



# $m\alpha^6$ order corrections of the hydrogen molecular ions

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# Outline

- 1 Introduction
- 2 Spin-averaged  $m\alpha^6$  order corrections
- 3 Progress of Numerical calculations
- 4 Acknowledgement



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1 Introduction

2 Spin-averaged  $m\alpha^6$  order corrections

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# Precision spectroscopy of Hydrogen Molecular Ions

## ① fundamental constants <sup>1</sup>

- ▶ mass ratios:  $m_p/m_e$ ,  $m_p/m_d$
- ▶ charge radii of proton and deuteron
- ▶ the Rydberg energy  $\mathcal{R}_\infty$
- ▶ ...

## ② precise optical clocks <sup>2</sup>

- ③ test QED calculations
- ④ search for new physics
- ⑤ ...

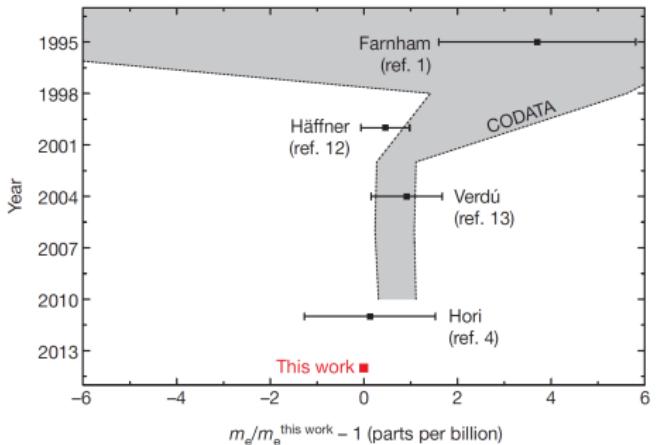
<sup>1</sup>J. Biesheuvel, et al., Nat. Comm. **7**, 10385 (2016).

<sup>2</sup>J.-Ph. Karr, J. Mol. Spectros. **300**, 37 (2014).

# Electron mass $m_e$

S. Sturm, et al., Nature **506**, 467-470 (2014).

the magnetic moment of a single electron bound to a carbon nucleus



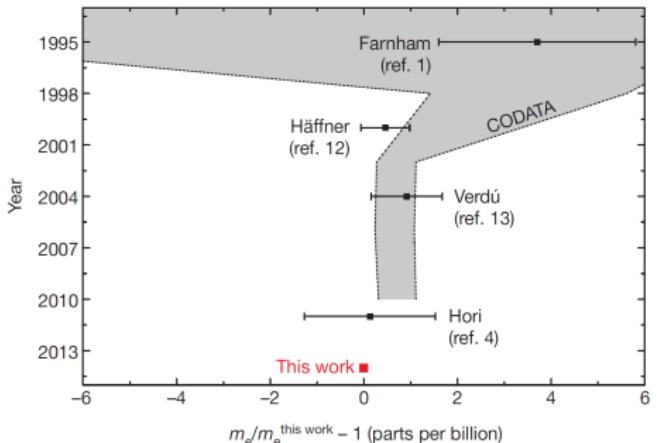
$$m_e = 0.000\ 548\ 579\ 909\ 067(14)(9)(2) \text{ } u \quad 30 \text{ ppt} \quad (1)$$

$$m_p/m_e = 1836.152\ 673\ 77(17) \quad 94 \text{ ppt} \quad (2)$$

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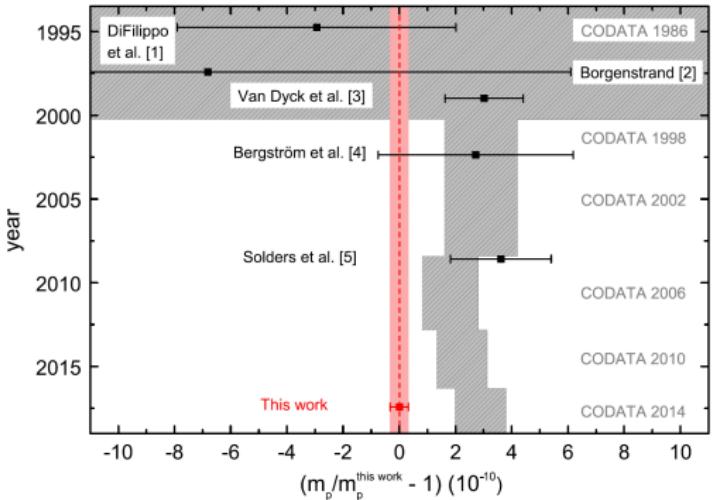
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It was limited by the uncertainty of the proton mass.

