Fundamental transitions and ionization energies of the hydrogen molecular ions at the few ppt level.

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We calculate ionization energies and fundamental vibrational transitions for $H^+_6$, $D^+_6$, and $H^+_2$ molecular ions. The NRQED expansion for the energy in terms of the fine structure constant $\alpha$ 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 to reduce the fractional uncertainty to the level of $7 \times 10^{-12}$ for fundamental transitions and to $4 \times 10^{-12}$ for the ionization energies.

The hydrogen molecular ions (HMI) play an essential role in testing molecular quantum mechanics [1, 2]. From the theoretical point of view the HMI is the simplest non-integrable quantum system, which still allows very accurate numerical treatment. As was pointed out already some time ago [3], and recently discussed more extensively [4], if the theory would be sufficiently precise, the comparison of spin-averaged energy levels and ro-vibrational spectroscopic studies [5–7] as well as in the CODATA evaluation of spin-averaged energy levels and ro-vibrational spectroscopic studies [5–7] as well as in the CODATA and dissociation energies of the hydrogen molecule from spectroscopic studies [8, 9, 10] as well as in the CODATA adjustment [8] for the determination of atomic masses of particles.

The aim of this Letter is to improve the theoretical precision of spin-averaged energy levels and ro-vibrational transition frequencies in HMI. To this end we consider the largest QED contributions which had not been evaluated in our previous works [2, 11], namely, corrections to orders $m\alpha^6$ and $m\alpha^7$ due to vibrational motion of nuclei and the leading contributions to order $m\alpha^8$. As it was shown recently [12], taking into account the vibrational motion of nuclei allows to resolve the discrepancy between theory and experiment in the hyperfine structure of $H^+_2$ ion.

These new achievements reduce the relative uncertainty in the fundamental vibrational transitions of HMI to the level of $7 \times 10^{-12}$ and allow to obtain the most precise theoretical values for the ionization energies of $H^+_6$, $D^+_2$, and $H^+_2$ molecular ions. In conclusion we discuss how these new results may have impact on fundamental physical constants such as the Rydberg constant, proton-to-electron mass ratio, and proton charge radius.

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

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

(1)

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

$$[H_{el} - E_{el}(R)]\phi_{el} = 0,$$

(2)

where $H_{el} = p^2/(2m) + V + Z_1Z_2/R$ 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

$$(H_{vb} - E_0)\chi_{\text{BO}} = \left[\frac{\nabla^2_{n}}{2\mu_n} + E_{el}(R) - E_0\right]\chi_{\text{BO}} = 0,$$

(3)

where $\mu_n$ 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 [13, 14] by the effective Hamiltonian:

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

(4)

and the second order contribution of the Breit-Pauli Hamiltonian,

$$\Delta E_B = \langle H_B Q(E_{el} - H_{el})^{-1}QH_B\rangle.$$

(5)

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

$$H_B = -\frac{p^4}{8m^3} + \frac{\pi\rho}{2m^2} + H_{B}^{\text{sc}},$$

(6)
The total contribution to the one-loop self energy correction at order $m\alpha^7$ similarly should be written

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

and

$$\Delta E_{\text{vb}}^{(7)} = \left< \chi_{\text{ad}} | \mathcal{E}_{\text{B}}(R) Q' (E_0 - H_{\text{vb}})^{-1} Q' \mathcal{E}_{\text{SE}}(R) | \chi_{\text{ad}} \right>,$$

where $\mathcal{E}_{\text{1loop-SE}}^{(7)}(R)$ is an effective potential of the $m\alpha^7$-order correction (see Eq. (11), in [10]), to the energy of the bound electron in the two-center problem, and

$$\mathcal{E}_{\text{SE}}^{(5)}(R) = \alpha^3 \left[ \frac{1}{\alpha^2} - \beta(R) + \frac{5}{6} - \frac{3}{8} \right],$$

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. [10] or in [20].

A similar separation between electronic and vibrational contributions also occurs for the one-loop vacuum polarization term, which was obtained in [21].

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. (14), (23)–(25) of [10]. 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.

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The leading contribution was obtained in [10] by averaging this effective potential over $R$:

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This shows that the third term (linear in ln(Zα)^{−2}) is the largest one, contrary to our intuition on hierarchy of the consecutive terms in the Zα expansion.

In case of a two-center system the corrections can still be written in the form of Eq. (11) (with n = 1). The first three coefficients B_{6α} can be obtained from the results of [24] as

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

\[ Z^6 B_{61} = -2 \left[ \frac{1}{9} \left\langle \nabla^2 V Q(E_0 - H)^{-1} Q \nabla^2 V \right\rangle_{\text{fin}} \right. \]
\[ + \frac{1}{18} \left( \nabla^4 V \right)_{\text{fin}} \ln 2 + \frac{4}{3} N(n,l) \]
\[ + \frac{19}{135} \left( \nabla^2 V Q(E_0 - H)^{-1} Q \nabla^2 V \right)_{\text{fin}} \]
\[ + \frac{19}{270} \left( \nabla^4 V \right)_{\text{fin}} + \frac{1}{24} \left( 2i \sigma^{ij} P^i \nabla^2 V P^j \right) \]
\[ + \left[ \frac{48781}{64800} + \frac{2027 \pi^2}{864} + \frac{56 \ln 2 - \frac{2 \pi^2}{3}}{27} \ln 2 \right. \]
\[ + 8 \ln^2 2 \right\} Z^3 \langle \pi \delta(r) \rangle. \]

