

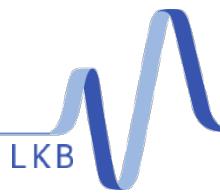
Theoretical study of molecular hydrogen ions in the low parts-per-trillion range

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Credits

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WIPM Wuhan



M. Sc.:
Louis Ritchie

+ VU team Amsterdam !

LKB Paris
experimental
team (H_2^+
spectroscopy)



Julian
Schmidt



Thomas
Louvradoux



Laurent
Hilico

Albane Douillet
Johannes Heinrich
Nicolas Sillitoe
Malcolm Simpson

M. Sc.:
Abdessamad Mbardi
Emmanuel Martins Seromenho

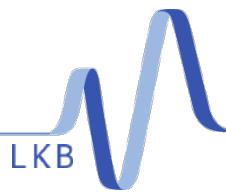


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* île de France

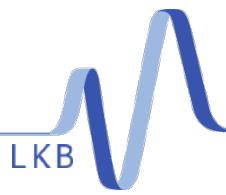
nano-K
Réseau Francilien
DES ATOMES FROIDS AUX NANOSCIENCES

IUF



Bound-state QED calculations in light few-body systems

- H, He⁺ proton radius, Rydberg constant, He nuclear radius } 2-body
- Ps, Mu “pure” QED test, BSM physics }
- H₂⁺, HD⁺, D₂⁺... nuclear-to-electron mass ratios, fifth-force tests }
- pHe antiproton-to-electron mass ratio: CPT test } 3-body
- He squared radii difference ; fine-structure constant }
- H₂, HD, D₂ ... dissociation energy } 4-body
(and more)
- Li, Be... isotope shifts }
- g-factor calculations in hydrogenlike, lithiumlike ions...



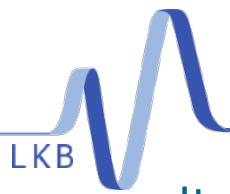
Approaches for calculation of QED corrections

- Bound states in QED
 - 1-body problem (e.g. H atom neglecting nuclear motion): Dirac equation
 - 2-body problem: Bethe-Salpeter equation, effective Dirac equation
 - 3-body and beyond: very complex!
- NonRelativistic Quantum Electrodynamics (NRQED) avoids these difficulties and is a powerful approach to calculate QED corrections in weakly bound ($Za \ll 1$) few-body systems, using the nonrelativistic (Schrödinger) wavefunctions.

Step 1: derive from QED the NRQED Lagrangian of interaction between a particle (electron or nucleon) and the EM field

Step 2: use it to determine QED corrections by systematic application of the nonrelativistic perturbation theory.

- effective Hamiltonian at the desired order
- numerical evaluation



Step 1: NRQED Lagrangian

It contains all possible local interactions satisfying the required symmetries: gauge invariance, parity, time reversal, Galilean invariance, hermiticity.

Coefficients fixed by imposing that the NRQED and QED scattering amplitudes coincide to the desired order in α .

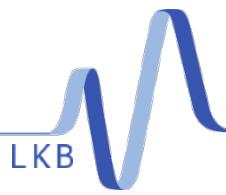
$$\begin{aligned} L_{\text{main}} = & \psi_e^* \left(i\partial_t - eA_0 + \frac{\mathbf{D}^2}{2m} + \frac{\mathbf{D}^4}{8m^3} + \frac{\mathbf{D}^6}{16m^5} + \dots \right) \psi_e & \mathbf{D} = \nabla - ie\mathbf{A} \\ & + \psi_e^* \left(c_F \frac{e}{2m} \boldsymbol{\sigma} \cdot \mathbf{B} + c_D \frac{e}{8m^2} (\mathbf{D} \cdot \mathbf{E} - \mathbf{E} \cdot \mathbf{D}) + c_S \frac{ie}{8m^2} \boldsymbol{\sigma} \cdot (\mathbf{D} \times \mathbf{E} - \mathbf{E} \times \mathbf{D}) \right. \\ & + \frac{e}{8m^3} \left\{ \mathbf{D}^2, \boldsymbol{\sigma} \cdot \mathbf{B} \right\} + \frac{3ie}{16m^4} \left\{ \mathbf{D}^2, \boldsymbol{\sigma} \cdot (\mathbf{D} \times \mathbf{E} - \mathbf{E} \times \mathbf{D}) \right\} \\ & \left. - \frac{3e}{64m^4} \left\{ \mathbf{D}^2, [\nabla, \mathbf{E}] \right\} - \frac{5e}{128m^4} [\mathbf{D}^2, (\mathbf{D} \cdot \mathbf{E} + \mathbf{E} \cdot \mathbf{D})] - \frac{e^2}{8m^3} \mathbf{E}^2 \right) \psi_e + \dots \end{aligned}$$

