# $m\alpha^7$-Order Corrections in the Hydrogen Molecular Ions and Antiprotonic Helium

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We present a calculation of the complete set of QED corrections of order $m\alpha^7$ for one-electron two-center systems. Leading corrections of order $m\alpha^8$ are also considered, which allows us to estimate the magnitude of yet uncalculated contributions. The theoretical uncertainty on the frequencies of rovibrational transitions in the hydrogen molecular ions $H_2^+$ and $HD^+$, and of two-photon transition in antiprotonic helium is reduced by about 1 order of magnitude, down to (3–4) $\times 10^{-11}$ and $10^{-10}$, respectively. These results open new perspectives for improved determination of the proton- and antiproton-to-electron mass ratios by precision spectroscopy experiments.

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In recent years, high-precision spectroscopy of three-body molecular or moleculelike systems has opened new possibilities for metrology of nucleus-to-electron mass ratios and/or tests of few-body bound-state QED [1]. One-photon ro-vibrational transitions were observed in $HD^+$ molecular ions with a relative uncertainty of 1–2 ppb [2,3]. Spectroscopy of two-photon transitions in antiprotonic helium at the 2–5 ppb level yielded a new value of the antiproton-to-electron mass ratio [4]. These experiments, as well as others [5,6], are currently being developed towards higher precision. The importance of the $m_p/m_e$ problem is supported by recent experiments [7] with rubidium atoms, which allow us to deduce a new value of the fine structure constant, $\alpha = e^2/(\hbar c)$, with a relative uncertainty $6.6\times 10^{-10}$. Further improvement may be hindered by the present limits on the proton-to-electron mass ratio, which, according to the present CODATA adjustment [8] is known with a relative uncertainty of $4.1\times 10^{-10}$.

Theoretical calculation of the complete set of QED corrections up to order $m\alpha^6$ has brought the theoretical uncertainty down to 0.3–0.4 ppb in $H_2^+$ or $HD^+$ [9], and about 1 ppb in antiprotonic helium [10]. Very accurate leading order relativistic corrections are also available from [11]. In the present work, we compute the complete set of $m\alpha^7$ order corrections including the one-loop self-energy contribution, which represents the main source of theoretical uncertainty. This allows us to improve the accuracy by about one order of magnitude, thus making real the possibility of improving the knowledge of nucleus-to-electron mass ratios.

The major part of this Letter concerns the one-loop self-energy at $m\alpha^7$ order, which is the most difficult contribution to evaluate. As a starting point of our consideration we take the general result of Refs. [12,13] for a bound electron in a field of external Coulomb potential. Its derivation does not use the exact form $V(r)$; thus, it is possible to extend it to a system with two Coulomb centers. Significant work is involved for two reasons. (i) The definition of the relativistic Bethe logarithm in [12,13] uses the energy scale $Z^2E_h$, which is well suited for the hydrogenic case, but becomes irrelevant for a system with two Coulomb centers of charges $Z_1$ and $Z_2$. It has to be carefully redefined in atomic units. (ii) The result of [12,13] is only valid for states with nonzero angular momentum and for the normalized difference of $S$ states, $\Delta_n = n^3\Delta E(nS) - \Delta E(1S)$. Some terms are actually divergent for individual $S$ states. First we need to determine finite expectation values for the divergent operators. Then we will use a comparison with the known result for the $1S$ state of hydrogen [14,15] to obtain the missing part, which appears as a contact term of the type $\pi Z^3\delta(\mathbf{r})$, and may be generalized to the two-center problem by using the distribution

$$V_\delta = \pi[Z_1^3\delta(\mathbf{r}_1) + Z_2^3\delta(\mathbf{r}_2)]. \tag{1}$$

We begin with the low-energy part and the redefinition of the relativistic Bethe logarithm $\mathcal{L}(Z,n,l)$. Here we use atomic units.

The relativistic Bethe logarithm is determined as an integral over photon energy [16]

$$\mathcal{L}(Z,n,l) = \frac{2}{3}\int_0^{E_h} kdkP_{\alpha^2}^{(1)}(k) + \frac{2}{3}\int_{E_h}^{\infty} kdkP_{\alpha^2}^{(2)}(k), \tag{2}$$

where $E_h$ is the Hartree energy. The quantities $P_{\alpha^2}^{(i)}(k)$ are defined in Eq. (10).

