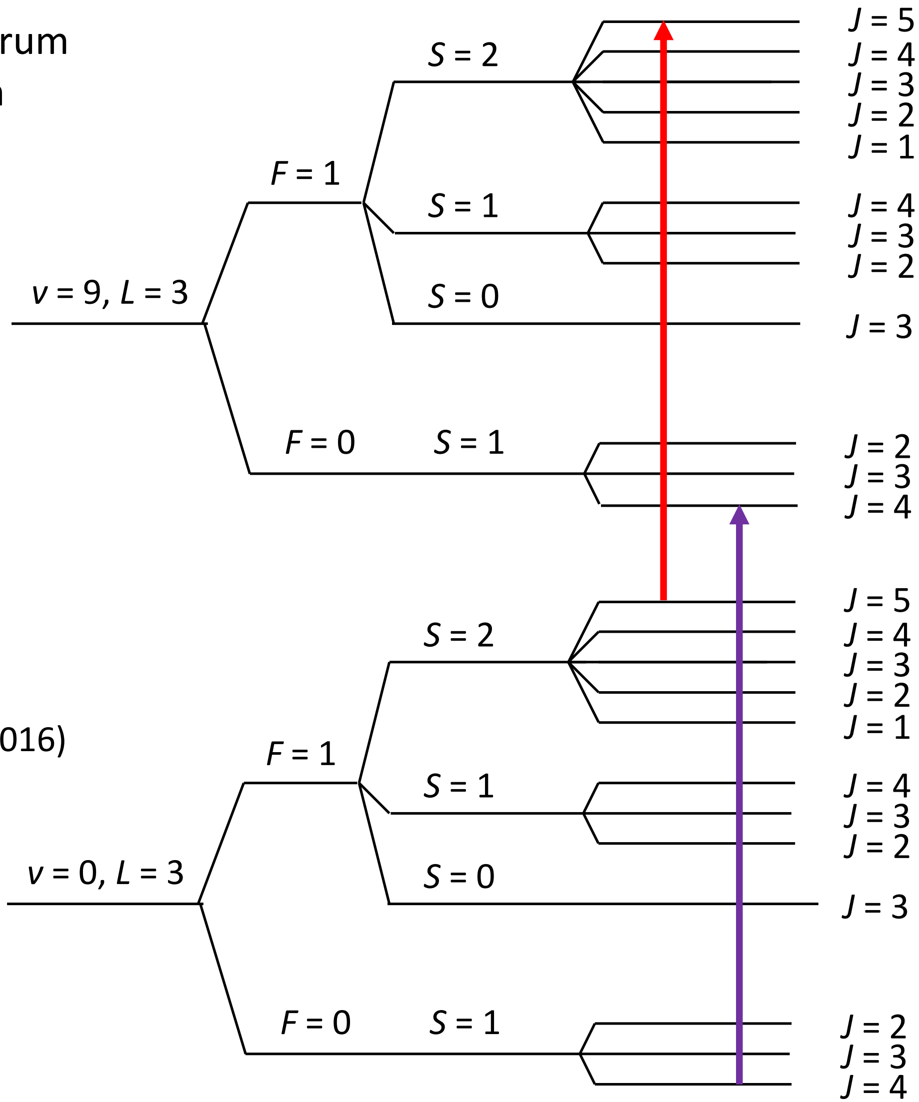


J.-Ph. Karr, S. Patra et al., J. Phys. Conf. Ser. **723**, 012048 (2016)