T. Kinoshita and M. Nio, PRD **53**, 4909 (1996)

R.J. Hill, G. Lee, G. Paz, M.P. Solon, PRD **87**, 053017 (2013)

Foldy-Wouthuysen transformation: e.g. V. Patkos, V.A. Yerokhin, K. Pachucki, PRA **94**, 052508 (2016)

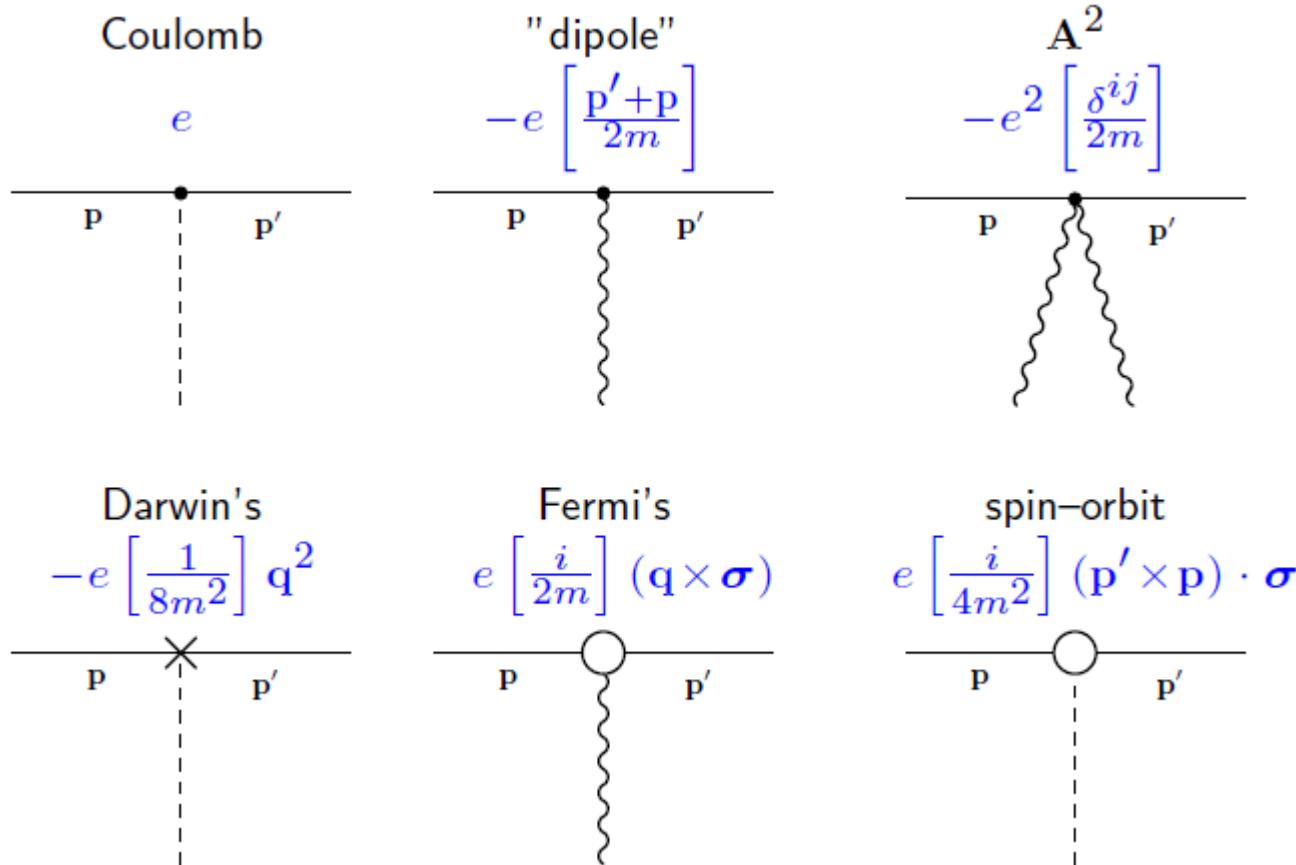
- Cutoff on the photon momentum: $k < \Lambda \sim m_e$
- Physics from relativistic momenta incorporated in the form of contact terms.

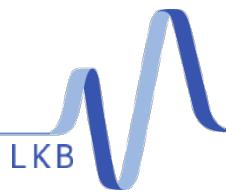


Step 2: perturbation theory

- Expansion in Feynman diagrams similarly to QED

In NRQED, interaction vertices are more numerous, but each NRQED diagram is simpler to calculate.