The integrand is the function of energy and is a sum of various contributions [12,16]:

(a) relativistic corrections to the wave function

$$\begin{aligned} P_{\rm rc}^{(1)}(k) &= 2\langle H_B Q(E_0-H)^{-1}Q\mathbf{p}(E_0-H-k)^{-1}\mathbf{p}\rangle \\ &\quad + \langle \mathbf{p}(E_0-H-k)^{-1}(H_B-\langle H_B\rangle) \\ &\quad \times (E_0-H-k)^{-1}\mathbf{p}\rangle; \end{aligned} \tag{3}$$

(b) modification of the vertex interactions

$$P_{\mathrm{rc}}^{(2)}(k)=\left\langle\left(-p^2p^i-\frac{1}{2}\sigma^{ij}\nabla^jV\right)(E_0-H-k)^{-1}p^i\right\rangle; \quad (4)$$

(c) nonrelativistic quadrupole contribution

$$P_{\mathrm{nq}}(k)=\frac{3k^2}{8\pi}\int_S d\Omega_{\mathbf{n}}(\delta^{ij}-n^in^j)\{\langle p^i(n\cdot r)(E_0-H-k)^{-1} \times(n\cdot r)p^i\rangle-\langle p^i(n\cdot r)^2(E_0-H-k)^{-1}p^i\rangle\}, \quad (5)$$

where $\mathbf{k}=k\mathbf{n}$. The angular brackets denote averaging on the nonrelativistic bound state wave function $\psi_0$, $E_0$, and $H=p^2/2+V$ are, respectively, the nonrelativistic energy of the state and the nonrelativistic Hamiltonian. Here, $Q$ is a projector operator on the subspace orthogonal to $\psi_0$.

The complete contribution is $P_{\alpha^2}(k)=P_{\mathrm{rc}}^{(1)}(k)+P_{\mathrm{rc}}^{(2)}(k)+P_{\mathrm{nq}}(k)$. Its asymptotic expansion for large $k$ may be written in operator form up to terms of $\mathcal{O}(1/k^2)$,

$$\begin{aligned}P_{\alpha^2}(k)=&-\frac{1}{2}\langle\nabla^2\rangle+\frac{2}{k}\langle(H_B-\langle H_B\rangle)(E_0-H)^{-1}\nabla^2\rangle+\frac{4}{5k}\langle\nabla^4\rangle-\frac{1}{2k}\langle(\nabla^2V)\rangle+\frac{\sqrt{2}}{k^{3/2}}\pi Z^2\langle\delta(\mathbf{r})\rangle\\&-\frac{3\ln k}{k^2}\pi Z^3\langle\delta(\mathbf{r})\rangle+\frac{1}{k^2}\left(5\ln 2+\frac{37}{10}\right)\pi Z^3\langle\delta(\mathbf{r})\rangle+\frac{1}{k^2}\langle(H_B-\langle H_B\rangle)(E_0-H)^{-1}(\nabla^2V)\rangle_{\mathrm{fin}}\\&+\frac{1}{k^2}\langle(\nabla V)^2\rangle_{\mathrm{fin}}+\frac{11}{80k^2}\langle(\nabla^4V)\rangle_{\mathrm{fin}}+\frac{1}{16k^2}\langle H_{\mathrm{so}}^{\delta}\rangle+\ldots, \end{aligned}\quad (6)$$

where

$$H_B=-\frac{p^4}{8}+\frac{\pi}{2}\rho+H_{\mathrm{so}},\qquad H_{\mathrm{so}}=\frac{1}{4}\sigma^{ij}\nabla^iVp^j,$$
$$H_{so}^{\delta}=2i\sigma^{ij}p^i(\nabla^2V)p^j,\qquad \sigma^{ij}=[\sigma^i\sigma^j]/(2i)=\epsilon^{ijk}\sigma^k.$$

Expression (6) determines the analytic form for the $1/k^2$ term via finite mean values of the divergent operators (see definitions below) and the term proportional to $Z^3\langle\delta(\mathbf{r})\rangle$; its derivation is similar to what was done in [17] for the $1/k^3$ term of the asymptotic expansion in the nonrelativistic Bethe logarithm case. That is the main advance with respect to the results obtained in [12,13], and is key for the redefinition of the relativistic Bethe logarithm in atomic units.

