Nonrelativistic and relativistic QED calculations in molecular hydrogen ions

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Introduction

Experimental progress in MHI spectroscopy

cf. talks S. Schiller, F. Schmid, M. Bohman

- Ro-vibrational spectroscopy ($\sim 10^{-12}$)
  - Determination of fundamental constants
  - Constraints on SI new physics

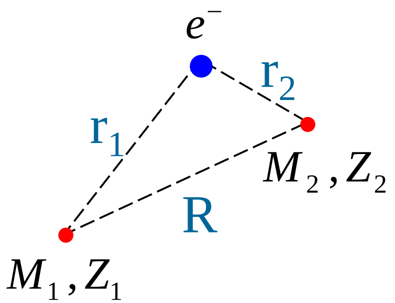
Energy level theory

- RF spectroscopy of the spin structure
  - Hyperfine structure ($\sim 10^{-8} - 10^{-9}$)
    - Extraction of spin-averaged RV frequencies
    - Constraints on SD new physics
  - g-factor ($\sim 10^{-10}$)
    - Test of molecular QED

HFS theory

g-factor theory

Theoretical approaches to MHIs



- Weakly relativistic ($Z_1 = Z_2 = 1$) three-body system

  $\Rightarrow$ ***Non Relativistic QED (NRQED) approach***

- NRQED Lagrangian of interaction between a particle (electron or nucleon) and the electromagnetic field.
  obtained via Foldy-Wouthuysen transformation [see e.g. K. Pachucki, PRA 71,012503 (2005)]
  or ab initio construction and matching with QED [see e.g. G. Paz, arXiv:1503.07216]

- Non relativistic perturbation theory
  Zero-order: numerical solution of three-body Schrödinger equation

- Corrections expanded in powers of $\alpha, Z\alpha, m/M$

- High-order corrections evaluated in the ***Adiabatic Approximation (AA)***

$$\psi_{\mathrm{ad}}(\mathbf{r}, R) = \phi_{\mathrm{el}}(\mathbf{r}; R)\, \chi_{\mathrm{ad}}(R)$$

1-body problem: bound electron in a two-center potential $V = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2}$

$\Rightarrow$ ***Nonrelativistic or relativistic QED calculations***

Numerical solution of electronic Schrödinger or Dirac equation

The bound-electron g factor

- Recently measured for $\mathrm{HD}^{+}(v = 0, L = 0)$ with $\sim 2 \times 10^{-10}$ accuracy
  single-ion Penning-trap experiment: ALPHATRAP (MPIK Heidelberg)
  cf. talk M. Bohman

- Previous theoretical calculations: $\sim 10^{-7}$ accuracy
  leading-order $[(Z\alpha)^2]$ relativistic corrections
  - nonrecoil, adiabatic approximation — R.A. Hegström, PRA **19**, 17 (1979)
  - with recoil, exact three-body approach — J.-Ph. Karr, PRA **104**, 032822 (2021)

- Possibility to test g-factor QED theory with high precision in a molecule

QED corrections to the g factor

NRQED expansion: $g = 2 + \frac{\alpha}{\pi} + \Delta g^{(2)} + \Delta g^{(3)} + \Delta g^{(4)} + \Delta g^{(5)} + \cdots$

for each $\Delta g^{(n)}$: expansion in m/M

✓ α^2 order: leading relativistic corrections ⟵ With recoil, three-body

- α^3 order: form factor correction (anomalous magnetic moment)
- α^4 order: next-to-leading order relativistic correction

  Dirac g-factor g^{rel}

  $\Longrightarrow \Delta g^{\mathrm{rel}(4+)} = \Delta g^{\mathrm{rel}} - \Delta g^{(2)-\mathrm{adiab}}$
- α^5 order: one-loop self-energy and vacuum polarization