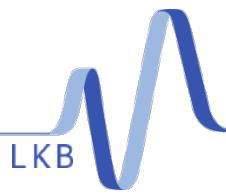


Classification of corrections

$m, -e$	$M, +Ze$	$\frac{v_e}{c} \approx Z\alpha$	$\frac{v_n}{c} \approx Z\alpha(m/M)$
 Electron	 Nuclei		

- NRQED is a “perturbative” method i.e. the binding potential is treated perturbatively \Rightarrow expansion in powers of $Z\alpha$ and m/M in addition to α
- In “nonperturbative” methods, only the α -expansion is done.
- Classification of corrections

$Z\alpha$	relativistic
$\alpha, Z\alpha$	radiative
$Z\alpha, m/M$	recoil
$\alpha, Z\alpha, m/M$	radiative-recoil



Theoretical “spin-averaged” transition frequency

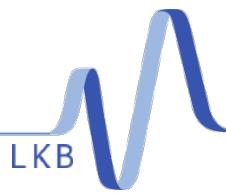
HD⁺ ($v = 0, L=3$) → ($v'=9, L'=3$) interval in kHz

with CODATA 2018 fundamental constants

HD ⁺	
ν_{nr}	415 260 910 672.1
$\Delta\nu_{m\alpha^4}$	5 666 221.7
$\Delta\nu_{m\alpha^5}$	-1 640 448.4
$\Delta\nu_{m\alpha^6}$	-11 666.7(1)
$\Delta\nu_{m\alpha^7}$	732.2(4)
$\Delta\nu_{m\alpha^8}$	-14.8(3.0)
ν_{tot}	415 264 925 496.2(3.1)

7.5 ppt

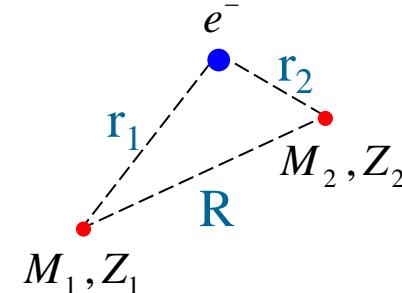
See V.I. Korobov, L. Hilico, J.-Ph. Karr, PRL **118**, 233001 (2017)



Nonrelativistic energy and wavefunction (1)

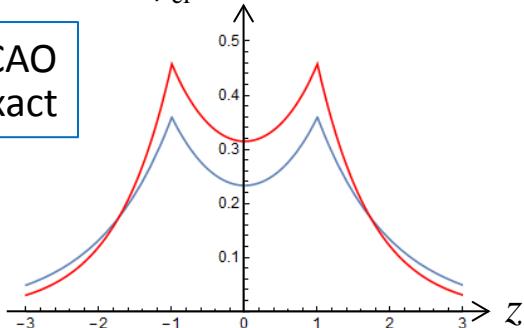
Born-Oppenheimer approximation:

$$\Psi^{\text{BO}} = \phi_{\text{el}}(\mathbf{r}; R) \chi_{\text{BO}}(R)$$



$$\phi_{\text{el}}(z) \quad (R = 2 \text{ a.u.})$$

— LCAO
— exact



$1s\sigma_g$ electronic wavefunction

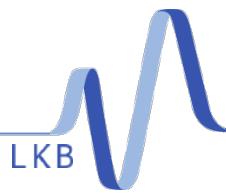
$$\phi_{\text{LCAO}}(r_1, r_2) = \frac{1}{\sqrt{2(1+S)}} [\phi_{1s}(r_1) + \phi_{1s}(r_2)]$$

Variational expansion:

$$\phi_{\text{el}}(r_1, r_2) = \sum_{i=1}^N C_i (e^{-\alpha_i r_1 - \beta_i r_2} + e^{-\beta_i r_1 - \alpha_i r_2})$$

Ts. Tsogbayar and V.I. Korobov, J. Chem. Phys. **125**, 024308 (2006)

- Energies accurate to $\sim(m/M)$; $(m/M)^2$ with adiabatic correction
- Wavefunctions accurate to $\sim(m/M)$



Nonrelativistic energy and wavefunction (2)

- Non-adiabatic corrections: perturbative expansion of E and ψ in powers of (m/M)
High orders required for 10^{-12} accuracy!
- Approach: nonadiabatic (3-body) calculations for NR energy and leading corrections
BO approximation for high-order corrections,
where $\sim(m/M)$ accuracy is enough to reach the precision goal.

