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Relativistic and QED corrections to the $2p\sigma_u(v=1)$ vibrational state of the H_2^+ molecular ion

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Abstract. Relativistic and QED corrections to the recently discovered first vibrational $2p\sigma_u$ state are presented. This state has an extremely small nonrelativistic binding energy $E_B = 1.085045252(1) \times 10^{-9}$ a.u. Its wave functions has a maximum at $R \approx 100$ a.u. and extends up to several hundreds. It is shown that this state does not disappear if higher order relativistic and QED corrections, including the Casimir–Polder effect, are taken into account.

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1. Introduction

We have recently reported [1, 2, 3] on the possible existence of a new bound state of the H_2^+ molecular ion. It corresponds to the first excitation of the $2p\sigma_u$ vibrational state, i.e. a state with total three-body orbital angular momentum $L = 0$ and with proton-proton spin coupled to $S_n = 1$. Its binding energy is extremely small, $E_B = 1.085045252(1) \times 10^{-9}$ a.u. (atomic units) with respect to the $p\text{-H}$ dissociation threshold, and its wave function extends over several hundreds a.u. Although not being populated, it results into a huge $p\text{-H}$ scattering length value of $a_t \approx 750$ a.u., which dominates the low energy $p\text{-H}$ scattering. Apart from its exotic character, the very existence of such a state can dramatically modify the $p + \text{H} \rightarrow \text{H}_2^+ + h\nu$ reaction rate and consequently can explain the H_2 molecular abundance [4, 5]. Our previous calculations were done in the framework of nonrelativistic quantum mechanics. Given the smallness of its binding energy, it is necessary to undertake a systematic study of the relativistic corrections in order to see to what extent they modify, or even question, the results previously found. This is the aim of the present paper.

At a first glance it may be expected that at very large distances a change of the asymptotic potential due to the Casimir–Polder (or retardation) effect can lead to

disappearance of this weakly bound state. For the charge–dipole case the asymptotic potential at distances $r \gg 100$ a.u. has a form [6]

$$V(R) = -\frac{\alpha_d}{2R^4} \left(1 - \frac{11\alpha}{2\pi} \frac{m_e}{m_p} \frac{1}{R} \right) \quad (1)$$

where α_d is the electric dipole polarizability of an atom (for the hydrogen atom $\alpha_d = 9/2$) and $\alpha \approx 1/137$ is the fine structure constant. The first term is the classical polarization potential, which results from the instant Coulomb interaction and is already included in the nonrelativistic solution. The second term represents the two transverse photon exchange between a neutral system (hydrogen atom) and a distant charged particle (proton). In order to evaluate the influence of this contribution on the binding energy one may use the value of the retardation potential — second term in Eq. (1) — at the maximum of the bound state wave function, $R_{max} \approx 100$ a.u., that gives:

$$V_{ret}(r_{max}) = -(9/4)(11\alpha/2\pi)(m_e/m_p)R_{max}^{-5} \approx 10^{-15} \text{ a.u..}$$

Thus the change of the $2p\sigma_u(v=1)$ binding energy is of the order $\Delta E_{ret} = E_B \times 10^{-6}$. The smallness of this quantity suggests that relativistic and QED corrections can be treated using the standard perturbation technique for bound states, and eventually at some stage should take in the Casimir–Polder effect.

2. Variational calculation of the nonrelativistic solution

The numerical calculations of the bound state wave function have been performed using the variational approach described in details in [7]. The variational wave function for an S state has the form,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^{\infty} \left\{ U_i \operatorname{Re} [e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r}] + W_i \operatorname{Im} [e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r}] \right\} - (1 \leftrightarrow 2), \quad (2)$$

where \mathbf{r}_1 and \mathbf{r}_2 are the position vectors of the electron with respect to two protons. Complex parameters α_i , β_i and γ_i are generated in a quasi-random manner:

$$\alpha_i = \left[\left[\frac{1}{2} i(i+1) \sqrt{p_\alpha} \right] (A_2 - A_1) + A_1 \right] + i \left[\left[\frac{1}{2} i(i+1) \sqrt{q_\alpha} \right] (A'_2 - A'_1) + A'_1 \right],$$

$[x]$ designates the fractional part of x , p_α and q_α are some prime numbers, $[A_1, A_2]$ and $[A'_1, A'_2]$ are real variational intervals which need to be optimized. Parameters β_i and γ_i are obtained in a similar way.

