



HAL
open science

Fundamental Transitions and Ionization Energies of the Hydrogen Molecular Ions with Few ppt Uncertainty

Vladimir I. Korobov, L. Hilico, J.-Ph. Karr

► **To cite this version:**

Vladimir I. Korobov, L. Hilico, J.-Ph. Karr. Fundamental Transitions and Ionization Energies of the Hydrogen Molecular Ions with Few ppt Uncertainty. *Physical Review Letters*, 2017, 118 (23), pp.233001. 10.1103/PhysRevLett.118.233001 . hal-01554919

HAL Id: hal-01554919

<https://hal.science/hal-01554919>

Submitted on 24 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Fundamental Transitions and Ionization Energies of the Hydrogen Molecular Ions with Few ppt Uncertainty

Vladimir I. Korobov

Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna 141980, Russia

L. Hilico and J.-Ph. Karr

Laboratoire Kastler Brossel, UPMC-Université Paris 6, ENS, CNRS, Collège de France 4 place Jussieu, F-75005 Paris, France

and Université d'Evry-Val d'Essonne, Boulevard François Mitterrand, F-91000 Evry, France

(Received 23 March 2017; published 8 June 2017)

We calculate ionization energies and fundamental vibrational transitions for H_2^+ , D_2^+ , and HD^+ molecular ions. The nonrelativistic quantum electrodynamics expansion for the energy in terms of the fine structure constant α is used. Previous calculations of orders $m\alpha^6$ and $m\alpha^7$ are improved by including second-order contributions due to the vibrational motion of nuclei. Furthermore, we evaluate the largest corrections at the order $m\alpha^8$. That allows us to reduce the fractional uncertainty to the level of 7.6×10^{-12} for fundamental transitions and to 4.5×10^{-12} for the ionization energies.

DOI: 10.1103/PhysRevLett.118.233001

The hydrogen molecular ions (HMIs) play an essential role in testing molecular quantum mechanics [1,2]. From the theoretical point of view, the HMI is one of the simplest nonintegrable quantum systems, which still allows very accurate numerical treatment. As has already been pointed out, some time ago [3], and recently discussed more extensively [4], if the theory would be sufficiently precise, the spectroscopy of HMIs may be used for determining fundamental physical constants such as the proton-to-electron mass ratio. The ionization energy of HMIs is also of high importance for the determination of ionization and dissociation energies of the hydrogen molecule from spectroscopic studies [5–7] as well as for the determination of atomic masses of light nuclei [8–10].

On the experimental side, there are many new projects started, which are now oriented towards Doppler-free spectroscopy with accuracy targeted to 1 ppt (one part per trillion) or better [4,11–13]. These perspectives bring strong motivation for theory.

The aim of this Letter is to improve the theoretical precision of spin-averaged energies and ro-vibrational transition frequencies in HMIs. To this end, we consider the largest QED contributions which had not been evaluated in our previous works [14–16], namely, corrections to orders $m\alpha^6$ and $m\alpha^7$ due to the vibrational motion of nuclei and the leading contributions to order $m\alpha^8$. As was recently shown [17], taking into account the vibrational motion of nuclei is essential for accurate theoretical description. It has allowed us to resolve the longstanding discrepancy between theory and experiment in the hyperfine structure of H_2^+ ions. These new achievements reduce the relative uncertainty in the fundamental vibrational transitions of HMIs to the level of 7.6×10^{-12} and allow us to obtain the most

precise theoretical values for the ionization energies of H_2^+ , D_2^+ , and HD^+ molecular ions. In conclusion, we discuss how these new results may have an impact on fundamental physical constants such as the Rydberg constant, proton-to-electron mass ratio, and the proton charge radius.

We use atomic units throughout this Letter.