3-body variational expansion

Separation of radial and angular variables:

$$\psi_{LM}^{\Pi}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{l_1+l_2=L \text{ or } L+1} Y_{LM}^{l_1 l_2}(\mathbf{r}_1, \mathbf{r}_2) F_{l_1}(r_1, r_2, r_{12})$$

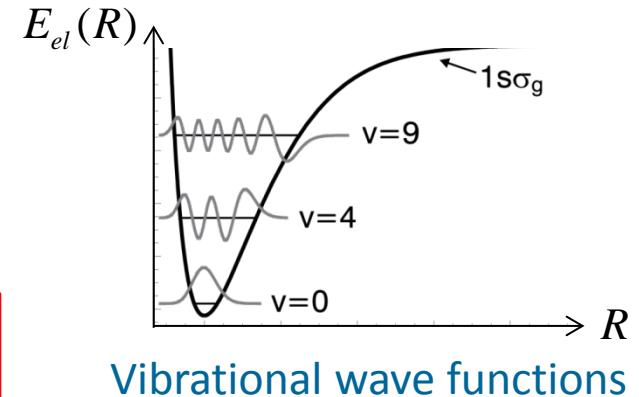
C. Schwartz, Phys. Rev. **123**, 1700 (1961)

Radial wavefunctions:

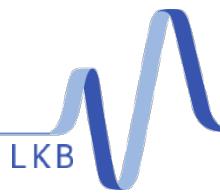
$$F(r_1, r_2, r_{12}) = \sum_{n=1}^N \left(C_n \operatorname{Re} \left(e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}} \right) + D_n \operatorname{Im} \left(e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}} \right) \right)$$

V.I. Korobov, Phys. Rev. A **61**, 064503 (2000)

Exponents generated pseudo-randomly in several intervals.



Vibrational wave functions



H_2^+ ground state : selected results

Author (year)	References	Method	N	Energy (a.u.)
Bishop (1977)	[17]	Var. elliptic	515	-0.5971390625
Moss (1993)	[25]	Transformed H		-0.59713906312(5)
Grémaud (1998)	[26]	Var. perimetric	31746*	-0.597139063123(1)
Moss (1999)	[27]	Var. elliptic		-0.5971390631234(1)
Hilico (2000)	[28]	Var. perimetric	66046*	-0.59713906312340(1)
Korobov (2000)	[19]	Var. exponential	2200	-0.597139063123405074
Bailey (2002)	[20]	Var. exponential	3500	-0.59713906312340507483
Cassar (2004)	[21]	Var. exponential	1052	-0.597139063123405074834338(3)
Li (2007)	[22]	Var. exponential	8381	-0.597139063123405074834134096026(5)
Hijikata (2009)	[29]	Free complement	19286	-0.5971390631234050748341340960260
Ning (2014)	[23]	Var. exponential	3806	-0.5971390631234050748341340960261899(1)

J.-Ph. Karr et al. in *Recent Progress in Few-Body Physics* (Springer, 2020)

What precision level is actually required ?

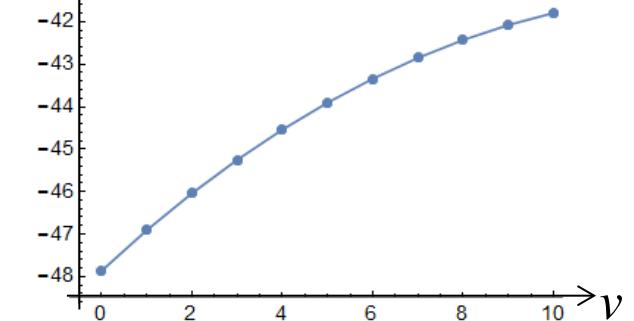
- In variational calculations: $\Delta\psi \sim \sqrt{\Delta E}$
- $\Delta E \sim 10^{-18}$ a.u. allows to get leading ($m\alpha^4$) corrections with sufficient accuracy.

Relativistic correction for the electron

$$E_{\text{rc}}^{(2)} = \alpha^2 \left\langle -\frac{\mathbf{p}_e^4}{8m_e^3} + \frac{4\pi}{8m_e^2} [Z_1 \delta(\mathbf{r}_1) + Z_2 \delta(\mathbf{r}_2)] \right\rangle$$

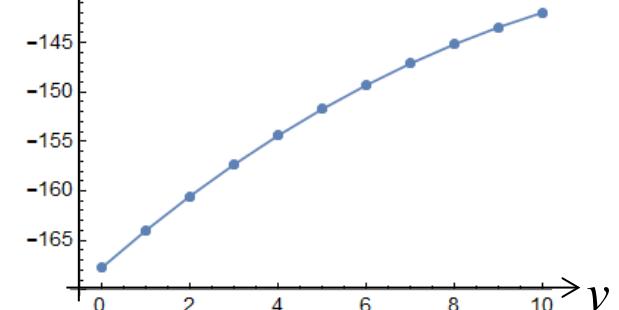
$E_{\text{rc}}^{(2)}$ (GHz)