The finite expectation values, which appear in Eq. (6) are defined as follows ($4\pi\rho=\nabla^2V$):

$$\langle[\nabla^4V]\rangle_{\mathrm{fin}}=-16\pi Z^2\mathcal{R}-32\pi Z^3\mathcal{Q}-8E_0\langle V^2\rangle+4\langle\mathbf{p}V^2\mathbf{p}\rangle+2\langle\mathbf{p}(4\pi\rho)\mathbf{p}\rangle-4E_0\langle 4\pi\rho\rangle, \quad (7a)$$

$$\begin{aligned}&\langle(\nabla^2V)Q(E-H)^{-1}QH_B\rangle_{\mathrm{fin}}\\&=\langle H'^{(1)}Q(E-H)^{-1}QH'^{(2)}\rangle+\frac{1}{4}[4\pi Z^2\mathcal{R}+16\pi Z^3\mathcal{Q}\\&\quad+8E_0\langle V^2\rangle-4E_0^2\langle V\rangle+\langle H^{(1)}\rangle\langle V\rangle-8\langle H^{(2)}\rangle\langle V\rangle]. \end{aligned}\quad (7b)$$

Here, $H'^{(1)}$ and $H'^{(2)}$ are obtained from transformation [18,19]

$$\begin{cases}H'^{(1)}=-(E_0-H_0)U_1-U_1(E_0-H_0)+(\nabla^2V)\\ H'^{(2)}=-(E_0-H_0)U_2-U_2(E_0-H_0)+H_B\end{cases}$$

to eliminate the divergent part from the second order term ($U_1=2V$ and $U_2=-\frac{1}{4}V$).

The functionals $\mathcal{Q}$ and $\mathcal{R}$ in (7) are defined as

$$\mathcal{Q}=\lim_{r_0\to 0}\left\{\left\langle\frac{1}{4\pi r^3}\right\rangle_{r_0}+(\ln r_0+\gamma_E)\langle\delta(\mathbf{r})\rangle\right\} \quad (8)$$

$$\mathcal{R}=\lim_{r_0\to 0}\left\{\langle\frac{1}{4\pi r^4}\rangle_{r_0}-\left[\frac{1}{r_0}\langle\delta(\mathbf{r})\rangle+(\ln r_0+\gamma_E)\langle\delta'(\mathbf{r})\rangle\right]\right\}, \quad (9)$$

where

$$\begin{aligned}\langle\phi_1|\delta'(\mathbf{r})|\phi_2\rangle&=\left\langle\phi_1\left|\frac{\mathbf{r}}{r}\nabla\delta(\mathbf{r})\right|\phi_2\right\rangle\\&=-\langle\partial_r\phi_1|\delta(\mathbf{r})|\phi_2\rangle-\langle\phi_1|\delta(\mathbf{r})|\partial_r\phi_2\rangle,\end{aligned}$$

and $\langle\rangle_{r_0}$ denotes integration outside a sphere of radius $r_0$.

As is discussed in [12,16] we have to subtract the leading terms of expansion (6)

$$P_{\alpha^2}^{(1)}(k)=P_{\alpha^2}(k)-F_{\alpha^2}-\frac{A_{\alpha^2}}{k}-\frac{B_{\alpha^2}}{k^{3/2}} \quad (10a)$$

and

$$P_{\alpha^2}^{(2)}(k)=P_{\alpha^2}(k)-F_{\alpha^2}-\frac{A_{\alpha^2}}{k}-\frac{B_{\alpha^2}}{k^{3/2}}-\frac{C_{\alpha^2}\ln k}{k^2}-\frac{D_{\alpha^2}}{k^2}. \quad (10b)$$

Constants $F$, $A$, $B$, $C$, and $D$ are taken by evaluating expectation values of operators appearing in the expansion (6) for the nonrelativistic wave function of a particular state.

The previous definition [12] of the relativistic Bethe logarithm $\mathcal{L}_H$ assumes scaling to $(Z\alpha) = 1$, and thus it may be expressed in atomic units as

$$\mathcal{L}_H(n,l) = Z^{-6}\left[\frac{2}{3}\int_0^{Z^2E_h} kdkP^{(1)}_{\alpha^2}(k) + \frac{2}{3}\int_{Z^2E_h}^{\infty} kdkP^{(2)}_{\alpha^2}(k)\right]. \tag{11}$$