# Proton mass $m_p$

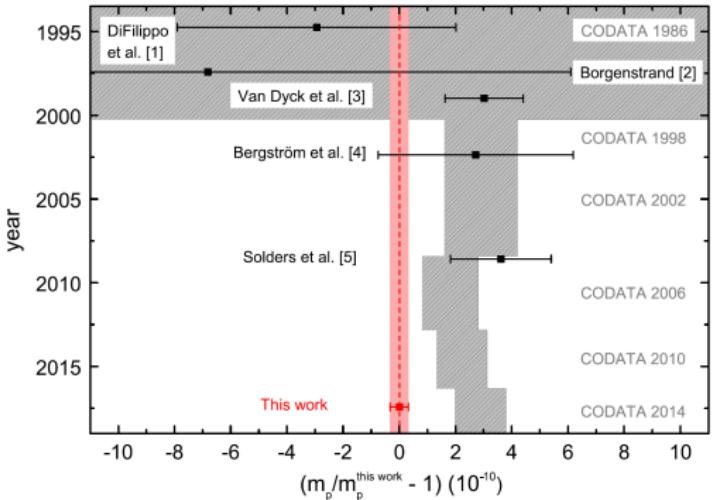
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$$m_p = 1.007\ 276\ 466\ 583(15)(29) \text{ } u \quad 32 \text{ ppt}$$

the difference is more than 3 standard deviations

$$m_p/m_e = 1836.152\ 673\ 346(81)$$



# Comparison of $m_p/m_e$

CODATA	2014	1836.152 673	89(17)
Sturm et al.	2014	1836.152 673	77(17)
Hiebe et al.	2017	1836.152 673	346(81)
Koelemeij et al. <sup>3</sup>	2016	1836.152 6695(53)	HD <sup>+</sup>
Hori et al. <sup>4</sup>	2016	1836.152 6734(15)	$\bar{p}\text{He}^+$

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the direct measurement of  $m_p/m_e$  may give us an answer

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# Spectroscopy measurements

- 2007, HHU<sup>5</sup>, HD<sup>+</sup>,  $(\nu, \mathcal{L}) : (0, 2) \rightarrow (4, 3)$ ,  
 $f = 214,978,560.6(5)$  MHz,  $2.3 \times 10^{-9}$
- 2016, VUU<sup>6</sup>, HD<sup>+</sup>,  $(\nu, \mathcal{L}) : (0, 2) \rightarrow (8, 3)$ ,  
 $f = 383,407,177.38(41)$  MHz,  $1.1 \times 10^{-9}$
- 2018, HHU<sup>7</sup>, HD<sup>+</sup>,  $(\nu, \mathcal{L}) : (0, 0) \rightarrow (0, 1)$ ,  
 $f = 1,314,935.8280(4)(3)$  MHz,  $3.8 \times 10^{-10}$   
 $m_p = 1.007,276,4669(13)$  u,  $1.3 \times 10^{-9}$

<sup>5</sup>J.C.J. Koelemeij, et. al., Phys. Rev. Lett. **98**, 173002 (2007).

<sup>6</sup>J. Biesheuvel, et al., Nat. Comm. **7**, 10385 (2016).

<sup>7</sup>S. Alighanbari, et. al., Nature Physics, **14**, 555-559 (2018).