HD⁺, L=0 states



Transverse photon exchange

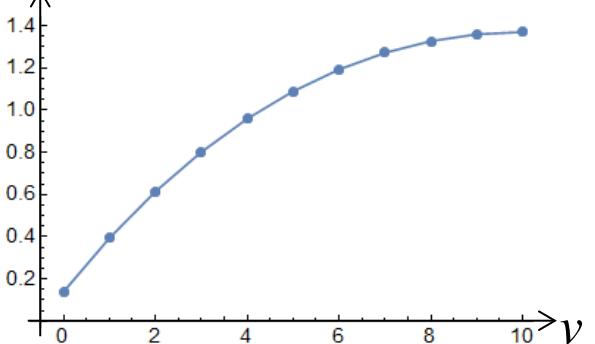
$E_{\text{tr-ph}}^{(2)e-n}$ (MHz)



Electron-nuclei

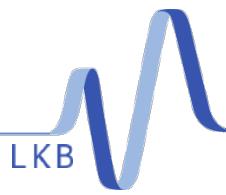
$$E_{\text{tr-ph}}^{(2)e-n} = \frac{\alpha^2 Z_1}{2m_e M_1} \left\langle \frac{\mathbf{p}_e \mathbf{P}_1}{r_1} + \frac{\mathbf{r}_1 (\mathbf{r}_1 \mathbf{p}_e) \mathbf{P}_1}{r_1^3} \right\rangle + 1 \leftrightarrow 2$$

$E_{\text{tr-ph}}^{(2)p-d}$ (MHz)



Between nuclei

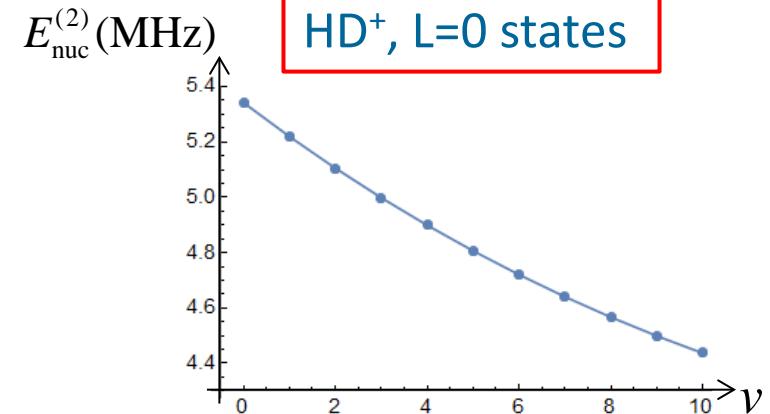
$$E_{\text{tr-ph}}^{(2)p-d} = -\frac{\alpha^2 Z_1 Z_2}{2M_1 M_2} \left\langle \frac{\mathbf{P}_1 \mathbf{P}_2}{R} + \frac{\mathbf{R}(\mathbf{R} \mathbf{P}_1) \mathbf{P}_2}{R^3} \right\rangle$$



Leading-order corrections (2)

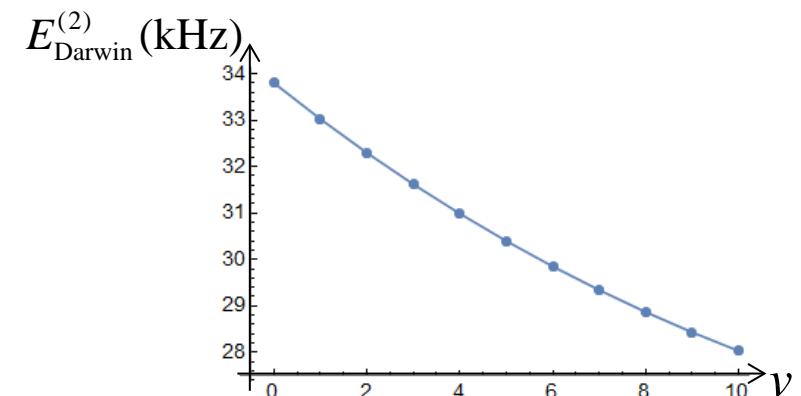
Leading nuclear finite-size shift

$$E_{\text{nuc}}^{(2)} = \sum_{i=1,2} \frac{2\pi Z_i (R_i/a_0)^2}{3} \langle \delta(\mathbf{r}_i) \rangle$$