$$\nu_{\text{theor}} = \nu_{\text{spin-avg}} + \nu_{\text{hfs}} \ ,$$

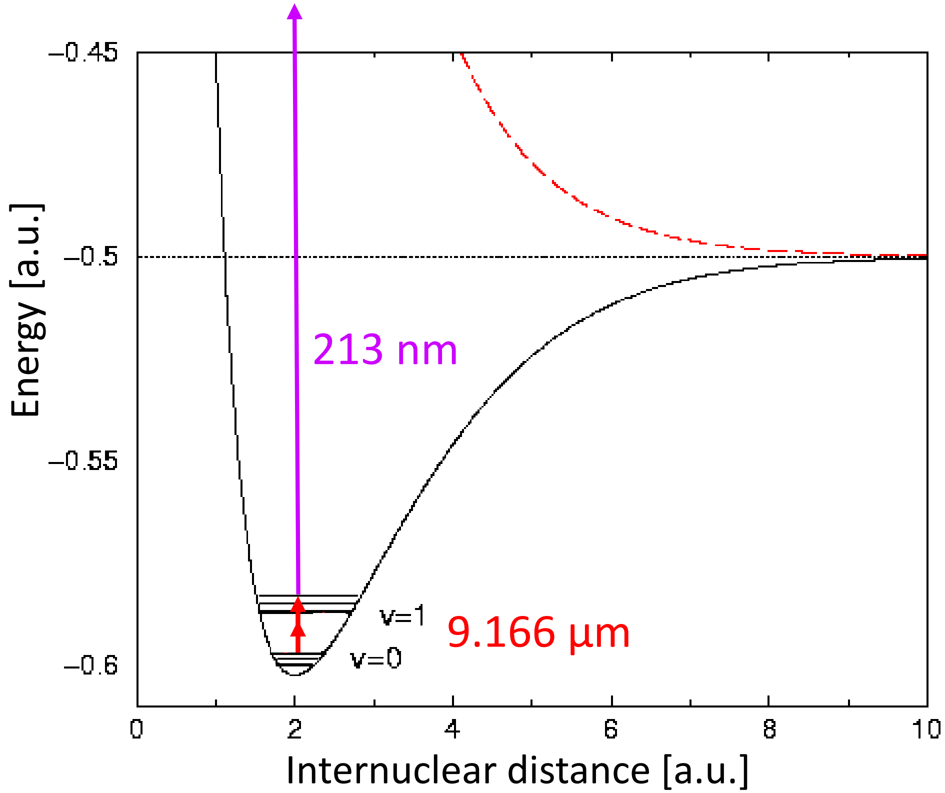
$\nu_{\text{spin-avg}}$ predicted with 7.5 10^{-12} accuracy

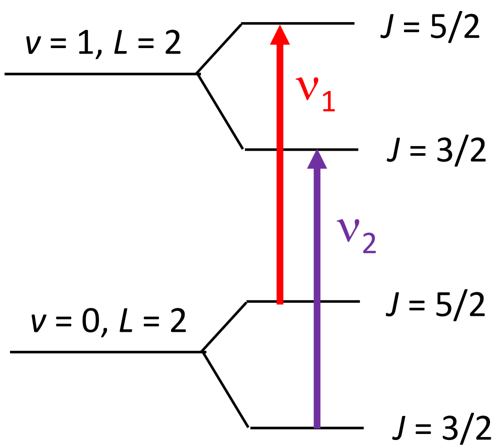
V.I. Korobov, L. Hilico, J.-Ph. Karr, PRL **118**, 233001



Current experiments: H_2^+

Doppler-free two-photon transition





$$\nu_{\text{spin-avg}} = (6\nu_1 + 4\nu_2)/10$$

! Poster on Wednesday !

J. Heinrich, PhD thesis (2018)

Status of HD^+ hyperfine structure theory

Spin-orbit | Nuclear spin-rotation | Spin-spin Fermi contact interaction

$$H_{\rm eff} = E_1(\mathbf{L}\cdot\mathbf{s}_e) + E_2(\mathbf{L}\cdot\mathbf{I}_p) + E_3(\mathbf{L}\cdot\mathbf{I}_d) + E_4(\mathbf{I}_p\cdot\mathbf{s}_e) + E_5(\mathbf{I}_d\cdot\mathbf{s}_e)$$

$$+ E_6\left\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_p)]\right\}$$

$$+ E_7\left\{2\mathbf{L}^2(\mathbf{I}_d\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_d)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_d)]\right\}$$

$$+ E_8\left\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{I}_d) - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{I}_d) + (\mathbf{L}\cdot\mathbf{I}_d)(\mathbf{L}\cdot\mathbf{I}_p)]\right\}$$