Comparing (11) with (2) one gets a relation between two definitions of the relativistic Bethe logarithm,

$$\begin{aligned}\mathcal{L}(Z,n,l) = Z^6\mathcal{L}_H(n,l) + \frac{Z^6}{n^3}\left[\ln^2 Z^{-2} + \ln Z^{-2}\left(\frac{10}{3}\ln 2 + \frac{37}{15}\right)\right] + \ln Z^{-2}\left[\frac{2}{3}\langle (H_B - \langle H_B\rangle)(E_0 - H)^{-1}(\nabla^2 V)\rangle_{\rm fin}\right.\\ \left. + \frac{2}{3}\langle (\nabla V)^2\rangle_{\rm fin} + \frac{11}{120}\langle (\nabla^4 V)\rangle_{\rm fin} + \frac{1}{24}\langle H^{\delta}_{so}\rangle\right].\end{aligned} \tag{12}$$

Now substituting this into expression (3.36) of Refs. [12,13] and comparing it with the result of [14,15] for the $1S$ state of hydrogen, we immediately get the general expression for the one-loop self-energy correction in the $m\alpha^7$ order in atomic units:

$$\begin{aligned}\Delta E^{(7)}_{\rm se} = \frac{\alpha^5}{\pi}\Bigg\{&\mathcal{L}(Z,n,l) + \left(\frac{5}{9} + \frac{2}{3}\ln\left[\frac{\alpha^{-2}}{2}\right]\right)\langle (\nabla^2 V)Q(E-H)^{-1}QH_B\rangle_{\rm fin} + 2\langle H_{\rm so}Q(E-H)^{-1}QH_B\rangle\\ &+ \left(\frac{779}{14400} + \frac{11}{120}\ln\left[\frac{\alpha^{-2}}{2}\right]\right)\langle \nabla^4 V\rangle_{\rm fin} + \left(\frac{23}{576} + \frac{1}{24}\ln\left[\frac{\alpha^{-2}}{2}\right]\right)\langle H^{\delta}_{\rm so}\rangle + \left(\frac{589}{720} + \frac{2}{3}\ln\left[\frac{\alpha^{-2}}{2}\right]\right)\langle (\nabla V)^2\rangle_{\rm fin}\\ &+ \frac{3}{80}\langle (\nabla^2 V)\mathbf{p}^2\rangle_{\rm fin} - \frac{1}{2}\langle \mathbf{p}^2 H_{\rm so}\rangle + Z^2\left[-\ln^2[\alpha^{-2}] + \left[\frac{16}{3}\ln 2 - \frac{1}{4}\right]\ln[\alpha^{-2}] - 0.81971202(1)\right]\langle \pi\rho\rangle\Bigg\}.\end{aligned} \tag{13}$$

This formula is the main analytical result of this Letter; it is quite general and may be extended to the case of the external electric field of two (or more) Coulomb sources. One may check that the above expression matches the result of Erickson and Yennie for the logarithmic term for an arbitrary $nS$ state of the hydrogen atom [20].

For the case of the two-center Coulomb problem one needs to replace the delta function in the last line of Eq. (13) by the distribution of Eq. (1).

To present our results we will adopt a similar notation as for hydrogenlike ions [21]:

$$\Delta E^{(7)}_{\rm se} = \frac{\alpha^5}{\pi}\langle V_\delta\rangle[A_{62}\ln^2[\alpha^{-2}] + A_{61}\ln[\alpha^{-2}] + A_{60}], \tag{14}$$

where $A_{62} = -1$; expressions for $A_{61}$ and $A_{60}$ coefficients are obtained from Eqs. (14).

$$\begin{aligned}A_{61}(R) &= \left[\frac{2}{3}\langle (\nabla^2 V)Q(E-H)^{-1}QH_B\rangle_{\rm fin} + \frac{11}{120}\langle \nabla^4 V\rangle_{\rm fin} + \frac{2}{3}\langle (\nabla V)^2\rangle_{\rm fin} + \left(\frac{16}{3}\ln 2 - \frac{1}{4}\right)\langle V_\delta\rangle,\right]/\langle V_\delta\rangle\\ A_{60}(R) &= \left[\left(\frac{5}{9} - \frac{2}{3}\ln 2\right)\langle (\nabla^2 V)Q(E-H)^{-1}QH_B\rangle_{\rm fin} + \left(\frac{779}{14400} - \frac{11}{120}\ln 2\right)\langle \nabla^4 V\rangle_{\rm fin}\right.\\ &\quad\left. + \left(\frac{589}{720} - \frac{2}{3}\ln 2\right)\langle (\nabla V)^2\rangle_{\rm fin} + \frac{3}{80}\langle 4\pi\rho\mathbf{p}^2\rangle_{\rm fin} - 0.81971202(1)\langle V_\delta\rangle + \mathcal{L}(R)\right]/\langle V_\delta\rangle.\end{aligned} \tag{15}$$

Here, $R$ is the distance between the Coulomb centers. Since we are interested in the spin-independent part of transition frequency we have dropped out the terms from Eq. (13), which correspond to the spin-orbit interaction. They will be considered elsewhere.