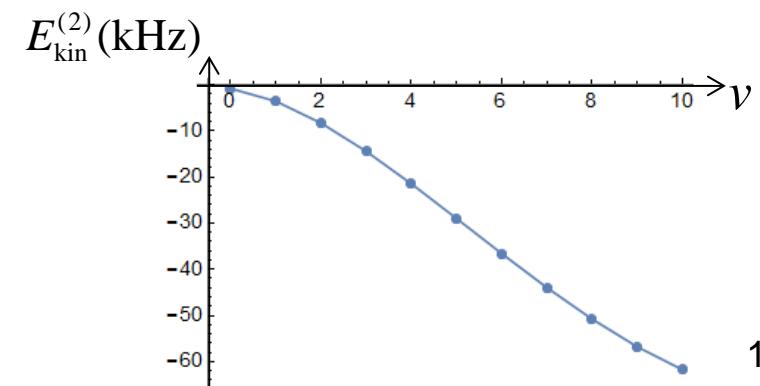
Nuclear Darwin term

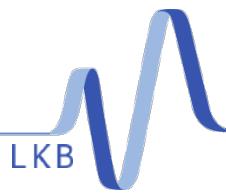
$$E_{\text{Darwin}}^{(2)} = \frac{\alpha^2 4\pi Z_p}{8M_p^2} \langle \delta(\mathbf{r}_p) \rangle$$



Nuclear kinetic correction

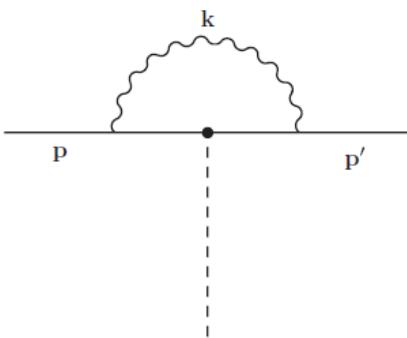
$$E_{\text{kin}}^{(2)} = -\alpha^2 \left\langle \frac{\mathbf{P}_1^4}{8M_1^3} + \frac{\mathbf{P}_2^4}{8M_2^3} \right\rangle$$



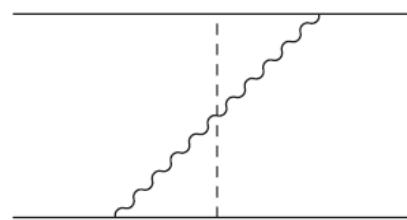


$m\alpha^5$: leading-order radiative corrections

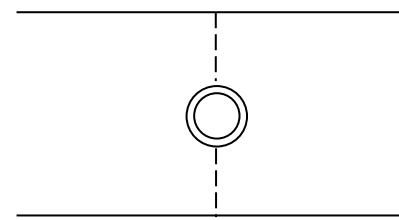
Self-energy



Retardation in transverse
photon exchange
 $[m\alpha^5(m/M)]$



Vacuum
polarization



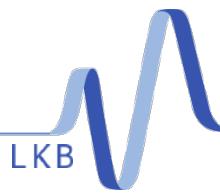
Anomalous
magnetic
moment



Bethe logarithm:

$$\beta(L, v) = \frac{\sum_i \langle 0 | \mathbf{J} | i \rangle^2 (E_i - E_0) \ln |E_i - E_0|}{\sum_i \langle 0 | \mathbf{J} | i \rangle^2 (E_i - E_0)} \quad \mathbf{J} = \sum_a \frac{z_a \mathbf{p}_a}{m_a}$$

- ✓ Calculated with 8-9 significant digits:
 $\beta(3,0) = 3.01220877(3)$
 $\beta(3,9) = 3.00959600(1)$



- 1-loop self energy $E_{se}^{(4)} = \alpha^4 \frac{4\pi}{m_e^2} \left(\frac{139}{128} - \frac{1}{2} \ln 2 \right) \langle Z_1^2 \delta(\mathbf{r}_1) + Z_2^2 \delta(\mathbf{r}_2) \rangle$
- 1-loop vacuum polarization, 2-loop corrections, anomalous magnetic moment
- Requiring independent calculation: ***relativistic corrections to the electron***
 - Calculation done in the ***adiabatic approximation***
 - Effective Hamiltonian $H^{(6)}$ derived in NRQED framework

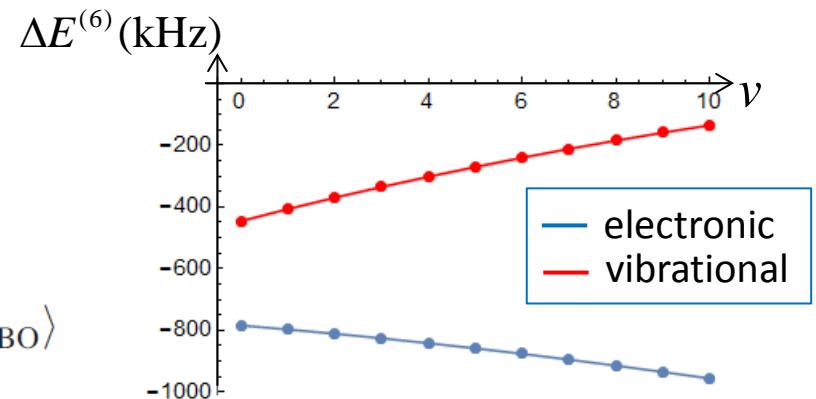
Correction curve: $\mathcal{E}_{RC}^{(6)}(R) = \langle H^{(6)} \rangle(R) + \langle H_{BP} Q(E_{el} - H_{el})^{-1} Q H_{BP} \rangle$