Spin-spin tensor interactions

$$+ E_9\left\{\mathbf{L}^2\mathbf{I}_d^2 - \frac{3}{2}(\mathbf{L}\cdot\mathbf{I}_d) - 3(\mathbf{L}\cdot\mathbf{I}_d)^2\right\}$$

Deuteron Quadrupole moment

✓ Calculations at the Breit-Pauli level (~α^2 relative accuracy)

D. Bakalov, V.I. Korobov, S. Schiller, PRL **97**, 043001 (2006)

(L=1,v=0) Unit: MHz	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9
	31.9846	-3.134[-02]	-4.809|-03]	924.629	142.146	8.6111	1.3218	-3.057[-03]	5.666[-03]
	2			1		3			

✓ Higher-order corrections to E_4, E_5

V.I. Korobov, J.C.J. Koelemeij, L. Hilico, J.-Ph. Karr, PRL **116**, 043001 (2016) (H_2^+)

➢ Next step: $(Z\alpha)^2$ relativistic correction to E_1 ; then E_6, E_7

2. Relativistic corrections to the spin-orbit interaction

! Poster by M. Haidar on Wednesday !

NRQED Lagrangian

$$\mathcal{L} = \psi^+ \Big\{ iD_t + \frac{\mathbf{D}^2}{2m} + \frac{\mathbf{D}^4}{8m^3} + c_F \frac{q}{2m}\boldsymbol{\sigma}\cdot\mathbf{B} + c_D \frac{q}{8m^2}(\nabla\cdot\mathbf{E} - \mathbf{E}\cdot\nabla) + c_S \frac{iq}{8m^2}\boldsymbol{\sigma}\cdot(\mathbf{D}\times\mathbf{E} - \mathbf{E}\times\mathbf{D})$$

$$+ c_{W1}\frac{q}{8m^3}\{\mathbf{D}^2, \boldsymbol{\sigma}\cdot\mathbf{B}\} - c_{W2}\frac{q}{4m^3}D^i\boldsymbol{\sigma}\cdot\mathbf{B}D^i + c_{p'p}\frac{q}{8m^3}(\boldsymbol{\sigma}\cdot\mathbf{D}\mathbf{B}\cdot\mathbf{D} + \mathbf{D}\cdot\mathbf{B}\boldsymbol{\sigma}\cdot\mathbf{D}) + ic_M\frac{q}{8m^3}\{\mathbf{D}^i, [\nabla\times\mathbf{B}]^i\}$$

$$+ c_{A1}\frac{q^2}{8m^3}(\mathbf{B}^2 - \mathbf{E}^2) - c_{A2}\frac{q^2}{16m^3}\mathbf{E}^2 + \ldots \Big\}\psi \quad + \quad \text{contact terms}$$

ψ : two-component spinor $\qquad D_t = \partial/\partial t + iqA^0 \qquad D^i = \partial/\partial x^i - iqA^i$