The coefficients $A_{61}$ and $A_{60}$ now may be calculated by averaging of the "effective" potentials over the vibrational wave function for individual three body states.

In the case of the fundamental vibrational transition $(v = 0, L = 0) \to (v = 1, L = 0)$ in $H_2^+$, the numerical value of the self-energy contribution is

$$\Delta E^{(7)}_{\rm se} \approx 125 \pm 2\ \text{kHz}. \tag{16}$$

The uncertainty here is primarily due to numerical inaccuracy in the calculated data for the relativistic Bethe logarithm [16].

TABLE I. Summary of contributions to the $(v = 0, L = 0) \rightarrow (v' = 1, L' = 0)$ fundamental transition frequency of $H_2^+$ and HD+ molecular ions (in MHz).

| | $H_2^+$ | $HD^+$ |
|---|---|---|
| $\Delta E_{nr}$ | 65 687 511.0714 | 57 349 439.9733 |
| $\Delta E_{\alpha^4}$ | 1091.0397 | 958.1510 |
| $\Delta E_{\alpha^5}$ | −276.5450 | −242.1263 |
| $\Delta E_{\alpha^6}$ | −1.9969 | −1.7481 |
| $\Delta E_{\alpha^7}$ | 0.138(2) | 0.120(2) |
| $\Delta E_{\alpha^8}$ | 0.001(1) | 0.001(1) |
| $\Delta E_{\mathrm{tot}}$ | 65 688 323.708(2) | 57 350 154.371(2) |

In addition to the one-loop self-energy correction, using the results from [22] we computed several other contributions at orders $m\alpha^7$ and $m\alpha^8$, which are proportional to $|\Psi(0)|^2$ [except the $V_{60}$ term in (17)] and easy to evaluate. In what follows, numerical values are the contributions to the fundamental transition in $H_2^+$.

(i) The one-loop vacuum polarization

$$\Delta E_{vp}^{(7)} = \frac{\alpha^5}{\pi}[V_{61}\ln(Z\alpha)^{-2} + V_{60}]\langle V_\delta\rangle \approx 2.9 \text{ kHz}. \quad (17)$$

The coefficients in (17) are taken as follows: $V_{61} = -\frac{2}{15}$, [23], and $V_{60} = \frac{4}{15}[\ln 2 - \frac{1289}{420}]$, as for the hydrogen atom in the $1S$ state [24]. For the nonlogarithmic contribution we approximate the electron wave function $\psi_e(\mathbf{r}_e) \approx N[\psi_{1s}(\mathbf{r}_1) + \psi_{1s}(\mathbf{r}_2)]$ by a sum of two wave functions of the hydrogen atom ground state at the Coulomb centers.

(ii) The Wichman-Kroll contribution [25]

$$\Delta E_{\mathrm{WK}}^{(7)} = \frac{\alpha^5}{\pi}W_{60}\langle V_\delta\rangle \approx -0.1 \text{ kHz}. \quad (18)$$

Here, $W_{60}(nS) = \frac{19}{45} - (\pi^2/27)$.

(iii) The complete two-loop contribution [26]

$$\Delta E_{\text{two-loop}}^{(7)} = \frac{\alpha^5}{\pi}[B_{50}]\langle Z_1^2\delta(\mathbf{r}_1) + Z_2^2\delta(\mathbf{r}_2)\rangle \approx 10.1 \text{ kHz}. \quad (19)$$

TABLE II. Summary of contributions to the $(36, 34) \rightarrow (34, 32)$ transition frequency of the ${}^4He^+\bar{p}$ atom (in MHz).

| | |
|---|---|
| $\Delta E_{nr}$ | 1 522 150 208.13 |
| $\Delta E_{\alpha^4}$ | −50 320.64 |
| $\Delta E_{\alpha^5}$ | 7 070.28 |
| $\Delta E_{\alpha^6}$ | 113.11 |
| $\Delta E_{\alpha^7}$ | −10.46(20) |
| $\Delta E_{\alpha^8}$ | −0.12(12) |
| $\Delta E_{\mathrm{total}}$ | 1 522 107 060.3(2) |

Here, $B_{50} = -21.55447(12)$, this contribution is valid for a bound electron in an arbitrary configuration of few point-like Coulomb sources.