The terms of $m\alpha^6$ and higher orders are calculated in the adiabatic approximation. For this purpose, we use the Born-Oppenheimer (BO) formalism. In this approach, the states of the molecule are taken in the form

$$\Psi^{\text{BO}} = \phi_{\text{el}}(\mathbf{r}; R)\chi_{\text{BO}}(R). \quad (1)$$

The electronic wave function obeys the clamped nuclei Schrödinger equation for a bound electron

$$[H_{\text{el}} - \mathcal{E}_{\text{el}}(R)]\phi_{\text{el}} = 0, \quad (2)$$

where $H_{\text{el}} = p^2/(2m) + V + Z_1Z_2/R$ is the electronic Hamiltonian, $V = -Z_1/r_1 - Z_2/r_2$, where Z_1 and Z_2 are the charges of the nuclei and r_1 , r_2 are the distances from the electron to nuclei 1 and 2, respectively. The wave function $\chi_{\text{BO}}(R)$ describes the relative nuclear motion and is a solution of

$$(H_{\text{vb}} - E_0)\chi_{\text{BO}} = \left[-\frac{\nabla_R^2}{2\mu_n} + \mathcal{E}_{\text{el}}(R) - E_0 \right] \chi_{\text{BO}} = 0, \quad (3)$$

where μ_n is the reduced mass of the nuclei.

Relativistic corrections of order $m\alpha^6$ to the energy of a bound electron in the two-center problem are determined [18,19] by the effective Hamiltonian

$$H^{(6)} = \frac{p^6}{16m^5} + \frac{[\nabla V]^2}{8m^3} - \frac{3\pi}{16m^4} \{p^2\rho + \rho p^2\} \\ + \frac{5}{128m^4} (p^4 V + V p^4) - \frac{5}{64m^4} (p^2 V p^2), \quad (4)$$

and the second-order contribution of the Breit-Pauli (BP) Hamiltonian

$$\Delta E_{\text{BP}} = \langle H_{\text{BP}} Q (E_{\text{el}} - H_{\text{el}})^{-1} Q H_{\text{BP}} \rangle. \quad (5)$$

Here, $\rho = \nabla^2 V / (4\pi)$, Q is a projection operator onto a subspace orthogonal to ϕ_{el} from Eq. (2). H_{BP} is the Breit-Pauli relativistic correction (RC) for a bound electron

$$H_{\text{BP}} = -\frac{p^4}{8m^3} + \frac{\pi\rho}{2m^2} + H_{\text{BP}}^{\text{so}}, \quad (6)$$

$H_{\text{BP}}^{\text{so}}$ is the electron spin-orbit contribution (see details in [19]). Both terms are divergent, but their sum is finite

$$\mathcal{E}_{\text{RC}}^{(6)}(R) = \alpha^4 [\Delta E_{\text{BP}}(R) + \langle H^{(6)} \rangle (R)]. \quad (7)$$

The leading contribution was obtained in [14] by averaging this effective potential over R

$$\Delta E_{\text{el}}^{(6)} = \langle \chi_{\text{BO}} | \mathcal{E}_{\text{RC}}^{(6)}(R) | \chi_{\text{BO}} \rangle. \quad (8a)$$

The next step is to consider the three-body correction to the energy E_0 of a molecular state, which we derive within the framework of the adiabatic approximation defined by Eqs. (1)–(3). This correction stems from the insertion of the Breit-Pauli effective potential $\mathcal{E}_{\text{BP}}(R) = \alpha^2 \langle H_{\text{BP}} \rangle$ into Eq. (3) and, in the order $m\alpha^6$, is expressed by

$$\Delta E_{\text{vb}}^{(6)} = \langle \chi_{\text{BO}} | \mathcal{E}_{\text{BP}}(R) Q' (E_0 - H_{\text{vb}})^{-1} Q' \mathcal{E}_{\text{BP}}(R) | \chi_{\text{BO}} \rangle, \quad (8b)$$

Q' is a projection operator onto a subspace orthogonal to $\chi_{\text{BO}}(R)$.

Obviously, instead of the Born-Oppenheimer solution $\chi_{\text{BO}}(R)$, one may use the adiabatic solution $\chi_{\text{ad}}(R)$, which includes, as well, the adiabatic corrections (see Ref. [20] for definitions, or a review by Carrington *et al.* [1]).

A complete set of the contributions at order $m\alpha^6$ is presented in Table I. Here, we include, as well, the relativistic recoil contribution at order $m(Z\alpha)^6(m/M)$ [21] and the radiative recoil contribution [22,23]. In the former case, the part which depends on the state wave function was evaluated with the help of LCAO approximation and its value had been used as an error bar for the recoil term.