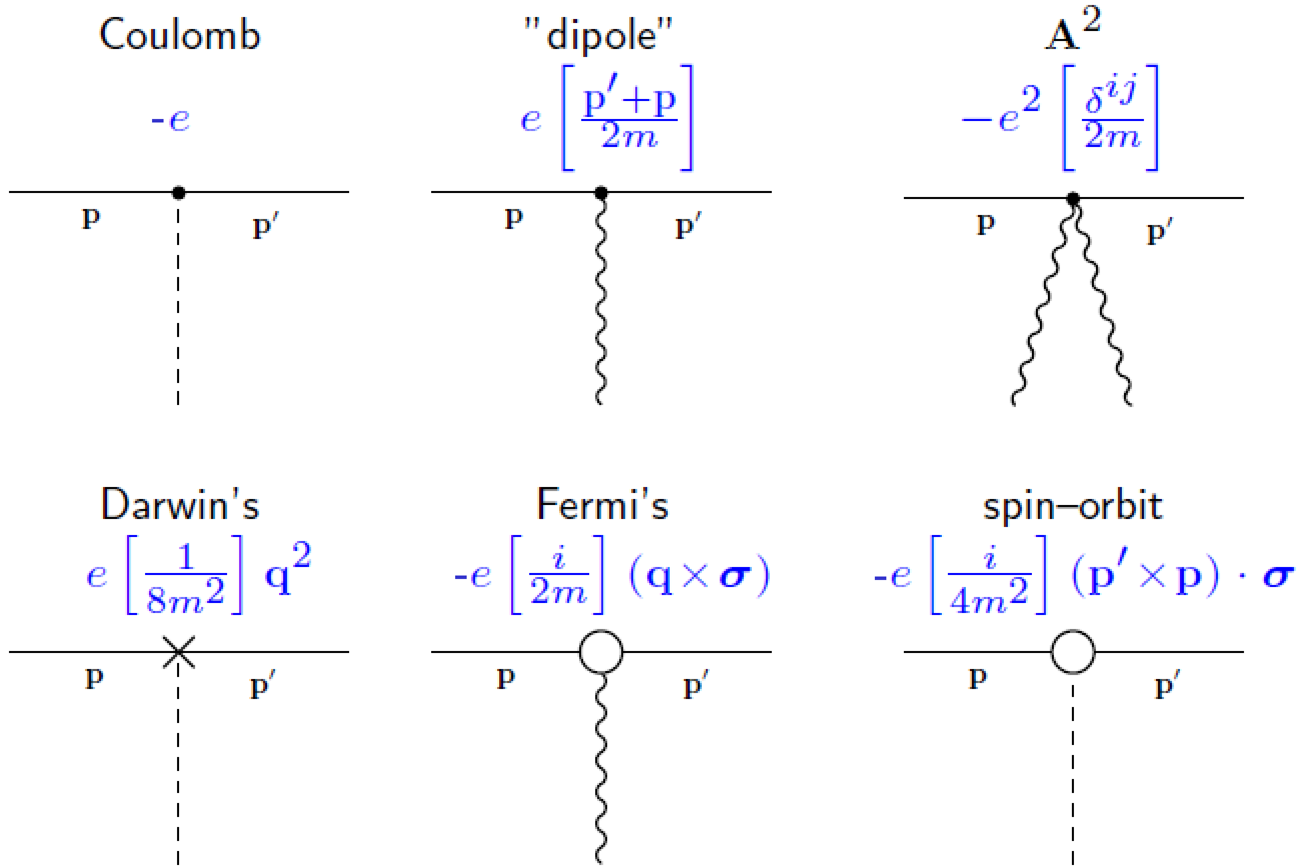
- The coefficients of the Lagrangian are fixed by imposing that the NRQED and QED scattering amplitudes coincide to the desired order in α.