In order to get the accurate result we use 5 sets of the basis functions of the type (2), for which the variational parameters have been searched independently. The proton-to-electron mass ratio, $m_p = 1836.152701 m_e$, has been adopted for this calculations.

In Table 1 we present the convergence of the computed binding energies as a function of N , number of the basis functions. One can see that the nonrelativistic binding energy for this weakly bound state has a relative accuracy of 10^{-9} , what is compliant with the requirements of the precise spectroscopy. The next question is how

Number of state (N)	Binding energy E_B (in a.u.)
2000	$1.08504520 \times 10^{-9}$
2500	$1.085045237 \times 10^{-9}$
3000	$1.0850452464 \times 10^{-9}$
3500	$1.0850452494 \times 10^{-9}$
∞	$1.085045252(1) \times 10^{-9}$

Table 1. Convergence of the binding energy (in a.u.) for the $2p\sigma_u(v=1)$ state with respect to a number of basis functions

to improve this value by taking into account the corrections imposed by a relativistic theory and QED. These aspects will be discussed in the following sections. As it was demonstrated in the introduction, these corrections can be evaluated using the standard perturbation expansion over the parameter $\alpha \approx 1/137$, which can be derived from the nonrelativistic QED effective field theory [8].

3. Corrections due to the Breit–Pauli Hamiltonian

The Breit–Pauli Hamiltonian provide us with the relative α^2 order corrections with respect to the nonrelativistic energy of a state.

The major contribution comes from the relativistic correction for the bound electron,

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

The other term of the Breit–Pauli Hamiltonian which has to be considered, is the transverse photon exchange contribution, which reads:

$$\begin{aligned} \delta E_{tr-ph}^{(2)} = & \frac{\alpha^2}{2M_p} \left\langle \frac{\mathbf{p}_e \mathbf{p}_1}{r_1} + \frac{\mathbf{r}_1 (\mathbf{r}_1 \mathbf{p}_e) \mathbf{p}_1}{r_1^3} + (1 \leftrightarrow 2) \right\rangle \\ & - \frac{\alpha^2}{2M_p^2} \left\langle \frac{\mathbf{p}_1 \mathbf{p}_2}{R} + \frac{\mathbf{R} (\mathbf{R} \mathbf{p}_1) \mathbf{p}_2}{R^3} \right\rangle. \end{aligned} \quad (4)$$

The remaining recoil corrections are negligibly small compared to uncertainty in the relativistic correction for the bound electron.

Beyond these terms, we have included as well the correction due to the finite size of the proton,

$$\delta E_{nuc} = \frac{2\pi(R_p/a_0)^2}{3} \left\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \right\rangle, \quad (5)$$

where $R_p = 0.862(12)$ fm is the proton root-mean-square radius.

As can be seen in the Table 2 the relativistic correction to the binding energy is of the order $\sim 10^{-3}$, what is in agreement with the work of Howells and Kennedy [9]. These authors studied the relativistic corrections for the high vibrational states of the $1s\sigma_g$ series in H_2^+ . They found that the Breit–Pauli relative contribution to the binding energy of the weakly bound states is of the order 10^{-3} , while in the case of low vibrational states it constitutes only a $\sim 10^{-5}$ part of the binding energy. The value of ΔE_{nr} in Table 2 agrees well with our previous estimate [3], based on the simplified approach of [9].

ΔE_{nr}	$-1.085\,045\,252 \times 10^{-9}$
ΔE_{rc}	$0.003\,285\,2(4) \times 10^{-9}$
ΔE_{tr-ph}	$0.000\,013\,371 \times 10^{-9}$
ΔE_{nuc}	$-0.000\,000\,067 \times 10^{-9}$
ΔE_{α^2}	$0.003\,298\,5(4) \times 10^{-9}$

Table 2. The Breit–Pauli Hamiltonian corrections (in a.u.) to the binding energy of the $2p\sigma_u(v=1)$ state

The uncertainty in the relativistic correction for the bound electron is considerably larger than other uncertainties in α^2 corrections. This is due to the strong cancellation between the correction terms for the H_2^+ molecular ion and the ground state of the hydrogen atom. The very accurate variational solution, providing the accuracy for the nonrelativistic energy to be $\sim 10^{-18}$ a.u., is still not enough to get the precise value for this relativistic contribution.