Among the terms presented in Eqs. (12), (13) all the distributions were determined and calculated in [10] except N(n,l), which is defined in Eq. (4.21a) of [24]. On the other hand the expression for N is similar to the one of Eq. (10) in Ref. [19]. 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 a good agreement with the value given in [24] 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)

\[ \Delta E^{(8)}_{\text{2loop}} = \alpha^6 \left[ B_{63} L^3(\alpha) + B_{62} L^2(\alpha) + B_{61} L(\alpha) + B_{60} \right] \]
\[ \approx 37.0 - 17.3 - 52.9 + 7.8. \]

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 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) → (L' = 0, v' = 1) (in kHz)

\[ \Delta\nu^{(8)}_{\text{2loop}} = \alpha^6 \left[ B_{63} L^3(\alpha) + B_{62} L^2(\alpha) + B_{61} L(\alpha) + B_{60} \right] \]
\[ \approx 0.97 - 1.68 - 0.84 + 0.21, \]
and for the uncertainty we take u(E_{2loop}) = 0.21 kHz.

The other significant contribution at the mα^8 order is the one-loop self-energy,

\[ E^{(8)}_{\text{1loop}} = \frac{\alpha}{\pi n^3} \left[ A_{71} \ln(Z\alpha)^{-2} + A_{70} \right], \]
where the leading term has analytic result [23]:

\[ A_{71}(nS) = \pi \left[ \frac{139}{64} - \ln 2 \right]. \]

For the hydrogen atom the nonlogarithmic contribution A_{70} of order mα(Zα)^7 has never been calculated directly. By extrapolation of the G_s(1S, Zα) function [24] with the expansion over Zα (see Eq. (5.1) from [23]) one may get A_{70} = 44.4. Similarly to the two-loop corrections above, we take the nonlogarithmic term as 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.

The main results of our work — frequencies for the fundamental transitions (L = 0, v = 0) → (0, 1) and ionization energies of the HMI — are presented in Tables IV and V respectively. To get precision data for the relativistic corrections of order mα^4 we have used the expectation values of the Breit-Pauli operators, which were obtained in [27–29] with 15 or even more significant digits.

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 (μ_p = m_p/m_e) to

\[ \Delta \mu_p/\mu_p = 1.5 \cdot 10^{-11}. \]
This uncertainty is smaller by a factor of 6 with respect to the present CODATA, $\Delta \mu_p/\mu_p = 9.5 \cdot 10^{-11}$ [8], which was recently improved by a high-precision measurement of the electron’s atomic mass [32] from the $g$-factor of a bound electron in a $^{12}$C$^{5+}$ ion, and is currently limited by uncertainty on the proton’s atomic mass. In terms of ultimate accuracy limits, the $1.5 \cdot 10^{-11}$ uncertainty that we have achieved for HMI spectroscopy is comparable to the current theoretical uncertainty of $1.3 \cdot 10^{-11}$ on the $g$-factor of $^{12}$C$^{5+}$ [8, 33].

The proton rms charge radius ($r_p$) uncertainty as defined in the CODATA14 adjustment may be in principle eliminated since the measured H-D isotope shift of the 1S-2S transition [34] determines the deuteron-proton charge radius difference [8, 35] $r_d^2 - r_p^2 = 3.81948(37)$ fm$^2$

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


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\begin{table}[h]
\centering
\caption{Fundamental transitions in H$_2^+$, D$_2^+$, and HD$^+$ (in MHz). CODATA14 recommended values of constants. The first error is the theoretical uncertainty, the second error is due to the uncertainty in mass ratios.}
\begin{tabular}{|c|c|c|}
\hline
 & H$_2^+$ & D$_2^+$ & HD$^+$ \\
\hline
$\Delta E_{n_2}$ & 65 687 511.0470 & 47 279 387.8184 & 57 349 439.9524 \\
$\Delta E_{o_2}$ & 1091.0405 & 795.3763 & 958.1517 \\
$\Delta E_{n_3}$ & $-276.5451$ & $-200.2780$ & $-242.1263$ \\
$\Delta E_{o_4}$ & $-1.9520(1)$ & $-1.4134(1)$ & $-1.7089(1)$ \\
$\Delta E_{o_5}$ & $0.1218(1)$ & $0.0881(1)$ & $0.1064(1)$ \\
$\Delta E_{o_6}$ & $-0.0023(5)$ & $-0.0017(4)$ & $-0.0020(5)$ \\
\hline
$\Delta E_{tot}$ & 65 688 323.7101(5)(29) & 47 279 981.5808(4)(8) & 57 350 154.3734(5)(17) \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Ionization energies in H$_2^+$, D$_2^+$, and HD$^+$ (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$^{-1}$.}
\begin{tabular}{|c|c|c|}
\hline
 & H$_2^+$ & D$_2^+$ & HD$^+$ \\
\hline
$E_{i,n_2}$ & 131 056.875 7465 & 131 418.947 7041 & 131 223.436 2578 \\
$E_{i,o_2}$ & 1.599 4995 & 1.604 8306 & 1.601 9142 \\
$E_{i,o_3}$ & $-0.350 9300$ & $-0.352 5527$ & $-0.351 6791$ \\
$E_{i,o_4}$ & $-0.002 4774(1)$ & $-0.002 4897(1)$ & $-0.002 4831(1)$ \\
$E_{i,o_5}$ & $0.000 1569(1)$ & $0.000 1576(1)$ & $0.000 1409(1)$ \\
$E_{i,o_6}$ & $-0.000 0021(6)$ & $-0.000 0021(6)$ & $-0.000 0021(6)$ \\
$E_{i,tot}$ & 131 058.121 9937(6) & 131 420.197 6480(6) & 131 224.684 1650(6) \\
\hline
\end{tabular}
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