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- LKB, L. Hilico and J.-Ph. Karr, H<sub>2</sub><sup>+</sup>,  $(\nu, \mathcal{L}) : (0, 0) \rightarrow (1, 0)$
- WIPM, X. Tong, HD<sup>+</sup>,  $(\nu, \mathcal{L}) : (0, 0) \rightarrow (6, 1)$

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# Bound state energy

By using NRQED, bound state energy can be expanded as (in a.u.)

$$E_{total} = E_{nr} + m\alpha^4 E^{(4)} + m\alpha^5 E^{(5)} + m\alpha^6 E^{(6)} + m\alpha^7 E^{(7)} + \dots \quad (3)$$

Here  $\alpha \approx 1/137$  is the fine structure constant, thus relativistic and radiative corrections are treated as perturbations.

In order to get spectroscopy with ppt precision, we need corrections up to  $m\alpha^7$  order or even more.



# Theoretical calculations

- 2006, relative uncertainty of 1 ppb<sup>8</sup>
  - ▶ leading order relativistic and radiative corrections

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<sup>8</sup>V. I. Korobov, Phys. Rev. A **74**, 052506(2006).

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- 2017, ppt level<sup>11</sup>
  - ▶ high precision expectation values of the Breit-Pauli operators
  - ▶  $m\alpha^6(m/\mathcal{M})$  order corrections
  - ▶  $m\alpha^8$  order QED corrections

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# Our works

Our previous works ( $m\alpha^4$  and  $m\alpha^5$  order corrections)

- expectation values of the Breit-Pauli operators  
PRA **79**, 064502 (2009); **86**, 064502 (2012); **93**, 032507 (2016).
- Bethe logarithm by using Drake-Goldman method  
PRA **88**, 052520 (2013).
- Bethe logarithm by using Schwartz's expand (with Korobov)  
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This work:  $m\alpha^6$  order corrections hydrogen molecular ions.



# $m\alpha^6$ order corrections

- 2007, Relativistic corrections of order  $m\alpha^6$  to the two-center problem.<sup>12</sup>
  - ▶ Born-Oppenheimer approximation.
  - ▶ adiabatic corrections
  - ▶ one electron  $m\alpha^6$  order effective Hamiltonian
- 2017, recoil contribution at order  $m\alpha^6(m/\mathcal{M})$  are taken from the two-body formulas.<sup>13</sup>

<sup>12</sup>V. I. Korobov and Ts. Tsogbayar, J. Phys. B **40**, 2661-2669 (2007).

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Theory beyond Born-Oppenheimer approximation is needed.

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# $m\alpha^6$ order corrections

$$E^{(6)} = \langle \Psi_0 | \mathcal{H}^{(4)} Q \frac{1}{(E_0 - \mathcal{H}_0)} Q \mathcal{H}^{(4)} | \Psi_0 \rangle + \langle \Psi_0 | \mathcal{H}^{(6)} | \Psi_0 \rangle \quad (4)$$



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- the second-order corrections for the Breit-Pauli Hamiltonian  $\mathcal{H}^{(4)}$ ,

$$E_{\text{sec}} = \langle \Psi_0 | \mathcal{H}^{(4)} Q \frac{1}{(E_0 - \mathcal{H}_0)} Q \mathcal{H}^{(4)} | \Psi_0 \rangle$$



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- $\mathcal{H}^{(6)}$ , the effective Hamiltonian of  $m\alpha^6$  order

$$\mathcal{H}^{(6)} = \mathcal{H}_{\text{rad}}^{(6)} + \mathcal{H}_{\text{red}}^{(6)} \quad (5)$$

- $\mathcal{H}_{\text{rad}}^{(6)}$ , the radiative corrections of  $m\alpha^6$  order
- $\mathcal{H}_{\text{rel}}^{(6)}$ , the relativistic corrections of  $m\alpha^6$  order