For an electron:
$$c_F = 1 + a_e$$
$$c_S = 1 + 2a_e$$
$$\ldots$$

T. Kinoshita, M. Nio, PRD **53**, 4909 (1996)
R.J. Hill, G. Lee, G. Paz, M.P. Solon, PRD **87**, 053017 (2013)

Perturbation theory

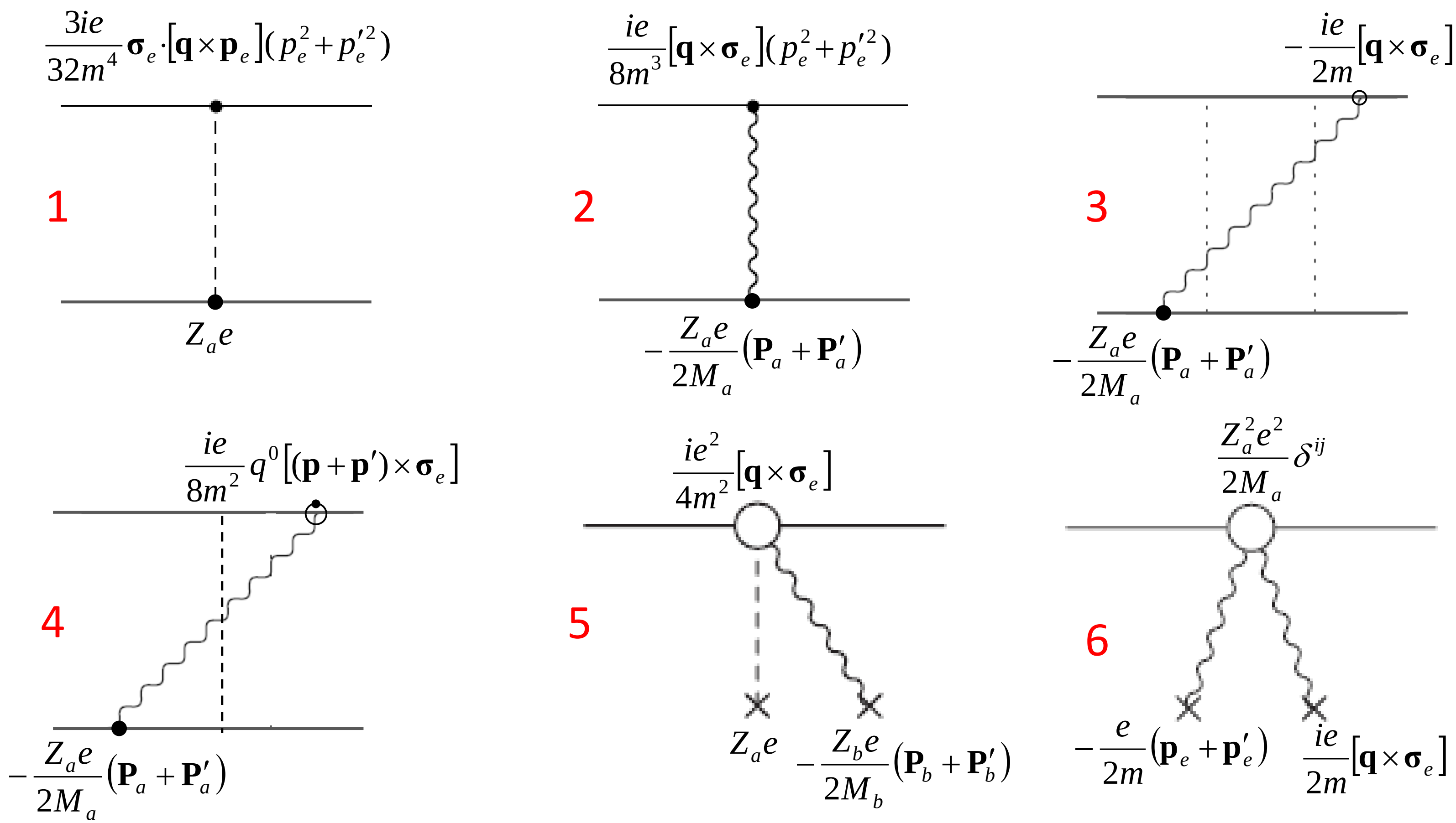
NRQED Feynam rules (electron case)



(Here $e > 0$ is the elementary charge)

Diagrams contributing to the spin-orbit interaction

at orders $m\alpha^6$ and $m\alpha^6(m/M)$



Effective potentials

Nonrecoil
[mα⁶]

$$\mathcal{U}_1 = -\frac{3Z_a}{16m^4}\left\{p_e^2, \frac{1}{r_a^3}[\mathbf{r}_a\times\mathbf{p}_e]\cdot\mathbf{s}_e\right\}$$

Recoil
[mα⁶(m/M)]