The total contribution to the one-loop self energy correction at order $m\alpha^7$ similarly should be written

TABLE I. Summary of contributions at order $m\alpha^6$ to the fundamental transitions in H_2^+ , D_2^+ , and HD^+ (in kHz). The first four contributions are defined as written in Eq. (1) of [14], $\Delta E_{\text{rel-el}}$ is the electronic contribution from Eq. (8), $\Delta E_{\text{rel-vb}}$ is the newly obtained vibrational contribution from Eq. (8b). The last contribution is the sum of the recoil and radiative-recoil corrections of order $m\alpha^6(m/M)$ (see text).

	H_2^+	D_2^+	HD^+
$\Delta E_{\text{1loop-SE}}$	-1881.2	-1362.3	-1647.0
ΔE_{anom}	21.2	15.3	18.5
ΔE_{VP}	-66.3	-48.0	-58.0
ΔE_{2loop}	-55.9	-40.5	-48.9
$\Delta E_{\text{rel-el}}$	-15.1	-10.5	-13.0
$\Delta E_{\text{rel-vb}}$	44.6	32.2	39.0
ΔE_{recoil}	0.75(3)	0.27(1)	0.49(2)
ΔE_{tot}	-1952.0(1)	-1413.4(1)	-1708.9(1)

$$\Delta E_{\text{el}}^{(7)} = \langle \chi_{\text{ad}} | \mathcal{E}_{\text{1loop-SE}}^{(7)}(R) | \chi_{\text{ad}} \rangle,$$

$$\Delta E_{\text{vb}}^{(7)} = \langle \chi_{\text{ad}} | \mathcal{E}_{\text{BP}}(R) Q' (E_0 - H_{\text{vb}})^{-1} Q' \mathcal{E}_{\text{SE}}^{(5)}(R) | \chi_{\text{ad}} \rangle, \quad (9)$$

where $\mathcal{E}_{\text{1loop-SE}}^{(7)}(R)$ is an effective potential of the $m\alpha^7$ -order correction [see Eq. (11), in [15]], to the energy of the bound electron in the two-center problem, and

$$\mathcal{E}_{\text{SE}}^{(5)}(R) = \alpha^3 \frac{4}{3} \left[\ln \frac{1}{\alpha^2} - \beta(R) + \frac{5}{6} - \frac{3}{8} \right] \\ \times \langle Z_1 \delta(\mathbf{r}_1) + Z_2 \delta(\mathbf{r}_2) \rangle \quad (10)$$

is the one-loop self-energy correction of order $m\alpha^5$. $\beta(R)$ is the nonrelativistic Bethe logarithm for the bound electron in the two-center problem, whose values as a function of R may be found in the Supplemental Material to Ref. [24] or in [25].

A similar separation between electronic and vibrational contributions also occurs for the one-loop vacuum polarization (VP) term, which was obtained in [26].

Contributions to order $m\alpha^7$ without the vibrational second-order term were considered in [15,16]. Here, we present final results, which appear in Table II. We have managed to significantly improve precision of the relativistic correction to the Bethe logarithm (see, for details, [27]), which allowed us to reduce the theoretical uncertainty in the one-loop self-energy by an order of magnitude.

Finally, we turn to the evaluation of $m\alpha^8$ -order corrections.

For hydrogenlike atoms, the two-loop correction at order $m\alpha^8$ may be written in the form

$$E_{\text{2loop}}^{(8)} = \left(\frac{1}{\pi} \right)^2 \frac{(Z\alpha)^6}{n^3} [B_{63} L^3(Z\alpha) + B_{62} L^2(Z\alpha) \\ + B_{61} L(Z\alpha) + B_{60}], \quad (11)$$

TABLE II. Summary of contributions at order $m\alpha^7$ to the fundamental transitions in H_2^+ , D_2^+ , and HD^+ (in kHz). The first two contributions are the one-loop self-energy and vacuum polarization corrections, which include the vibrational contribution (see text). The third line is the Wichman-Kroll (WK) contribution [28]. The last three contributions are defined in Eqs. (23)–(25) of [15].