# Radiative corrections $\langle \mathcal{H}_{\text{rad}}^{(6)} \rangle$ in external field approximation

## ① $m\alpha^6$ order radiative corrections

$$\mathcal{E}_{\text{se}}^{(6)} = \alpha^4 \frac{4\pi}{m_e^2} \left( \frac{139}{128} - \frac{1}{2} \ln 2 \right) \langle z_1^2 \delta(\vec{r}_1) + z_2^2 \delta(\vec{r}_2) \rangle, \quad (6)$$

$$\mathcal{E}_{\text{anom}}^{(6)} = \alpha^2 \frac{\pi}{m_e^2} \left[ \left( \frac{\alpha}{\pi} \right)^2 \left( \frac{197}{144} + \frac{\pi^2}{12} - \frac{\pi^2}{2} \ln 2 + \frac{3}{4} \zeta(3) \right) \right] \langle z_1 \delta(\vec{r}_1) + z_2 \delta(\vec{r}_2) \rangle, \quad (7)$$

$$\mathcal{E}_{\text{vp}}^{(6)} = \frac{4\alpha^3}{3m_e^2} \left[ \frac{5\pi\alpha}{64} \right] \langle z_1^2 \delta(\vec{r}_1) + z_2^2 \delta(\vec{r}_2) \rangle, \quad (8)$$

$$\mathcal{E}_{\text{2loop}}^{(6)} = \frac{\alpha^4}{m_e^2 \pi} \left[ -\frac{6131}{1296} - \frac{49\pi^2}{108} + 2\pi^2 \ln 2 - 3\zeta(3) \right] \langle z_1 \delta(\vec{r}_1) + z_2 \delta(\vec{r}_2) \rangle. \quad (9)$$

## ② $m\alpha^6(m/\mathcal{M})$ order radiative corrections

$$\mathcal{E}_{\text{rec}}^{(6)} = \alpha^4 \frac{4\pi}{m_e} \left( \ln 2 - \frac{7}{8} \right) \langle \frac{z_1^3}{m_1} \delta(\vec{r}_1) + \frac{z_2^3}{m_2} \delta(\vec{r}_2) \rangle, \quad (10)$$

$$\mathcal{E}_{\text{e-line}}^{(6)} = \frac{\alpha^4}{m_e^2 \pi} \left( 6\zeta(3) - 2\pi^2 \ln 2 + \frac{3\pi^2}{4} - 14 \right) \langle \frac{z_1^2}{m_1} \delta(\vec{r}_1) + \frac{z_2^2}{m_2} \delta(\vec{r}_2) \rangle, \quad (11)$$

$$\mathcal{E}_{\text{p-line}}^{(6)} = \frac{\alpha^4}{m_e^2 \pi} \left( \frac{2\pi^2}{9} - \frac{70}{27} \right) \langle \frac{z_1^2}{m_1} \delta(\vec{r}_1) + \frac{z_2^2}{m_2} \delta(\vec{r}_2) \rangle. \quad (12)$$

<sup>13</sup>M. I. Eides, H. Grotch and V. A. Shelyuto, *Theory of Light Hydrogenic Bound States* (Springer-Verlag Berlin Heidelberg 2007).



# Relativistic corrections $\langle \mathcal{H}_{\text{rel}}^{(6)} \rangle$

Effective Hamiltonian technique has been well developed by K. Pachucki for light atomic systems<sup>14</sup>.

PHYSICAL REVIEW A 71, 012503 (2005)

## Higher-order effective Hamiltonian for light atomic systems

Krzysztof Pachucki\*

Institute of Theoretical Physics, Warsaw University, Hoza 69, 00-681 Warsaw, Poland

(Received 29 September 2004; published 19 January 2005)

We present the derivation of the effective higher-order Hamiltonian, which gives an  $ma^6$  contribution to the energy levels of an arbitrary light atom. The derivation is based on the Foldy-Wouthuysen transformation of the one-particle Dirac Hamiltonian followed by perturbative expansion of the many-particle Green function. The obtained results can be used for the high precision calculation of relativistic effects in atomic systems.

- ① non-relativistic theory
- ② rigorous adaptation of bound state QED
- ③ relativistic and radiative corrections included systematically
- ④ singularities removed by cutting off momentum integrations at  $p \sim m_e$
- ⑤ correction terms due to the cutoff effects

<sup>14</sup>K. Pachucki, PRA 71, 012503 (2005); 74, 022512 (2006)



# Effective Hamiltonian technique

- Helium fine structure,  $m\alpha^6$  order Douglass and Kroll operators <sup>15</sup>
- Helium fine structure,  $m\alpha^6(m/M)$  order recoil corrections <sup>16</sup>
- Light atomic systems,  $m\alpha^6$  order effective Hamiltonian <sup>17</sup>
- Helium singlet states,  $m\alpha^6$  order spin-averaged effective Hamiltonian <sup>18</sup>
- QED of finite-size particles with arbitrary spin <sup>19</sup>
- Helium higher-order recoil corrections, spin-independent <sup>20</sup>

<sup>15</sup>K. Pachucki, J. Phys. B: At. Mol. Opt. Phys. (1999).