4. Radiative and higher order relativistic corrections

The complete spin-independent contribution of order α^3 and $\alpha^3(m/M)$ has the form [8, 10],

$$\begin{aligned} \delta E^{(3)} = \alpha^3 \sum_{i=1,2} \left[\frac{4}{3} \left(-\ln \alpha^2 - \beta(L, v) + \frac{5}{6} - \frac{1}{5} \right) \langle \delta(\mathbf{r}_i) \rangle \right. \\ \left. + \frac{2}{3M_p} \left(-\ln \alpha - 4\beta(L, v) + \frac{31}{3} \right) \langle \delta(\mathbf{r}_i) \rangle - \frac{14}{3M_p} Q(r_i) \right], \end{aligned} \quad (6)$$

where

$$\beta(L, v) = \frac{\langle \mathbf{p}_e (H_0 - E_0) \ln((H_0 - E_0)/R_\infty) \mathbf{p}_e \rangle}{4\pi \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle} \quad (7)$$

is the Bethe logarithm, H_0 is the three-body nonrelativistic Hamiltonian, \mathbf{p}_e is the electron momentum operator and $Q(r)$ is the Q -term introduced by Araki and Sucher [11],

$$Q(r) = \lim_{\rho \rightarrow 0} \left\langle \frac{\Theta(r - \rho)}{4\pi r^3} + (\ln \rho + \gamma_E) \delta(\mathbf{r}) \right\rangle.$$

In calculating the $2p\sigma_u(v=1)$ state of H_2^+ , the Bethe logarithm was taken equal to the hydrogenic limit, namely, $\beta(^3S, 1) \approx 2.9841$. This is justified since the electronic wave function for the $2p\sigma_u(v=1)$ state to a good extent can be approximated by the antisymmetrized hydrogenic wave function: $\psi_e(r_1, r_2; R) = (1/\sqrt{2})(\psi_H(\mathbf{r}_1) - \psi_H(\mathbf{r}_2))$. On the other hand, this accuracy is sufficient to get a relevant estimate of the α^3 order radiative correction.

Our calculations include also the α^4 order corrections in a non-recoil limit. Among them are the one-loop self-energy and vacuum polarization corrections for the bound electron (next to the leading term in α expansion of the external field approximation [12, 13])

$$\delta E_{1-loop}^{(4)} = \alpha^4 \left[4\pi \left(\frac{139}{128} - \frac{1}{2} \ln 2 \right) + \frac{5\pi}{48} \right] \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle,$$

ΔE_{nr}	$-1.085\,045\,252(1) \times 10^{-9}$
ΔE_{α^2}	$0.003\,298\,5(4) \times 10^{-9}$
ΔE_{α^3}	$-0.000\,470\,02(1) \times 10^{-9}$
ΔE_{α^4}	$-0.000\,003\,29 \times 10^{-9}$
E_B	$1.082\,219\,8(4) \times 10^{-9}$

Table 3. Relativistic and QED corrections to the $2p\sigma_u(v=1)$ state of the hydrogen molecular ion H_2^+ .

and two-loop QED corrections,

$$\delta E_{2-loop}^{(4)} = \frac{\alpha^4}{\pi} \left[-\frac{4358}{1296} - \frac{10\pi^2}{27} + \frac{3\pi^2}{2} \ln 2 - \frac{9}{4} \zeta(3) \right] \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle.$$

The last contribution is the relativistic corrections of order α^4 , $\delta E_{rc}^{(4)}$, for the bound electron (the $m\alpha^6$ order term in the expansion of the Dirac energy for the two-center problem).

$$\delta E_{rc}^{(4)} = \langle H_B Q (E_0 - H_0)^{-1} Q H_B \rangle + \langle H^{(4)} \rangle$$

where H_B is the Breit-Pauli Hamiltonian for the bound electron of the two center problem and Q is a projector orthogonal to the initial $2p\sigma_u$ electronic state, and

$$H^{(4)} = \alpha^4 \frac{p_e^6}{16m^5} + \alpha^4 \sum_{i=1,2} \left(\frac{1}{8m^3} \left[\mathbf{p}_e, \frac{1}{r_i} \right] - \frac{3\pi}{16m^4} \left\{ p_e^2, \left[\mathbf{p}_e, \left[\mathbf{p}_e, \frac{1}{r_i} \right] \right] \right\} + \frac{5}{128m^4} \left[p_e^2, \left[p_e^2, \frac{1}{r_i} \right] \right] \right).$$

In fact, the α^4 relativistic correction turns out to be negligibly small and can be omitted.