	H_2^+	D_2^+	HD^+
$\Delta E_{1\text{loop-SE}}$	109.0(1)	78.8(1)	95.4(1)
ΔE_{VP}	2.8	2.0	2.4
ΔE_{WK}	-0.08	-0.06	-0.07
$\Delta E_{2\text{loop}}$	10.1	7.3	8.9
$\Delta E_{3\text{loop}}$	-0.06	-0.05	-0.05
ΔE_{tot}	121.8(1)	88.1(1)	106.4(1)

where $L(Z\alpha) \equiv \ln(Z\alpha)^{-2}$. It is useful to recall the numerical values of the various terms for the ground state of the hydrogen atom [28]

$$\Delta E(1S) \approx \frac{(Z\alpha)^6}{\pi^2} [-282 - 62 + 476 - 61].$$

This shows that the third term [linear in $\ln(Z\alpha)^{-2}$] is the largest one, contrary to our intuition on the hierarchy of the consecutive terms in the $Z\alpha$ expansion.

In the case of a two-center system, the corrections can still be written in the form of Eq. (11) (with $n = 1$ and $Z_1 = Z_2 = Z$). The first three coefficients B_{6k} can be obtained from the results of [29] as

$$\begin{aligned} Z^6 B_{63} &= -\frac{8}{27} Z^3 \pi \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle, \\ Z^6 B_{62} &= \frac{1}{9} \langle \nabla^2 V Q (E_0 - H)^{-1} Q \nabla^2 V \rangle_{\text{fin}} + \frac{1}{18} \langle \nabla^4 V \rangle_{\text{fin}} \\ &\quad + \frac{16}{9} \left[\frac{31}{15} + 2 \ln 2 \right] Z^3 \pi \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle, \end{aligned} \quad (12)$$

and

$$\begin{aligned} Z^6 B_{61} &= -2 \left[\frac{1}{9} \langle \nabla^2 V Q (E_0 - H)^{-1} Q \nabla^2 V \rangle_{\text{fin}} \right. \\ &\quad \left. + \frac{1}{18} \langle \nabla^4 V \rangle_{\text{fin}} \right] \ln 2 + \frac{4}{3} N(R) \\ &\quad + \frac{19}{135} \langle \nabla^2 V Q (E_0 - H)^{-1} Q \nabla^2 V \rangle_{\text{fin}} \\ &\quad + \frac{19}{270} \langle \nabla^4 V \rangle_{\text{fin}} + \frac{1}{24} \langle 2i\sigma^{ij} p^i \nabla^2 V p^j \rangle \\ &\quad + \left[\frac{48781}{64800} + \frac{2027\pi^2}{864} + \frac{56}{27} \ln 2 - \frac{2\pi^2}{3} \ln 2 \right. \\ &\quad \left. + 8 \ln^2 2 + \zeta(3) \right] Z^3 \pi \langle \delta(\mathbf{r}_2) + \delta(\mathbf{r}_1) \rangle. \end{aligned} \quad (13)$$

Among the terms presented in Eqs. (12) and (13), all the distributions were determined and calculated in [15]

except N , which is defined in Eq. (4.21.a) of [29]. On the other hand, the expression for N is similar to the one of Eq. (10) in Ref. [24]. Using the same technique, which has been used for calculations of the relativistic Bethe logarithm, we were able to get N for the hydrogen atom ground state $N(1S) = 17.8556720362(1)$, which is in good agreement with the value given in [29] and even adds two more significant digits. Having validated our approach, we then did calculations of the $N(R)$ “effective” potential for the two-center problem. Putting it into Eq. (13) and then averaging over R , we get, for the ionization energy of H_2^+ (in kHz),

$$\begin{aligned} \Delta E_{2\text{loop}}^{(8)} &= \alpha^6 [B_{63} L^3(\alpha) + B_{62} L^2(\alpha) + B_{61} L(\alpha) + B_{60}] \\ &\approx 37.0 - 17.3 - 52.9 + 7.8. \end{aligned}$$

The last term in the second line has been evaluated in the LCAO approximation using the atomic hydrogen ground state value for B_{60} . We take the error bar on the two-loop contribution as equal to this approximate value of the nonlogarithmic term. In our previous studies, we used the same kind of estimates for the uncertainty resulted from the yet uncalculated terms, and further improvements of the theory showed the good relevance of this approach.