<sup>16</sup>K. Pachucki and J. Sapirstein, J. Phys. B **36**, 803 (2003).

<sup>17</sup>K. Pachucki, Phys. Rev. A **71**, 012503 (2005).

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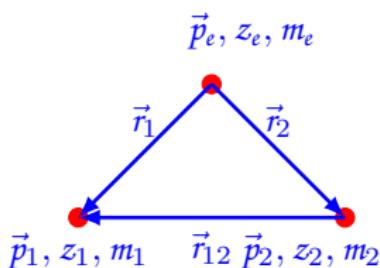
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# Spin-averaged effective Hamiltonian

$$\delta\mathcal{H}_1 = \frac{p_e^6}{16m_e^5}, \quad (13)$$

$$\delta\mathcal{H}_2 = \frac{1}{128m_e^4} [p_e^2, [p_e^2, \mathcal{V}]] + \frac{3\alpha}{64m_e^4} \{p_e^2, 4\pi \sum_a z_a z_e \delta(\vec{r}_a)\}, \quad (14)$$

$$\delta\mathcal{H}_3 = \sum_a -\frac{1}{32m_e^3 m_a} [p_a^2, [p_e^2, \mathcal{V}_a]], \quad (15)$$

$$\delta\mathcal{H}_4 = -\frac{1}{8m_e^2} \{p_e^2, 2\mathcal{H}_{\mathcal{R}}\}, \quad (16)$$

$$\begin{aligned} \delta\mathcal{H}_5 = & \sum_a \frac{z_a^2}{2m_a} \left\{ \left[ \frac{z_e\alpha}{2r_a} \left( \delta^{ij} + \frac{r_a^i r_a^j}{r_a^2} \right) \frac{p_e^j}{m_e} \right] \left[ \frac{z_e\alpha}{2r_a} \left( \delta^{il} + \frac{r_a^i r_a^l}{r_a^2} \right) \frac{p_e^l}{m_e} \right] \right. \\ & \left. + \frac{z_e^2 \alpha^2}{4m_e^2} \frac{\vec{\sigma}_e \times \vec{r}_a \cdot \vec{\sigma}_e \times \vec{r}_a}{r_a^6} \right\}, \end{aligned} \quad (17)$$

$$\delta\mathcal{H}_6 = \sum_a -\frac{\alpha}{m_e m_a} \left\{ [p_e^i, \mathcal{V}] \mathcal{X}^{ij}(r_a) [\mathcal{V}, p_a^j] + p_e^i [\mathcal{X}^{ij}(r_a), \frac{p_e^2}{2m_e}] [\mathcal{V}, p_a^j] \right\}, \quad (18)$$

where

$$\mathcal{X}^{ij}(r) = \int d^3k \frac{4\pi}{k^4} \left( \delta^{ij} - \frac{k^i k^j}{k^2} \right) (e^{ik \cdot \vec{r}} - 1) = \frac{1}{8r} [r^i r^j - 3\delta^{ij} r^2]. \quad (19)$$



# The second-order corrections

$$\mathcal{E}_{sec} = \langle \mathcal{H}^{(4)} Q \frac{1}{\mathcal{E}_0 - \mathcal{H}_0} Q \mathcal{H}^{(4)} \rangle, \quad (20)$$

where

$$\mathcal{H}^{(4)} = \mathcal{H}_B + \mathcal{H}_R + \mathcal{H}_S, \quad (21)$$

$$\mathcal{H}_B = -\frac{1}{8m_e^3} \vec{p}_e^4 - \frac{\pi}{2m_e^2} [z_1 z_e \delta(\vec{r}_1) + z_2 z_e \delta(\vec{r}_2)], \quad (22)$$