The summary of the relativistic and QED contributions up to and including term of order α^4 is presented in Table 3. The uncertainty in the final value is determined by the uncertainty in calculating the leading relativistic correction for the bound electron. The other corrections have been obtained with much better accuracy.

5. Spin effects

In the preceding evaluations, the spin effects were ignored. For the $2p\sigma_u(v=1)$ state, the spin-spin interaction has a form:

$$H_{H_2^+}^{\text{HFS}} = \alpha^2 \frac{8\pi}{3} \mu_e \mathbf{s}_e \left[\mu_p \mathbf{s}_{p_1} \delta(\mathbf{r}_1) + \mu_p \mathbf{s}_{p_2} \delta(\mathbf{r}_2) \right],$$

where $\mu_e = (1 + a_e)/m_e$ and $\mu_p = (1 + a_p)/M_p$ are the magnetic moments of an electron and a proton, respectively. For the lowest hyperfine state, $S_{\text{tot}} = 1/2$, the spin-dependent correction to the binding energy is

$$\delta E_{H_2^+}^{\text{HFS}} = \alpha^2 \frac{8\pi \mu_e \mu_p}{3} \langle \mathbf{S}_n \mathbf{s}_e \rangle \left[\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle_{H_2^+} \right],$$

where $\mathbf{S}_n = \mathbf{s}_{p_1} + \mathbf{s}_{p_2}$ is a total spin of protons, and $\langle \mathbf{S}_n \mathbf{s}_e \rangle = -1$. On the other hand, the $p + H$ asymptotic states should be antisymmetric with respect to exchange of two

protons as well. For the $2p\sigma_u(v=1)$ this can be realized only when proton spins are parallel ($S_n = 1$). In this case the threshold energy should be

$$E_H^{\text{HFS}}(S_{\text{tot}} = 1/2) = -\alpha^2 \frac{8\pi\mu_e\mu_p}{3} \left[\langle \delta(\mathbf{r}) \rangle_{\text{H}} \right].$$

Then the change of the binding energy due to the spin-spin interaction is

$$\Delta E_{S_{\text{tot}}=1/2}^{\text{HFS}} = \left(\delta E_{H_2^+}^{\text{HFS}} - E_H^{\text{HFS}} \right)_{S_{\text{tot}}=1/2} = -8.223 \times 10^{-14} \text{ a.u.}$$

6. Conclusions

The relativistic and QED corrections to the $2p\sigma_u(v=1)$ vibrational state of the H_2^+ molecular ion have been evaluated. Calculations include up to α^4 order terms.

The main conclusion of this work is that, despite the smallness of its binding energy, the existence of this state is not questioned by the impact of the relativistic and radiative effects. By including all these corrections one gets a binding energy $E_B = 1.0822198(4) \times 10^{-9}$ a.u., or $E_B = 2.944\,870(1) \times 10^{-8}$ eV, what represents a relative modification $\Delta E_B/E_B = 2.61 \times 10^{-3}$ of the nonrelativistic value.

While the nonrelativistic binding energy is now known to a relative precision of about 10^{-9} , the final value for the physical binding energy has an uncertainty by two orders of magnitude larger. Generally, for the low vibrational "gerade" states of the hydrogen isotope molecular ions, the convergence with respect to α is better. The most conceivable explanation is that, for the weakly bound states, the cancelation of the different correction terms in the molecular ion and the atom has the strongest effect and this slows down the convergence of the expansion. It manifests already in the leading order corrections of the Breit-Pauli Hamiltonian and was observed before in [9] for the $1s\sigma_g$ series of states.

The contribution of the spin-spin interaction is rather small: its magnitude is by three orders smaller than the relativistic correction for the bound electron.

Finally, we would like to mention that the existence of this weakly bound H_2^+ molecular ion state is of fundamental importance. It manifests itself in a huge p -H scattering length $a \approx 750$ a.u. [1], which determines the low energy scattering of proton by atomic hydrogen. The H_2^+ formation rate is substantially influenced by the p -H resonant cross section. This can help to explain the abnormal abundance of H_2 molecules in the interstellar space [4, 5]. Experimental confirmation of the considered state would be very appreciated, despite being difficult to realize [2].

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