Similarly, for the fundamental transition ($L = 0$, $v = 0$) \rightarrow ($L' = 0$, $v' = 1$) (in kHz),

$$\begin{aligned} \Delta \nu_{2\text{loop}}^{(8)} &= \alpha^6 [B_{63}^\nu L^3(\alpha) + B_{62}^\nu L^2(\alpha) + B_{61}^\nu L(\alpha) + B_{60}^\nu] \\ &\approx 0.97 - 1.68 - 0.84 + 0.21, \end{aligned}$$

and for the uncertainty, we take $u_r(E_{2\text{loop}}) = 0.21$ kHz.

The other significant contribution at the $m\alpha^8$ order is the one-loop self-energy,

$$E_{1\text{loop}}^{(8)} = \frac{\alpha^6}{\pi n^3} Z^7 [A_{71} \ln(Z\alpha)^{-2} + A_{70}], \quad (14)$$

where the leading term has an analytic result [28,30]: $A_{71}(nS) = \pi[139/64 - \ln 2]$. For the hydrogen atom, the nonlogarithmic contribution A_{70} of order $m\alpha(Z\alpha)^7$ has never been calculated directly. By extrapolation of the $G_{\text{se}}(1S, Z\alpha)$ function [31] with the expansion over $Z\alpha$ [see Eq. (5.1) from [31]], one may get $A_{70} = 44.4$. Similar to the two-loop corrections above, we take the nonlogarithmic term as an estimate of the theoretical uncertainty.

The second order contributions, due to vibrational motion, both from one- and two-loop diagrams, were evaluated as well. The total frequency shift is about 100 Hz and may be neglected for the time being. Table III presents a set of calculated contributions at order $m\alpha^8$ and estimates of error bars due to yet uncalculated terms.

TABLE III. Summary of contributions at order $m\alpha^8$ to the fundamental transitions in H_2^+ , D_2^+ , and HD^+ (in kHz).

	H_2^+	D_2^+	HD^+
$\Delta E_{2\text{loop}}$	-1.34(21)	-0.97(15)	-1.17(18)
$\Delta E_{1\text{loop-SE}}$	-0.97(48)	-0.70(35)	-0.85(42)
ΔE_{VP}	-0.017	-0.013	-0.015
ΔE_{tot}	-2.3(5)	-1.7(4)	-2.0(5)

The main results of our work, frequencies for the fundamental transitions ($L=0, v=0$) \rightarrow (0, 1) and ionization energies of the HMIs, are presented in Tables IV and V, respectively. To get precision data for the relativistic corrections of order $m\alpha^4$ we have used the expectation values of the Breit-Pauli operators, which were obtained in [32–34] with 15 or even more significant digits. As may be extracted from the Tables, the new theoretical relative uncertainty for the fundamental transition frequency is $u_r(\nu(\text{H}_2^+)) = 0.5/(66 \times 10^9) \approx 7.6 \times 10^{-12}$, and accordingly, for the ionization energy, one gets $u_r(E_I) = 4.5 \times 10^{-12}$. The CODATA14 [35] uncertainty of the Rydberg constant is $u_r(R_\infty) = 5.9 \times 10^{-12}$. Since this constant enters in the data of the Tables as a multiplier, an uncertainty in the energies due to the uncertainty in the Rydberg constant can be easily evaluated and is not shown.

These results have direct impact on the potential determination of the fundamental constants. For example, the theoretical uncertainty on the fundamental transition in H_2^+ sets the following limit on the achievable precision of the proton-to-electron mass ratio ($\mu_p = m_p/m_e$) to

$$\Delta\mu_p/\mu_p = 1.5 \times 10^{-11}. \quad (15)$$

This uncertainty is smaller by a factor of 6 with respect to the present CODATA, $u_r(\mu_p) = 9.5 \times 10^{-11}$ [10], which is currently limited by uncertainty on the proton's atomic mass. The electron's atomic mass has recently been improved [$u_r(A_r(e)) = 3.1 \times 10^{-11}$] by a high-precision measurement of the g factor of a bound electron in a $^{12}\text{C}^{5+}$

TABLE IV. Fundamental transition frequencies ν_{01} for H_2^+ , D_2^+ , and HD^+ molecular ions (in kHz). CODATA14 recommended values of constants. The first error is the theoretical uncertainty, the second error is due to the uncertainty in mass ratios.