$$\mathcal{H}_R = -\sum_{n=1}^2 \frac{z_e z_n}{2m_e m_0} \left[ \frac{\vec{p}_e \vec{p}_n}{r_n} + \frac{\vec{r}_n (\vec{r}_n \cdot \vec{p}_e) \vec{p}_n}{r_n^3} \right], \quad (23)$$

$$\mathcal{H}_S = \left\{ -\frac{1+2\kappa_e}{2m_e^2} \left( \frac{\vec{r}_1 \times \vec{p}_e}{r_1^3} + \frac{\vec{r}_2 \times \vec{p}_e}{r_2^3} \right) + \frac{1+\kappa_e}{m_e m_1} \frac{\vec{r}_1 \times \vec{p}_1}{r_1^3} + \frac{1+\kappa_e}{m_e m_2} \frac{\vec{r}_2 \times \vec{p}_2}{r_2^3} \right\} \vec{s}_e \quad (24)$$



# Cancellation of singularities

Total singularity of  $\langle \mathcal{H}^{(6)} \rangle$ :

$$S_{1\text{st}} = \sum_a \frac{1}{32} \left[ \left(1 - \frac{13}{m_a}\right) \langle \varepsilon_a^2 \rangle_S - 4 \left(1 - \frac{6}{m_a}\right) \langle \mathcal{V}_a^3 \rangle_S \right]. \quad (25)$$

Singularity from the second-order contributions

$$S_{2\text{nd}} = - \sum_a \frac{1}{32} \left[ \left(1 - \frac{13}{m_a}\right) \langle \varepsilon_a^2 \rangle_S - 4 \left(1 - \frac{6}{m_a}\right) \langle \mathcal{V}_a^3 \rangle_S \right]. \quad (26)$$

- $S_{1\text{st}} + S_{2\text{nd}} \equiv 0$
- the singularity for each pair of electron-nucleus interactions is in agreement with hydrogen atom



## Spin-averaged effective Hamiltonian of orders $m\alpha^6$ and $m\alpha^6(m/M)$ for hydrogen molecular ions

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The spin-averaged effective Hamiltonian of orders  $m\alpha^6$  and  $m\alpha^6(m/M)$  for a one-electron two-center Coulombic system is derived by using the theory of nonrelativistic quantum electrodynamics (NRQED), without assuming the Born-Oppenheimer approximation. The separated singularities from the first- and second-order perturbations are shown to be canceled out analytically for both order  $m\alpha^6$  and  $m\alpha^6(m/M)$  corrections by regularizing the effective Hamiltonian. Our results can be used to perform high-precision spectroscopic calculations of hydrogen molecular ions.

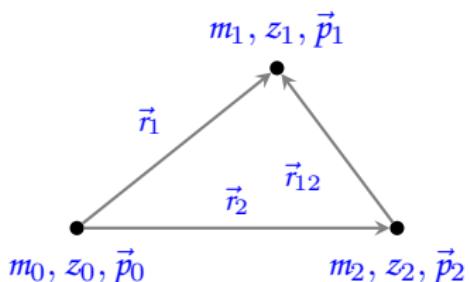
DOI: [10.1103/PhysRevA.98.032502](https://doi.org/10.1103/PhysRevA.98.032502)



# Outline

- 1 Introduction
- 2 Spin-averaged  $m\alpha^6$  order corrections
- 3 Progress of Numerical calculations
- 4 Acknowledgement

# Non-relativistic wave functions



Schrödinger equation :

$$\mathcal{H}_0 \Psi_0 = E_0 \Psi_0 , \quad (27)$$

$$\mathcal{H}_0 = \frac{1}{2} \left( \frac{1}{m_0} + \frac{1}{m_1} \right) \vec{p}_1^2 + \frac{1}{2} \left( \frac{1}{m_0} + \frac{1}{m_2} \right) \vec{p}_2^2 + \frac{1}{m_0} \vec{p}_1 \cdot \vec{p}_2 + \frac{z_0 z_1}{r_1} + \frac{z_0 z_2}{r_2} + \frac{z_1 z_2}{r_{12}} .$$

$$\Psi_0 = \sum_n \sum_{ij\kappa}^{i+j+\kappa \leq \Omega} r_1^i r_2^{j_0+j} r_{12}^\kappa e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}} \mathcal{Y}_{LM}^{l_1 l_2}(\vec{r}_1, \vec{r}_2) ,$$

where  $j_0$  is a big number for hydrogen molecular ions.