$$\begin{aligned}
\mathcal{U}_2 &= \frac{Z_a}{4m^3M_a}p_e^2\frac{1}{r_a^3}[\mathbf{r}_a\times\mathbf{P}_a]\cdot\mathbf{s}_e\\
\mathcal{U}_3 &= \frac{Z_a^2}{2m^2M_a}\left[\frac{1}{r_a^4}[\mathbf{r}_a\times\mathbf{p}_e] - \frac{iZ_b}{r_a^3R^3}[\mathbf{r}_a\times\mathbf{R}] + \frac{Z_b}{r_aR^3}[\mathbf{R}\times\mathbf{p}_e] + \frac{Z_b}{r_a^3R^3}[\mathbf{r}_a\times\mathbf{R}](\mathbf{r}_a\cdot\mathbf{p}_e)\right]\cdot\mathbf{s}_e\\
\mathcal{U}_{5a} &= \frac{Z_a^2}{4m^2M_a}\frac{1}{r_a^4}[\mathbf{r}_a\times\mathbf{P}_a]\cdot\mathbf{s}_e\\
\mathcal{U}_{5b} &= \frac{Z_aZ_b}{4m^2M_a}\left[\frac{1}{r_ar_b^3}[\mathbf{r}_b\times\mathbf{P}_a] - \frac{1}{r_a^3r_b^3}[\mathbf{r}_a\times\mathbf{r}_b](\mathbf{r}_a\cdot\mathbf{P}_a)\right]\cdot\mathbf{s}_e\\
\mathcal{U}_6 &= -\frac{Z_a^2}{2m^2M_a}\frac{1}{r_a^4}[\mathbf{r}_a\times\mathbf{p}_e]\cdot\mathbf{s}_e
\end{aligned}$$

Total $m\alpha^6$-order correction

The total energy shift is

$$\Delta E^{(6)} = \left\langle H^{(6)} \right\rangle + \left\langle H^{(4)} Q (E_0 - H_0)^{-1} H^{(4)} \right\rangle$$

For spin-orbit interactions, the following second-order terms contribute:

Nonrecoil [$m\alpha^6$]

$$\Delta E^{(6)}_{B-SO} = 2\left\langle H_B Q (E_0 - H_0)^{-1} Q H_{SO} \right\rangle$$

$$\Delta E^{(6)}_{SO-SO} = \left\langle H_{SO} Q (E_0 - H_0)^{-1} Q H_{SO} \right\rangle$$

Recoil [$m\alpha^6(m/M)$]

$$\Delta E^{(6)}_{B-SO_M} = 2\left\langle H_B Q (E_0 - H_0)^{-1} Q H_{SO_M} \right\rangle$$

$$\Delta E^{(6)}_{SO-SO_M} = 2\left\langle H_{SO} Q (E_0 - H_0)^{-1} Q H_{SO_M} \right\rangle$$

$$\Delta E^{(6)}_{SO-rec} = 2\left\langle H_{SO} Q (E_0 - H_0)^{-1} Q H_{rec} \right\rangle$$

Where

$$H_{SO} = \frac{Z_a \alpha (1 + 2a_e)}{2m^2} \frac{[\mathbf{r}_a \times \mathbf{p}_e]}{r_a^3} \cdot \mathbf{s}_e \qquad H_{SO_M} = -\frac{Z_a \alpha (1 + a_e)}{m M_a} \frac{[\mathbf{r}_a \times \mathbf{P}_a]}{r_a^3} \cdot \mathbf{s}_e$$

$$H_B = -\frac{p_e^4}{8m^3} + \frac{\pi Z_a \alpha}{2} \delta(\mathbf{r}_a) \qquad H_{rec} = \frac{Z_a \alpha}{2 m M_a} p_e^i \left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i r_a^j}{r_a^3} \right) P_a^j$$

Alternative form of the NRQED Lagrangian

$$H_{FW} = eA^0 + \frac{\pi^2}{2m} - \frac{e}{4m}\sigma^{ij}B^{ij} - \frac{\pi^4}{8m^3} + \frac{e}{16m^3}\{\sigma^{ij}B^{ij}, p^2\}$$
$$- \frac{e}{8m^2}(\vec{\nabla}\cdot\vec{E}_{\parallel} + \sigma^{ij}\{E^i_{\parallel}, p^j\}) + \frac{e^2}{2m^2}\sigma^{ij}E^i_{\parallel}A^j$$
$$+ \frac{ie}{16m^3}[\sigma^{ij}\{A^i, p^j\}, p^2] + \frac{e^2}{8m^3}\vec{E}^2_{\parallel}$$
$$+ \frac{3e}{32m^4}\{p^2, \sigma^{ij}E^i_{\parallel}p^j\} + \frac{5}{128m^4}[p^2, [p^2, eA^0]]$$
$$- \frac{3}{64m^4}\{p^2, \nabla^2(eA^0)\} + \frac{1}{16m^5}p^6,$$