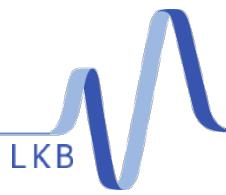
“electronic” contribution:

$$\Delta E_{el}^{(6)} = \langle \chi_{BO} | \mathcal{E}_{RC}^{(6)}(R) | \chi_{BO} \rangle$$

“vibrational” contribution:

$$\Delta E_{vb}^{(6)} = \langle \chi_{BO} | \mathcal{E}_{BP}(R) Q' (E_0 - H_{vb})^{-1} Q' \mathcal{E}_{BP}(R) | \chi_{BO} \rangle$$





$m\alpha^6$ order: recoil terms

- Pure recoil correction

“State-independent” part: $\Delta E_{\text{rec}}^{(6)} = \alpha^4 \pi \left(4 \ln 2 - \frac{7}{2} \right) \sum_{i=1,2} \frac{\langle \delta(r_i) \rangle}{M_i}$

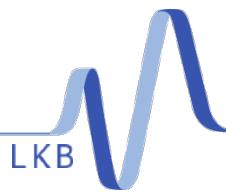
Uncertainty \equiv “State-dependent” part: $\Delta E_{\text{rec}}^{(6)} \approx \alpha^4 \pi \left(-\frac{1}{16} \right) \sum_{i=1,2} \frac{\langle \delta(r_i) \rangle}{M_i}$

K. Pachucki, Phys. Rev. Lett. **79**, 4120 (1997) ; M.I. Eides and H. Grotch, Phys. Rev. A **55**, 3351 (1997)

- Calculation of $m\alpha^6$ -order relativistic corrections including recoil-terms ***in a full 3-body approach*** in progress (Z.-X. Zhong, Wuhan)

Effective Hamiltonian: Z.-X. Zhong, W.-P. Zhou, X.-S. Mei, Phys. Rev. A **98**, 032502 (2018)

- Radiative-recoil correction



- ✓ 2-loop and 3-loop corrections, Wichmann-Kroll vacuum polarization

- 1-loop self-energy $\Delta E_{se}^{(7)} = \frac{\alpha^5}{\pi} \langle V_\delta \rangle [A_{62} \ln^2[\alpha^{-2}] + A_{61} \ln[\alpha^{-2}] + A_{60}]$

Effective Hamiltonian $H^{(7)}$ **without contact terms**:

U.D. Jentschura, A. Czarnecki, K. Pachucki, Phys. Rev. A **72**, 062102 (2005)

- + Full calculation for 1S state:

K. Pachucki, Ann. Phys. **226**, 1 (1993)

⇒ Complete effective Hamiltonian

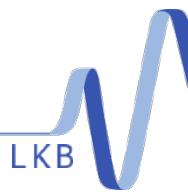
V.I. Korobov, L. Hilico, J.-Ph. Karr, PRL **112**, 103003 and PRA **89**, 032511 (2014)

Low-energy part: relativistic corrections to the Bethe logarithm

V.I. Korobov, L. Hilico, J.-Ph. Karr, PRA **87**, 062506 (2013)

- 1-loop vacuum polarization $\Delta E_{vp}^{(7)} = \frac{\alpha^5}{\pi} [V_{61} \ln(Z\alpha)^{-2} + G_{VP}^{(1)}(R)] \langle V_\delta \rangle$
(Uehling potential)
calculated in adiabatic and 3-body approaches.