## Basical integrals $I_q(\mathcal{R}'\mathcal{R})$



	Yan and Drake <sup>1</sup>	General Type <sup>2</sup>
$I_q(\mathcal{R}'\mathcal{R})$	$I_q(a, b, c; \alpha, \beta)$	$\Gamma_{\ell, m, n}(\alpha, \beta, \gamma)$ and $q = 0$
$\mathcal{R}'\mathcal{R}$	$r_1^i r_2^k r_{12}^k e^{-\alpha r_1 - \beta r_2} P_q(\cos \theta)$	$r_1^i r_2^k r_{12}^k e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}$
Nonsingular	$a + b + c + 5 \geq 5$ $a, b, c \geq -2$ $I_q = \frac{2}{2q+1} \sum_k C_{cqk} I_{\mathcal{R}}(\dots)$	$\ell, m, n \geq 0$ $\Gamma_{000} = \frac{2}{(\alpha+\beta)(\alpha+\gamma)(\beta+\gamma)}$ $\Gamma_{\ell+1, m, n} = -\frac{\partial}{\partial \alpha} \Gamma_{\ell, m, n}$
Singular rel&QED	$I_0(a, b, -2 - n)$ $I_0(-n, b, c)$ $I_0(-n, b, -m)$ $I_0(-n, -m, c)$	$\Gamma_{-p, 0, 0}$ $\Gamma_{-p, m+1, n} = -\frac{\partial}{\partial \beta} \Gamma_{-p, m, n}$ $\Gamma_{-p, -1, 0}$ $\Gamma_{-p, -1, n+1} = -\frac{\partial}{\partial \gamma} \Gamma_{-p, -1, n}$ $\Gamma_{-2, -2, 0}$ <sup>3</sup>

<sup>1</sup>Yan and Drake, Can. J. Phys. **72**, 822 (1994); Chem. Phys. Lett., **259**, 96 (1996).

<sup>2</sup>Korobov, J. Phys. B, **35**, 1959 (2002); Harris et al., J. Chem. Phys. **121**, 6323 (2004).

<sup>3</sup>Korobov, Phys. Rev. A **85**, 042514 (2012).

# Non-relativistic energy of $H_2^+$ ground state

TABLE II. Nonrelativistic energy for the ground state of  $H_2^+$ .

$\Omega$	No. of terms	$E(\Omega)$ (a.u.)	$R(\Omega)$
3	32	-0.597 138 982 249 839 766 674 228 437 022 897	
4	58	-0.597 139 062 095 593 487 466 938 942 979 182	
5	94	-0.597 139 063 075 853 406 303 378 173 871 251	81.45
6	144	-0.597 139 063 122 676 395 625 438 654 740 649	20.93
7	208	-0.597 139 063 123 384 395 608 334 606 353 522	66.13
8	290	-0.597 139 063 123 404 506 047 653 790 245 369	35.20
9	390	-0.597 139 063 123 405 064 624 580 206 465 343	36.00
10	512	-0.597 139 063 123 405 074 540 495 404 209 463	56.33
11	656	-0.597 139 063 123 405 074 824 265 899 599 489	34.94
12	826	-0.597 139 063 123 405 074 833 826 471 754 663	29.68
13	1022	-0.597 139 063 123 405 074 834 129 700 384 551	31.52
14	1248	-0.597 139 063 123 405 074 834 133 821 134 784 73	73.58
15	1504	-0.597 139 063 123 405 074 834 134 092 642 376 75	15.17
16	1794	-0.597 139 063 123 405 074 834 134 095 975 150 09	81.46
17	2118	-0.597 139 063 123 405 074 834 134 096 025 192 00	66.59
18	2480	-0.597 139 063 123 405 074 834 134 096 025 843 47	76.81
19	2880	-0.597 139 063 123 405 074 834 134 096 026 176 93	1.95
20	3322	-0.597 139 063 123 405 074 834 134 096 026 188 92	27.81
21	3806	-0.597 139 063 123 405 074 834 134 096 026 189 87	12.64
$\infty$		-0.597 139 063 123 405 074 834 134 096 026 189 9(1)	

- 34 digits are obtained for the gound state of  $H_2^+$  by Y. Ning and Z.-C. Yan<sup>21</sup>
- As increasing of vibrational quantum number  $v$ , the preicsion is decreasing rapidly.