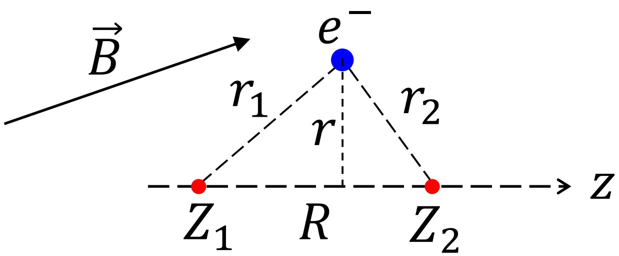
} Nonrecoil, adiabatic

Molecular g-factor anisotropy

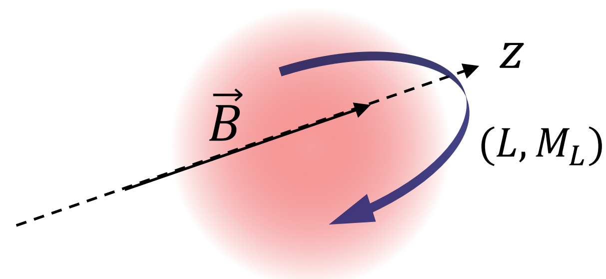
In molecular systems: anisotropy → g ***tensor***

$$H_{\text{eff}} = \frac{e}{2m_e} \sum_{ij} g_{ij} s_e^i B^j$$

Adiabatic approximation



3-body description



$g_\parallel = g_{zz}\,;\, g_\perp = g_{xx} = g_{yy}$ ⟷ $g = g_s + g_t$

scalar rank 2

$$g_s = (2g_\perp + g_\parallel)/3 \;\;,$$

$$g_t = \sqrt{\frac{L(L+1)}{(2L-1)(2L+3)}}(g_\perp - g_\parallel)$$

$$g(v, L, M_L) = g_s(v, L) + \frac{3M_L^2 - L(L+1)}{L(L+1)(2L-1)(2L+3)} g_t(v, L)$$

Dirac g-factor calculation

$$H_{\rm int} = -\frac{c}{2}\boldsymbol{\alpha}\cdot(\mathbf{r}\times\mathbf{B})$$

Electronic ground state ($1s\sigma$): two degenerate $m = \langle J_z \rangle = \pm 1/2$ states

$$|\Psi_+\rangle = \begin{bmatrix} \psi_1 \\ \psi_2\, e^{i\phi} \\ i\psi_3 \\ i\psi_4\, e^{i\phi} \end{bmatrix} \qquad |\Psi_-\rangle = \widehat{\mathcal{T}}|\Psi_+\rangle = \begin{bmatrix} -\psi_2\, e^{-i\phi} \\ \psi_1 \\ i\psi_4\, e^{-i\phi} \\ -i\psi_3 \end{bmatrix}$$

$$H_{\rm int}^{(0)} = \begin{bmatrix} \langle\Psi_+|H_{\rm int}|\Psi_+\rangle & \langle\Psi_+|H_{\rm int}|\Psi_-\rangle \\ \langle\Psi_-|H_{\rm int}|\Psi_+\rangle & \langle\Psi_-|H_{\rm int}|\Psi_-\rangle \end{bmatrix}$$

$$g_{\parallel}^{\rm rel} = 8\pi\, c\,(\langle\psi_1|\rho|\psi_4\rangle_{\rm rad} - \langle\psi_2|\rho|\psi_3\rangle_{\rm rad})$$
$$g_{\perp}^{\rm rel} = 4\pi\, c\,(\langle\psi_1|\rho|\psi_4\rangle_{\rm rad} + \langle\psi_2|\rho|\psi_3\rangle_{\rm rad} + 2\langle\psi_1|z|\psi_3\rangle_{\rm rad})$$

- Numerical calculation for a range of internuclear distances using min-max finite-element method

  O. Kullie and S. Schiller, PRA **105**, 052801 (2022) ; O. Kullie, PRA **110**, 052808 (2024).

- Averaging over relativistically corrected vibrational wavefunctions

Radiative corrections

- α^3 order: form factor correction (anomalous magnetic moment)

$$\Delta g_{\perp}^{(3+)} = \frac{\alpha^2}{4}\,(g_e - 2)\langle p_e^2 + p_{ez}^2\rangle$$

$$\Delta g_{\parallel}^{(3+)} = \frac{\alpha^2}{2}\,(g_e - 2)\langle p_e^2 - p_{ez}^2\rangle$$

R.A. Hegström, PRA **19**, 17 (1979)

Estimated uncertainty $\sim 2\,(m_e/m_p)\,\Delta g^{(3+)}$

- α^5 order: one-loop self-energy and vacuum polarization

From H atom theory:

$$\Delta g_{SE}^{(5)\ln} = \frac{32}{9}\alpha^5 \ln(\alpha^{-2})\,\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle$$

$$\Delta g_{SE}^{(5)} \simeq a_{40}(1S)\alpha^5\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle$$