	H_2^+	D_2^+	HD^+
ν_{nr}	65 687 511 047.0	47 279 387 818.4	57 349 439 952.4
ν_{α^2}	1 091 040.5	795 376.3	958 151.7
ν_{α^3}	-276 545.1	-200 278.0	-242 126.3
ν_{α^4}	-1952.0(1)	-1413.4(1)	-1708.9(1)
ν_{α^5}	121.8(1)	88.1(1)	106.4(1)
ν_{α^6}	-2.3(5)	-1.7(4)	-2.0(5)
ν_{tot}	65 688 323 710.1(5)(2.9)	47 279 981 589.8(4)(8)	57 350 154 373.4(5)(1.7)

ion [36]. In terms of ultimate accuracy limits, the 1.5×10^{-11} theoretical uncertainty that we have achieved for HMI spectroscopy is comparable to the current theoretical uncertainty of 1.3×10^{-11} on the g factor of $^{12}\text{C}^{5+}$ [10,37].

The proton rms charge radius (r_p) uncertainty as determined in the CODATA14 adjustment has a much smaller contribution $\sim 5 \times 10^{-12}$ to the uncertainty in the fundamental transitions. However, replacing the CODATA value of r_p with that obtained from muonic hydrogen spectroscopy [38,39] leads to a 3 kHz blueshift of the transition, i.e., a relative shift of 5×10^{-11} . If we assume that the muonic hydrogen adjusted Rydberg constant should be used as a proper constant when using the muonic hydrogen proton radius [40], then we get a global shift of 1.1 kHz, which is still feasible for detection (see, also, the more detailed discussion in [4]).

Finally, since the fundamental transitions have the potentiality to be used for adjustment of the fundamental constants, here, we present, in explicit form, the frequency dependence of transition lines on the masses and on the proton and deuteron charge radii

$$\begin{aligned} \nu(\text{H}_2^+) &= \nu_0(\text{H}_2^+) + \frac{\Delta R_\infty}{R_\infty} \nu_0(\text{H}_2^+) + 2(R_\infty c) \\ &\times [-2.55528 \times 10^{-6} \Delta\mu_p - 8.117 \times 10^{-12} \Delta r_p], \end{aligned} \quad (16a)$$

where $\Delta R_\infty = R_\infty - R_{\infty,0}$, $\Delta\mu_p = \mu_p - \mu_{p,0}$, and $\Delta r_p = r_p^2 - r_{p,0}^2$, here, the subscript 0 stands for the CODATA14 value, and ν_0 is the transition frequency presented in Table IV, which was calculated with the CODATA14 values of the constants

$$\begin{aligned} \nu(\text{D}_2^+) &= \nu_0(\text{D}_2^+) + \frac{\Delta R_\infty}{R_\infty} \nu_0(\text{D}_2^+) + 2(R_\infty c) \\ &\times [-9.37686 \times 10^{-7} \Delta\mu_d - 5.877 \times 10^{-12} \Delta r_d], \end{aligned} \quad (16b)$$

here, $\Delta\mu_d = \mu_d - \mu_{d,0}$ and $\Delta r_d = r_d^2 - r_{d,0}^2$,

TABLE V. Ionization energies E_I for H_2^+ , D_2^+ , and HD^+ molecular ions (in cm^{-1}). CODATA14 recommended values of constants. The error is the theoretical uncertainty. The error due to the uncertainty in mass ratio is below 10^{-7} cm^{-1} .