J.-Ph. Karr, L. Hilico, V.I. Korobov, PRA **90**, 062516 (2014) and **95**, 042514 (2017)



- 2-loop self-energy

$$\Delta E_{\text{2loop}}^{(8)} \approx \frac{\alpha^6}{\pi^2} \langle V_\delta \rangle [B_{63} \ln^3(\alpha^{-2}) + B_{62} \ln^2(\alpha^{-2}) + B_{61} \ln(\alpha^{-2}) + B_{60}]$$

Effective Hamiltonian $H^{(8)}$ **without contact terms**:

U.D. Jentschura, A. Czarnecki, K. Pachucki, Phys. Rev. A **72**, 062102 (2005)

⇒ Calculation of B_{63} , $B_{62}(R)$, $B_{61}(R)$

V.I. Korobov, L. Hilico, J.-Ph. Karr, PRL **118**, 233001 (2017)

Nonlogarithmic term estimated using LCAO approximation: $B_{60} \equiv B_{60}(1S)$

Uncertainty ≡ total value of this term = **1.2 kHz**

- 1-loop self-energy

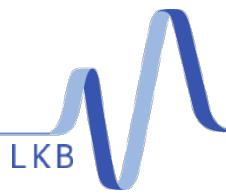
$$\Delta E_{\text{1loop}}^{(8)} \approx \alpha^6 [A_{71} \ln(\alpha^{-2}) + A_{70}(1S)] \langle Z_1^3 \delta(\mathbf{r}_1) + Z_2^3 \delta(\mathbf{r}_2) \rangle$$

A_{71} : S.G. Karshenboim, Z. Phys. D **39**, 109 (1997)

A_{70} : estimated from nonperturbative calculations

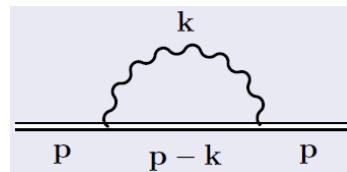
U.D. Jentschura, P.J. Mohr, G. Soff, PRA 63, 042512 (2001).

Uncertainty ≡ total value of nonlogarithmic term = **2.8 kHz**



What next ?

- The main sources of theoretical uncertainty:
 - one-loop self energy at $m\alpha^8$ order [A₇₀ coefficient]
 - two-loop corrections at $m\alpha^8$ order [B₆₀ coefficient]
- Top priority is the **one-loop self-energy**



- Switch to non-perturbative approach ?

H atom: U.D. Jentschura, P.J. Mohr, G. Soff, PRL **82**, 53 (1999).
Requires high-precision numerical resolution of **Dirac equation** for the electron in a two-center potential.
- The theoretical accuracy could then be improved to $\sim 3 \times 10^{-12}$.



Work in progress: hyperfine structure

- High-precision study of hyperfine structure becomes possible
- Perspective: improved determination of the deuteron quadrupole moment

$$H_{\text{eff}} = \underbrace{E_1(\mathbf{L} \cdot \mathbf{s}_e) + E_2(\mathbf{L} \cdot \mathbf{I}_p) + E_3(\mathbf{L} \cdot \mathbf{I}_d)}_{\text{Spin-orbit}} + \underbrace{E_4(\mathbf{I}_p \cdot \mathbf{s}_e) + E_5(\mathbf{I}_d \cdot \mathbf{s}_e)}_{\text{Nuclear spin-rotation}} + \underbrace{\left[E_6 \left\{ 2\mathbf{L}^2(\mathbf{I}_p \cdot \mathbf{s}_e) - 3[(\mathbf{L} \cdot \mathbf{I}_p)(\mathbf{L} \cdot \mathbf{s}_e) + (\mathbf{L} \cdot \mathbf{s}_e)(\mathbf{L} \cdot \mathbf{I}_p)] \right\} + E_7 \left\{ 2\mathbf{L}^2(\mathbf{I}_d \cdot \mathbf{s}_e) - 3[(\mathbf{L} \cdot \mathbf{I}_d)(\mathbf{L} \cdot \mathbf{s}_e) + (\mathbf{L} \cdot \mathbf{s}_e)(\mathbf{L} \cdot \mathbf{I}_d)] \right\} + E_8 \left\{ 2\mathbf{L}^2(\mathbf{I}_p \cdot \mathbf{I}_d) - 3[(\mathbf{L} \cdot \mathbf{I}_p)(\mathbf{L} \cdot \mathbf{I}_d) + (\mathbf{L} \cdot \mathbf{I}_d)(\mathbf{L} \cdot \mathbf{I}_p)] \right\} \right]}_{\text{Spin-spin tensor interactions}} + E_9 \left\{ \mathbf{L}^2 \mathbf{I}_d^2 - \frac{3}{2}(\mathbf{L} \cdot \mathbf{I}_d) - 3(\mathbf{L} \cdot \mathbf{I}_d)^2 \right\} \underbrace{\text{Deuteron quadrupole moment}}$$

D. Bakalov, V.I. Korobov, S. Schiller, PRL **97**, 243001 (2006)

Largest coefficients: ✓ E_4, E_5 : higher-order corrections evaluated
see V.I. Korobov, J. Koelemeij, L. Hilico, J.-Ph. Karr, PRL **116**, 053003 (2016) (H_2^+)
➤ E_1] $m\alpha^6$ -order effective Hamiltonian
 $E_{6,7}$] and first numerical results