K. Pachucki et al., PRL **93**, 150401 (2004)

with $a_{40}(1S) = -10.236\,524\,318(1)$

Estimated uncertainty $\sim 100\%$ of $\Delta g_{SE}^{(5)}$

$$\Delta g_{VP}^{(5)} \simeq -\frac{16}{15}\alpha^5\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle$$

S.G. Karshenboim, Phys. Lett. A **266**, 380 (2000)

Results for HD^+

Order	Type of contrib.	$g(v=0,L=0)$	$g_s(v=0,L=1)$	$g_t(v=0,L=1)$
1	Free	−2.002 319 304 36	−2.002 319 304 36	
$(Z\alpha)^2(m/M)^n$	Relativistic + rec.	0.000 040 812 41	0.000 040 783 24	0.000 001 064 00
$\alpha(Z\alpha)^2$	One-loop radiative	−0.000 000 049 05(5)	−0.000 000 049 02(5)	0.000 000 004 66
$(Z\alpha)^4 + \mathrm{h.o.}$	Relativistic (*)	0.000 000 000 52	0.000 000 000 51	0.000 000 000 01
$\alpha(Z\alpha)^4$	One-loop SE	−0.000 000 000 20(9)	−0.000 000 000 20(9)	0.000 000 000 00
	Total [1]	−2.002 278 540 70(10)	−2.002 278 569 83(10)	0.000 001 068 66(1)
	Previous [2]	−2.002 278 5(2)		
	Experiment [3]	−2.002 278 540 96(40)		

- ✓ Accuracy improved from 10^{-7} to 5.0×10^{-11}
- ✓ Good agreement with experimental value

[1] O. Kullie, H.D. Nogueira, J.-Ph. Karr, PRA **112**, 052813 (2025)
[2] R.E. Hegstrom, PRA **19**, 17 (1979)
[3] C. König et al., PRL **136**, 143002 (2026)

Hyperfine structure effects

D. Bakalov
S. Schiller

- Higher-order terms involving hyperfine interactions need to be considered

$$h^{\text{pert}} = h^{\text{Z}} + h^{\text{spin}} + h^{\text{D}}$$

$$h^{\text{Z}} = -\mu_{\text{B}}\left(g_{\text{e}}\mathbf{B}\cdot\mathbf{s}_e + g_{\text{p}}\mathbf{B}\cdot\mathbf{I}_p + g_{\text{d}}\mathbf{B}\cdot\mathbf{I}_d\right)$$
$\approx$ 112 GHz

$$h^{\text{D}} = h^{\text{D0}} + h^{\text{D2}}, \quad \approx 10\ \text{kHz}$$
$$h^{\text{D0}} = \frac{e^2}{12m_{\text{e}}}\mathbf{B}^2\mathbf{r}_e^2$$
$$h^{\text{D2}} = -\frac{e^2}{24m_{\text{e}}}\left(3(\mathbf{r}_e\cdot\mathbf{B})^2 - \mathbf{B}^2\mathbf{r}_e^2\right)$$

$$h^{\text{spin}} = h^{\text{F}} + h^{\text{SO}} + h^{\text{T}},$$
$$h^{\text{F}} = \frac{8\pi}{3}\mu_{\text{B}}^2\big(g_{\text{p}}g_{\text{e}}\delta(\mathbf{r}_{pe})(\mathbf{I}_p\cdot\mathbf{s}_e) \quad \approx 1\ \text{GHz}$$
$$+g_{\text{d}}g_{\text{e}}\delta(\mathbf{r}_{de})(\mathbf{I}_d\cdot\mathbf{s}_e)\big)$$
$$h^{\text{T}} = -\mu_{\text{B}}^2\Bigg(\frac{g_{\text{e}}g_{\text{p}}}{r_{pe}^5}\left(3(\mathbf{r}_{pe}\cdot\mathbf{s}_e)(\mathbf{r}_{pe}\cdot\mathbf{I}_p) - \mathbf{r}_{pe}^2(\mathbf{s}_e\cdot\mathbf{I}_p)\right)$$
$$+\frac{g_{\text{e}}g_{\text{d}}}{r_{de}^5}\left(3(\mathbf{r}_{de}\cdot\mathbf{s}_e)(\mathbf{r}_{de}\cdot\mathbf{I}_d) - \mathbf{r}_{de}^2(\mathbf{s}_e\cdot\mathbf{I}_d)\right)\Bigg)$$