(iv) The three-loop contribution is already negligible. For the hydrogen molecular ion fundamental transition it gives [27]

$$\Delta E_{\text{three-loop}}^{(7)} = \frac{\alpha^5}{\pi^2}[0.42]\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle \approx -60 \text{ Hz}. \quad (20)$$

The above is the complete set of contributions at $m\alpha^7$ order in the nonrecoil limit.

In the next order ($m\alpha^8$) we evaluate only the leading $\ln^3(Z\alpha)^{-2}$ contribution. It represents the second order perturbation with two one-loop self-energy operators $[m\alpha^2(Z\alpha)^6]$ [28]:

$$\Delta E_{\text{two-loop}}^{(8)} = \frac{\alpha^6}{\pi^2}\left[-\frac{8}{27}\right]\ln^3(Z\alpha)^{-2}\langle V_\delta\rangle \approx 1 \text{ kHz}. \quad (21)$$

Using its value we determine the theoretical uncertainty of yet uncalculated terms in the $m\alpha^8$ order and higher.

Adding these results to previously calculated contributions [9,10], one obtains precise theoretical predictions for the transition frequencies (see Tables I and II). Nonrelativistic energies and leading order corrections were obtained with the CODATA10 [8] recommended values. It is necessary to note that we used improved calculations for the leading order relativistic corrections ($m\alpha^4$) and updated values for the Bethe logarithm [29], which were the major source of inaccuracy in the leading order radiative corrections ($m\alpha^5$). That allowed us to significantly reduce numerical uncertainties in the contributions at these orders.

In the $m\alpha^7$ order the uncertainty on the contribution stems from numerical uncertainty in calculation of the relativistic Bethe logarithm [16]. The recoil terms at order $m\alpha^6(m/M)$ are negligible.

The contribution from the finite charge distributions of nuclei deserves special discussion. For the fundamental transition in the $H_2^+$ ion the CODATA10 uncertainty results in 250 Hz uncertainty for the transition energy. If we use instead the charge radius from the muonic hydrogen measurements [30], the frequency will move by 3 kHz; ro-vibrational spectroscopy of $H_2^+$ is thus sensitive to the discrepancy between determinations of the proton radius. The CODATA10 uncertainty due to the deuteron rms charge radius for the $HD^+$ fundamental transition is 215 Hz and is so far negligible. In the antiprotonic helium the value of the rms charge radius of the alpha particle is taken from [31] and results in a frequency uncertainty of 7 kHz, while the corresponding uncertainty from the antiproton rms charge radius is more than 1 order of magnitude less, the antiproton-electron interaction being repulsive.

TABLE III. Comparison with most accurate experimental measurements of transition frequencies for $\mathrm{HD}^+$ and antiprotonic helium (in MHz).

| | Experiment | Theory |
|---|---|---|
| $\mathrm{HD}^+(v, L)$ | | |
| $(0,2) \to (4,3)$ [2] | 214 978 560.6(5) | 214 978 560.948(8) |
| $(0,0) \to (1,1)$ [3] | 58 605 052.00(6) | 58 605 052.156(2) |
| $^4\mathrm{He}^+\bar{p}(n, L)$ [4] | | |
| $(36,34) \to (34,32)$ | 1 522 107 062(4) | 1 522 107 060.3(2) |
| $(33,32) \to (31,30)$ | 2 145 054 858(5) | 2 145 054 858.1(2) |

At present, most accurate experimental results are available for the $\mathrm{HD}^+$ molecular ion and for the antiprotonic helium. In Table III we compare our theoretical results with the best experimental ones. Agreement is excellent in all cases except for the $v = 0 \to v = 1$ transition in $\mathrm{HD}^+$, where the discrepancy is $2.6\sigma_{\mathrm{exp}}$.

In conclusion, we have completed the calculation of the $m\alpha^7$ corrections and obtain new theoretical estimates of experimentally relevant transition frequencies. The theoretical accuracy has been improved by about 1 order of magnitude and has reached a level of 0.03 ppb (0.13 ppb) in molecular hydrogen ions (antiprotonic helium). This is an important milestone, since the achieved accuracy allows for improved determination of the proton- and antiproton-to-electron mass ratios [8].

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