	H_2^+	D_2^+	HD^+
$E_{I,nr}$	131 056.875 746 5	131 418.947 704 1	131 223.436 257 8
E_{I,α^2}	1.599 499 5	1.604 830 6	1.601 914 2
E_{I,α^3}	-0.350 930 0	-0.352 552 7	-0.351 679 1
E_{I,α^4}	-0.002 477 4(1)	-0.002 489 7(1)	-0.002 483 1(1)
E_{I,α^5}	0.000 156 9(1)	0.000 157 6(1)	0.000 140 9(1)
E_{I,α^6}	-0.000 002 1(6)	-0.000 002 1(6)	-0.000 002 1(6)
$E_{I,\text{tot}}$	131 058.121 993 7(6)	131 420.197 648 0(6)	131 224.684 165 0(6)

$$\begin{aligned} \nu(\text{HD}^+) &= \nu_0(\text{HD}^+) + \frac{\Delta R_\infty}{R_\infty} \nu_0(\text{HD}^+) + 2(R_\infty c) \\ &\times [-1.49998 \times 10^{-6} \Delta\mu_p - 3.75470 \times 10^{-7} \Delta\mu_d \\ &- 3.555 \times 10^{-12} \Delta r_p - 3.550 \times 10^{-12} \Delta r_d]. \end{aligned} \quad (16c)$$

In the last equation, Δr_d may be, in principle, eliminated since the measured H-D isotope shift of the 1S-2S transition [41] determines the deuteron-proton charge radius difference [10,42]

$$r_d^2 - r_p^2 = 3.81948(37) \text{ fm}^2,$$

with much smaller error than the CODATA14 uncertainties for r_p and r_d .

In summary, we have considered several new contributions to the binding energies of HMIs, which result in an essential improvement of the theoretical uncertainty both for the ionization energies and for the transition frequencies of the HMIs. This level of precision allows us to use the HMI spectroscopy as an alternative way for determination of the fundamental physical constants.

This work was supported by Université Pierre et Marie Curie (UPMC), which is gratefully acknowledged. J.-Ph. K. acknowledges support from a Fellowship of the Institut Universitaire de France. V. I. K. acknowledges support from the Russian Foundation for Basic Research under Grant No. 15-02-01906-a. The authors also very much appreciate valuable discussions with K. Pachucki.

-
- [1] A. Carrington, I. R. McNab, and Ch. A. Montgomerie, *J. Phys. B* **22**, 3551 (1989).
 [2] Ch. A. Leach and R. E. Moss, *Annu. Rev. Phys. Chem.* **46**, 55 (1995).
 [3] W. H. Wing, G. A. Ruff, W. E. Lamb, Jr., and J. J. Spezeski, *Phys. Rev. Lett.* **36**, 1488 (1976).
 [4] J.-Ph. Karr, L. Hilico, J. C. J. Koelemeij, and V. I. Korobov, *Phys. Rev. A* **94**, 050501(R) (2016).
 [5] Jinjun Liu, E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, and F. Merkt, *J. Chem. Phys.* **130**, 174306 (2009).
 [6] Jinjun Liu, D. Sprecher, Ch. Jungen, W. Ubachs, and F. Merkt, *J. Chem. Phys.* **132**, 154301 (2010).
 [7] D. Sprecher, J. Liu, Ch. Jungen, W. Ubachs, and F. Merkt, *J. Chem. Phys.* **133**, 111102 (2010).
 [8] E. G. Myers, A. Wagner, H. Kracke, and B. A. Wesson, *Phys. Rev. Lett.* **114**, 013003 (2015).
 [9] S. L. Zafonte and R. S. Van Dyck, Jr., *Metrologia* **52**, 280 (2015).
 [10] P. J. Mohr, B. N. Taylor, and D. B. Newell, *Rev. Mod. Phys.* **88**, 035009 (2016).
 [11] V. Q. Tran, J.-Ph. Karr, A. Douillet, J. C. J. Koelemeij, and L. Hilico, *Phys. Rev. A* **88**, 033421 (2013).