- Largest term: 3rd-order hyperfine-dependent correction to *g*-factor, few 10^{-11}

$$\Delta^{(\text{TZT})}E_{00,n}(B) = (E_{00}^{(0)} - E_{02}^{(0)})^{-2}\sum_{n',n''}\langle 00,n|h^{\text{T}}|02,n'\rangle\langle 02,n'|h^{\text{Z}}|02,n''\rangle\langle 02,n''|h^{\text{T}}|00,n\rangle$$
$$-\langle 00,n|h^{\text{Z}}|00,n\rangle\sum_{n'}\langle 00,n|h^{\text{T}}|02,n'\rangle^2(E_{00}^{(0)} - E_{02}^{(0)})^{-2}$$

- Much larger corrections w.r.t. atoms, due to small (ro-vibr.) energy denominators

C. König et al., PRL 2026, Supplemental Material

Perspectives

- Hyperfine effects complicate theoretical calculations

  ...but absent in para-$\mathrm{H}_2^+/\mathrm{D}_2^+/\mathrm{T}_2^+$

- Next terms to consider

  radiative-recoil correction of order $\alpha(Z\alpha)^2(m/M)$

  one-loop self-energy correction of order $\alpha(Z\alpha)^4$

- Experimental possibilities: g-factor differences [1]

  SM test: comparison $\mathrm{He}^+/\mathrm{H}_2^+$ or $\mathrm{H}_2^+(v,L)/\mathrm{H}_2^+(v',L')$

  Compare e^+/e^- g-factors with e^+/He^+ ... or e^+/H_2^+ (LSYM project, MPIK Heidelberg)

[1] T. Sailer et al., Nature **606**, 479 (2022)

Status of theory – Example: HD^+, $(v, L) = (0,3) \rightarrow (9,3)$

Nonrelativistic transition frequency (3-body Schrödinger eq.): f_{09}^{nr} = 415 260 910 671.9 kHz

Type of correction	Framework	Evaluated orders	Δf_{09} (kHz)
Relativistic	3-body **AA→3-body**	$m(Z\alpha)^4$ (with recoil) $m(Z\alpha)^6$	5 667 052.3 129.6(0.1)
Relativistic-recoil	3-body 3-body	$m(Z\alpha)^5(m/M)$ $m(Z\alpha)^6(m/M)$ (partial + estimated)	-320.8 1.2(0.1)
1-loop self-energy	3-body AA AA	$m\alpha(Z\alpha)^4$, $m\alpha(Z\alpha)^5$ $m\alpha(Z\alpha)^6$ $m\alpha(Z\alpha)^7$ (partial) + estimated HO	-1 695 245.8(0.1) 651.1(0.3) -6.3**(2.6)**
1-loop vacuum polarization muonic VP hadronic VP	3-body AA 3-body 3-body	$m\alpha(Z\alpha)^4$, $m\alpha(Z\alpha)^5$ $m\alpha(Z\alpha)^6$, $m\alpha(Z\alpha)^7$ Leading order Leading order	43 650.3 15.8 1.0 0.7
2-loop radiative	3-body AA	$m\alpha^2(Z\alpha)^4$, $m\alpha^2(Z\alpha)^5$ $m\alpha^2(Z\alpha)^6$ (partial) + estimated HO	-272.4 0.9(1.8)
3-loop radiative	3-body	$m\alpha^3(Z\alpha)^4$	-0.4
Nuclear finite size and polarizability (+ rad. corr.)	3-body 3-body	$m(Z\alpha)^4$; for deuteron only : $m(Z\alpha)^5, m(Z\alpha)^6$(partial)	-830.6 1.8
Radiative-recoil	3-body	$m\alpha(Z\alpha)^5(m/M)$	2.1

Talk D. Ferenc
Poster M. Panet

Total transition frequency: f_{09} = 415 264 925 502.7**(3.2)** kHz

$u_r = 7.8 \times 10^{-12}$

V.I. Korobov and J.-Ph. Karr, PRA **104**, 032806 (2021)