V. Patkos, V.A. Yerokhin, K. Pachucki, PRA **94**, 052508 (2016)

- Obtained from the QED Lagrangian by Foldy-Wouthuysen transformation
- The last step eliminates the term involving $\mathbf{E}_{\perp} = -\partial_t \mathbf{A}$ ("time derivative vertex"), and modifies the transverse photon exchange and seagull terms

✓ Cross-checks:
- both forms reproduce known results for the FS and HFS of H(2p)
- they give identical results for HMI

Singularities in second-order terms

- No divergences, but some second-order terms are singular

$$\Delta E^{(6)}_{B-SO} = 2\langle\psi_0|H_{SO}Q(E_0-H_0)^{-1}QH_B|\psi_0\rangle = 2\langle\psi_0|H_{SO}|\psi^{(1)}\rangle,$$

$$(E_0-H_0)\psi^{(1)} = QH_B\psi_0$$

$$\psi^{(1)} \sim \frac{c_1}{r_1}+\frac{c_2}{r_2}$$

- The $1/r$ singularity is separated in the following way:

$$\langle H_{SO}Q(E_0-H_0)^{-1}QH_B\rangle = \langle H_{SO}Q(E_0-H_0)^{-1}QH'_B\rangle + \langle H_{SO}U\rangle - \langle H_{SO}\rangle\langle U\rangle$$

$$U = \frac{c_1}{r_1}+\frac{c_2}{r_2} \qquad H'_B = H_B-(E_0-H_0)U-U(E_0-H_0)$$

- a $\ln(r)$ singularity remains, leading to slow convergence.

V.I. Korobov and Z.-X. Zhong, PRA **80**, 042506 (2009)

Numerical calculations

- "Exponential" variational expansion V.I. Korobov, PRA **61**, 064503 (2000)

$$\psi^{\Pi}_{LM}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{l_1+l_2=L\ \mathrm{or}\ L+1}\mathcal{Y}^{l_1l_2}_{LM}(\mathbf{r}_1,\mathbf{r}_2)F_{l_1}(r_1,r_2,r_{12})$$

where $\mathcal{Y}^{l_1l_2}_{LM}(\mathbf{r}_1,\mathbf{r}_2)=r_1^{\,l_1}r_2^{\,l_2}Y^{l_1l_2}_{LM}(\theta_1,\phi_1,\theta_2,\phi_2)$

$$F(r_1,r_2,r_{12})=\sum_{n=1}^{N}\left(C_n\,\mathrm{Re}\left(e^{-\alpha_n r_1-\beta_n r_2-\gamma_n r_{12}}\right)+D_n\,\mathrm{Im}\left(e^{-\alpha_n r_1-\beta_n r_2-\gamma_n r_{12}}\right)\right)$$

- Matrix elements for all effective operators are calculated analytically.

- Typically:

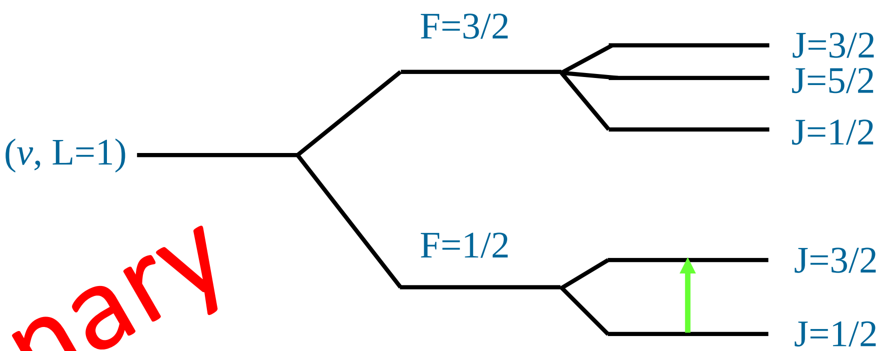
  N ~ 2000-4000 for first-order terms and regular second-order terms