- [12] S. Schiller, D. Bakalov, and V. I. Korobov, *Phys. Rev. Lett.* **113**, 023004 (2014).
 [13] S. Schiller, I. Kortunov, M. Hernández Vera, F. Gianturco, and H. da Silva, Jr., *Phys. Rev. A* **95**, 043411 (2017).
 [14] V. I. Korobov, *Phys. Rev. A* **77**, 022509 (2008).
 [15] V. I. Korobov, L. Hilico, and J.-Ph. Karr, *Phys. Rev. A* **89**, 032511 (2014).
 [16] V. I. Korobov, L. Hilico, and J.-Ph. Karr, *Phys. Rev. Lett.* **112**, 103003 (2014).
 [17] V. I. Korobov, J. C. J. Koelemeij, L. Hilico, and J.-Ph. Karr, *Phys. Rev. Lett.* **116**, 053003 (2016).
 [18] K. Pachucki, *Phys. Rev. A* **56**, 297 (1997).
 [19] V. I. Korobov and Ts. Tsogbayar, *J. Phys. B* **40**, 2661 (2007).
 [20] L. Wolniewicz and J. D. Poll, *J. Chem. Phys.* **73**, 6225 (1980).
 [21] K. Pachucki, *Phys. Rev. Lett.* **79**, 4120 (1997).
 [22] K. Pachucki, *Phys. Rev. A* **52**, 1079 (1995).
 [23] A. Czarnecki and K. Melnikov, *Phys. Rev. Lett.* **87**, 013001 (2001); I. Blokland, A. Czarnecki, and K. Melnikov, *Phys. Rev. D* **65**, 073015 (2002).
 [24] V. I. Korobov, L. Hilico, and J.-Ph. Karr, *Phys. Rev. A* **87**, 062506 (2013).
 [25] R. Bukowski, B. Jeziorski, R. Moszyński, and W. Kołos, *Int. J. Quantum Chem.* **42**, 287 (1992).
 [26] J.-Ph. Karr, L. Hilico, and V. I. Korobov, *Phys. Rev. A* **95**, 042514 (2017).
 [27] V. I. Korobov, L. Hilico, and J.-Ph. Karr, *Hyperfine Interact.* **233**, 75 (2015).
 [28] M. I. Eides, H. Grotch, and V. A. Shelyuto, *Theory of Light Hydrogenic Bound States*, Springer Tracts in Modern Physics Vol. 222 (Springer, Berlin, 2007).
 [29] U. D. Jentschura, A. Czarnecki, and K. Pachucki, *Phys. Rev. A* **72**, 062102 (2005).
 [30] S. G. Karshenboim, *Z. Phys. D* **39**, 109 (1997).
 [31] U. D. Jentschura, P. J. Mohr, and G. Soff, *Phys. Rev. A* **63**, 042512 (2001).
 [32] Z.-X. Zhong, Z.-C. Yan, and T.-Y. Shi, *Phys. Rev. A* **79**, 064502 (2009).
 [33] Z.-X. Zhong, P.-P. Zhang, Z.-C. Yan, and T.-Y. Shi, *Phys. Rev. A* **86**, 064502 (2012).
 [34] P.-P. Zhang, Z.-X. Zhong, Z.-C. Yan, and T.-Y. Shi, *Phys. Rev. A* **93**, 032507 (2016).
 [35] The Committee on Data of the International Council for Science (ICSU), <http://www.codata.org/about-codata>.
 [36] S. Sturm, F. Köhler, J. Zatorski, A. Wagner, Z. Harman, G. Werth, W. Quint, C. H. Keitel, and K. Blaum, *Nature (London)* **506**, 467 (2014).
 [37] K. Pachucki, A. Czarnecki, U. D. Jentschura, and V. A. Yerokhin, *Phys. Rev. A* **72**, 022108 (2005).
 [38] R. Pohl *et al.*, *Nature (London)* **466**, 213 (2010).
 [39] A. Antognini *et al.*, *Science* **339**, 417 (2013).
 [40] R. Pohl, R. Gilman, G. A. Miller, and K. Pachucki, *Annu. Rev. Nucl. Part. Sci.* **63**, 175 (2013).
 [41] C. G. Parthey, A. Matveev, J. Alnis, R. Pohl, T. Udem, U. D. Jentschura, N. Kolachevsky, and T. W. Hänsch, *Phys. Rev. Lett.* **104**, 233001 (2010).
 [42] U. D. Jentschura, A. Matveev, C. G. Parthey, J. Alnis, R. Pohl, T. Udem, N. Kolachevsky, and T. W. Hänsch, *Phys. Rev. A* **83**, 042505 (2011).