$m\alpha^6$ relativistic and recoil corrections: 3-body calculation

- $m\alpha^6$-order NRQED Hamiltonian

Nonrecoil : $H^{(6)} = \frac{p_e^6}{16m^5} - \frac{3}{64m^4}\{p_e^2, \Delta V\} + \frac{5}{128m^4}\{p_e^4, V\} - \frac{5}{64m^4}\left(p_e^2 V p_e^2\right) + \frac{1}{8m^3}\mathbf{E}^2$

$$\Delta E^{2^{nd}-order} = \left\langle H_B Q(E_0 - H_0)^{-1} Q H_B \right\rangle + \left\langle H_{so} Q(E_0 - H_0)^{-1} Q H_{so} \right\rangle^{(0)}$$

Recoil, low-energy part :

$$H_{rec}^{(6)} = -\frac{1}{4}\{p_e^2, H_{ret}\} + \frac{3}{8}\left[\frac{Z_1^2}{M_1}\frac{1}{r_1^4} + \frac{Z_2^2}{M_2}\frac{1}{r_2^4}\right] + \frac{1}{4}\left[\frac{Z_1^3}{M_1}\frac{1}{r_1^3} + \frac{Z_2^3}{M_2}\frac{1}{r_2^3} + \frac{Z_1^2 Z_2}{M_1}\frac{(\boldsymbol{r}_1\boldsymbol{r}_2)}{r_1^2 r_2^3} + \frac{Z_1 Z_2^2}{M_2}\frac{(\boldsymbol{r}_1\boldsymbol{r}_2)}{r_1^3 r_2^2}\right]$$
$$+\frac{1}{4}\left[\frac{Z_1^2}{M_1}\mathbf{p}_e\frac{1}{r_1^2}\mathbf{p}_e + \frac{Z_2^2}{M_2}\mathbf{p}_e\frac{1}{r_2^2}\mathbf{p}_e\right]$$

$$\Delta E_{rec}^{2^{nd}-order} = 2\left\langle H_B Q(E_0 - H_0)^{-1} Q H_{ret} \right\rangle$$

V.I. Korobov, J.-Ph. Karr, M. Haidar, and Z.-X Zhong, PRA **102**, 022804 (2020)
Z.-X. Zhong, W.-P. Zhou, and X.-S. Mei, PRA **98**, 032502 (2018)
V. Patkós, V.A. Yerokhin, and K. Pachucki, PRA **94**, 052508 (2016) (helium)

- Singularities in first- and second-order contributions require regularization
  - ✓ Nonrecoil part, adiabatic approximation: V.I. Korobov, J. Phys. B **40**, 2661 (2007)

Separation of divergences

Example: $\langle p_e^6 \rangle$

$p_e^2\psi_0 = -2V_\mu\psi_0 + \psi_{reg}$, $\quad$ $\mathrm{V}_\mu = -\mu_1\frac{Z_1}{r_1} - \mu_2\frac{Z_2}{r_2}$ $\quad$ $\mu_i = \frac{mM_i}{m+M_i}$

$\Rightarrow$ "regularized" p_e^2 operator : $p_\mu^2 = p_e^2 + 2V_\mu$

$p_\mu^2\psi_0$ is a regular function.

Similarly: $p_\mu^4 = p_e^4 - 2\big(4\pi\rho_\mu\big)$, $\quad$ $\rho_\mu = \mu_1 Z_1\delta(\mathbf{r_1}) + \mu_2 Z_2\delta(\mathbf{r_2})$

$p_\mu^4\psi_0 \sim 1/r_i^2$ at $r_i \to 0$.

$$\langle p_e^6\rangle = \boxed{-4\big\langle V_\mu\big(4\pi\rho_\mu\big)\big\rangle} + 2\big\langle p_\mu^2\big(4\pi\rho_\mu\big)\big\rangle + \langle p_\mu^2 p_\mu^4\rangle - 2\big\langle V_\mu\big(p_e^2 p_\mu^2\big)\big\rangle + 4\langle \mathbf{p}_e V_\mu^2 \mathbf{p}_e\rangle$$

Singular part

Regular expectation values:

- Expansion and "direct" calculation, or
- "product" calculation, e.g. $\langle\psi_0|p_\mu^2 p_\mu^4|\psi_0\rangle = \sum_n \langle\psi_0|p_\mu^2|\psi_n\rangle\langle\psi_n|p_\mu^4|\psi_0\rangle$

V.I. Korobov, PRA **112**, 022808 and 022813 (2025)

First numerical evaluation: Z.-X. Zhong et al., arXiv:2603.07858

Numerical results: nonrecoil part

Unit: kHz

$L = 0$ states		H_2^+ $v=0$	H_2^+ $v=1$	H_2^+ $v=0\to1$	HD^+ $v=0$	HD^+ $v=1$	HD^+ $v=0\to1$
$\langle H'^{(6)} \rangle$	AA [1]	4569.22	4448.40	-120.82	4578.10	4472.44	-105.66
	Z26 [2]				4556.65	4427.15	-129.50
	TW	4543.13			**4556.61**		
$E'^{(6)}_{2nd}$	E'_B(AA) [1]	-5637.67	-5498.52	139.16	-5648.01	-5526.05	121.96
	E'_B(3-b) [3]	-5595.92	-5431.84	164.08	-5614.86	-5470.54	144.32
	E'_S(AA) [1]	-159.46	-148.37	11.09	-160.27	-150.58	9.68
	E'_S(3-b) [3]	-159.36	-148.29	11.08	-160.19	-150.52	9.68
Total	AA [1]	-1227.91	-1198.49	**29.42**	-1230.18	-1204.19	25.99
	Z26 [2]				-1218.41	-1193.91	24.50
	TW	-1212.15			**-1218.45**		

[1] V.I. Korobov, J.-Ph. Karr, PRA **104**, 032806 (2021)
[2] Z.-X. Zhong et al., arXiv:2603.07858
[3] V.I. Korobov, J.-Ph. Karr, Z.-X. Zhong, Mol. Phys. e2563023 (2025)

Numerical results: recoil part (PRELIMINARY!)

Unit: kHz

$L = 0$ states		H_2^+			HD^+		
		$v = 0$	$v = 1$	$v = 0 \to 1$	$v = 0$	$v = 1$	$v = 0 \to 1$
$\langle H'^{(6)}_{\rm rec} \rangle$	Z26 [2]				24.23	23.57	-0.66
	TW	7.74			5.83		
$E'^{(6)2\rm nd}_{\rm rec}$	3-b [3]	-29.51	-28.63	0.88	-22.19	-21.60	0.59
Total	Est. [1]	-10.43	-10.15	**0.27**	-7.84	-7.66	**0.18**
	Z26 [2]				2.04	1.96	**-0.08**
	TW	-21.77			-16.36		

[1] V.I. Korobov, J.-Ph. Karr, PRA **104**, 032806 (2021)

[2] Z.-X. Zhong et al., arXiv:2603.07858

[3] V.I. Korobov, J.-Ph. Karr, Z.-X. Zhong, Mol. Phys. e2563023 (2025)

$m\alpha^6$-order corrections: conclusions

- Nonrecoil part
  - good agreement with Zhong's results
  - unexpectedly large deviation (~1%) between adiabatic and 3-body results

- Recoil part
  - work in progress !

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Corrections to the g-factor : expanded version

Contribution	Order	$HD^+(v=0, N=0)$	H-like atom (1s) $(Z=1)$
free electron: g_e		−2.002 319 304 36	
relativistic	$(Z\alpha)^2$	0.000 040 776 46	0.000 035 500 90
	$(Z\alpha)^4$	0.000 000 000 52	0.000 000 000 47
one-loop QED	$\alpha(Z\alpha)^2$	−0.000 000 028 07	−0.000 000 020 62
	$\alpha(Z\alpha)^4$	−0.000 000 000 20(9)	−0.000 000 000 16
two-loop QED	$\alpha^2(Z\alpha)^2$	0.000 000 000 04	0.000 000 000 03
recoil	$(Z\alpha)^2(m/M)^n$	0.000 000 014 90	−0.000 000 021 77
radiative-recoil	$\alpha(Z\alpha)^2(m/M)^n$	0.000 000 000 01(5)	0.000 000 000 02
sum: $g_{e,\text{bound}}$		−2.002 278 540 70(10)	−2.002 283 845 48