  N ~ 7000-10000 for singular second-order terms (3 digits accuracy)

Comparison with experiments: H_2^+

$$H_{eff} = b_F\left(\mathbf{I}.\mathbf{s}_\mathbf{e}\right) + c_e\left(\mathbf{L}.\mathbf{s}_\mathbf{e}\right) + c_I\left(\mathbf{L}.\mathbf{I}\right) + \frac{d_1}{(2L-1)(2L+3)}\left\{\frac{2}{3}\mathbf{L}^2\left(\mathbf{I}.\mathbf{s}_\mathbf{e}\right) - \left[(\mathbf{L}.\mathbf{I})(\mathbf{L}.\mathbf{s}_\mathbf{e}) + (\mathbf{L}.\mathbf{s}_\mathbf{e})(\mathbf{L}.\mathbf{I})\right]\right\}$$

$$+ \frac{d_2}{(2L-1)(2L+3)}\left\{\frac{1}{3}\mathbf{L}^2\mathbf{I}^2 - \frac{1}{2}(\mathbf{L}.\mathbf{I}) - (\mathbf{L}.\mathbf{I})^2\right\}$$



Preliminary

RF spectroscopy experiments

S.C. Menasian, PhD Thesis (1973)

ro-vibrational level	Δc_e (kHz)
$(L=1, v=4)$	0.81
$(L=1, v=5)$	0.74
$(L=1, v=6)$	0.67

[1]	This work (present)	Experiment
15.371049	15.371447	15.371407(2)
14.381189	14.381553	14.381513(2)
13.413169	13.413498	13.413460(2)

Unit : MHz

[1] V.I. Korobov, J.C.J. Koelemeij, L. Hilico, J.-Ph. Karr, PRL **116**, 043001 (2016)

Summary

- Relativistic corrections to the spin-orbit interaction coefficient in the hfs of HMI have been calculated.

- Agreement with H_2^+ RF spectroscopy data is improved by about 1 order of magnitude ;

  Further improvement may be obtained by including the $m\alpha^7\ln(\alpha)$ radiative correction.

- Numerical calculations of the correction to ***tensor interactions*** are in progress.

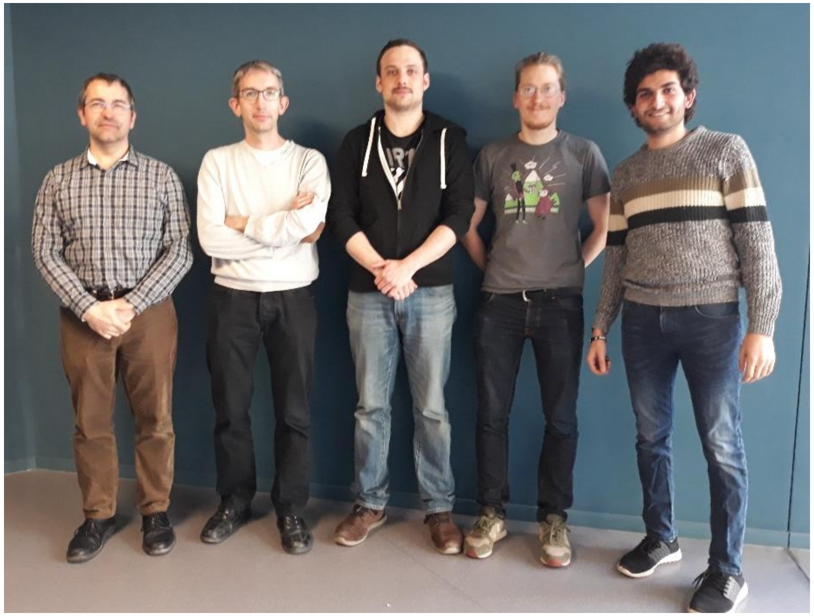
- Theoretical predictions should then no longer be limited by hfs

- Next priority will be to improve further the theory of spin-averaged transition frequencies.

Acknowledgements

LKB Paris

Laurent Hilico, JPK, Thomas Louvradoux, Julian Schmidt, **Mohammad Haidar**



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