<sup>21</sup>Y. Ning and Z.-C. Yan, Phys. Rev. A **90**, 032516 (2014).



# High vibrational states

PHYSICAL REVIEW A **99**, 012501 (2019)

## Leading-order relativistic corrections to the rovibrational spectrum of $\text{H}_2^+$ and $\text{HD}^+$ molecular ions

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High-precision variational calculations of the operators for the relativistic corrections in the leading  $m\alpha^4$  order are presented. The rovibrational states in the range of the total orbital angular momentum  $L = 0\text{--}4$  and vibrational quantum number  $v = 0\text{--}10$  for the  $\text{H}_2^+$  and  $\text{HD}^+$  molecular ions are considered. We estimate that about 10 significant digits are obtained. This high precision is required for making theoretical predictions for transition frequencies at the level of  $10^{-12}$  relative uncertainty.

DOI: [10.1103/PhysRevA.99.012501](https://doi.org/10.1103/PhysRevA.99.012501)



# Operator $\langle \vec{p}_e^4 \rangle$ <sup>22</sup>

TABLE I. Convergence of the mean value of  $\langle \vec{p}_e^4 \rangle$  for the vibrational states  $v = 4$  and 10 in  $\text{HD}^+$  for various  $L$ .

	$N$	$L = 0$	$L = 3$
$v = 4$	8 000	5.792 077 3804	5.765 200 6482
	10 000	5.792 077 3799	5.765 200 6473
	12 000	5.792 077 3798	5.765 200 6468
	14 000	5.792 077 3798	5.765 200 6466
	$\infty$	5.792 077 3798(1)	5.765 200 6465(1)
	Ref. [15]	5.792 077 379 5339(5)	5.765 200 6889(6)

Ref. [15] : Z.-X. Zhong, et al., Phys. Rev. A **86**, 064502 (2012).

<sup>22</sup>D. T. Aznabayev, A. K. Bekbaev and V. I. Korobov, Phys. Rev. A **99**, 012501 (2019).



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The differences are due to the fundamental constants.

<sup>22</sup>D. T. Aznabayev, A. K. Bekbaev and V. I. Korobov, Phys. Rev. A **99**, 012501 (2019).



# The second-order contribution due to $\mathcal{H}_B$

$$\mathcal{E}_B = \langle \mathcal{H}'_B Q (\mathcal{E}_0 - \mathcal{H}_0)^{-1} \mathcal{H}'_B \rangle, \quad (28)$$

$$\mathcal{H}'_B = \mathcal{H}_B - \{ \mathcal{E}_0 - \mathcal{H}_0, \mathcal{U} \}, \quad (29)$$

$$\mathcal{H}_B = -\frac{\vec{p}_e^4}{8m_e^3} - \frac{\pi}{2m_e^2} \sum_a z_a z_e \delta(\vec{r}_a), \quad (30)$$

$$\mathcal{U} = \sum_a \lambda_a \frac{z_a z_e}{r_a}, \quad \lambda_a = -\frac{1}{4} \left( 1 - \frac{3}{m_a} \right). \quad (31)$$



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Numerical calculation for this term is still ongoing ...



# Outline

1 Introduction

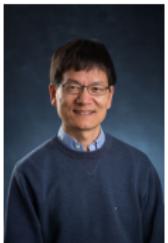
2 Spin-averaged  $m\alpha^6$  order corrections

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4 Acknowledgement



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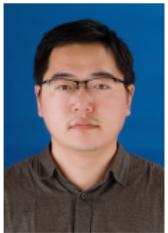
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