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Highly accurate evaluation of the singular properties for the positronium and hydrogen negative ions

Alexei M Frolov

Department of Applied Mathematics, University of Western Ontario, London, Ontario, N6A 5B7, Canada

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Abstract

A large number of regular and some singular bound state properties of the ground $1^1S(L=0)$-states of the positronium Ps^- and hydrogen $^\infty H^-$ negative ions are determined to a very high numerical accuracy. The highly accurate variational wavefunctions are constructed with the use of exponential basis functions written in the three-body perimetric coordinates. In particular, the total energy of the ground state of the Ps^- ion determined in our calculations is $E = -0.262\,005\,070\,232\,980\,107\,770\,3745$ au, while the analogous ground state energy for the $^\infty H^-$ ion is $E = -0.527\,751\,016\,544\,377\,196\,589\,733$ au. These values are the best-to-date variational energies obtained for these systems.

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In this paper, we report a large number of bound state properties of the ground $1^1S(L=0)$-states in the Ps^- and $^\infty H^-$ ions. Each of these properties has been determined to a very high accuracy from direct variational calculations. It should be mentioned that many bound state properties of these two ions have been reported in our earlier works (see, e.g., [1]) and in numerous papers of other authors (see, e.g., [2]). However, some of the bound state properties obtained in these works were not determined even to a relatively high accuracy. In addition to this, for a number of properties, e.g., for the triple delta-function $\langle\delta_{321}\rangle$, the actual/observed convergence was very slow. In this study, we have significantly improved the overall quality of the variational wavefunctions. In particular, the total energies of the ground 1^1S-states of the Ps^- and $^\infty H^-$ ions obtained in this study are the best-to-date values. By using these wavefunctions we also determine a large number of bound state properties in the Ps^- and $^\infty H^-$ ions. Note that some bound state properties considered below are singular, i.e. the corresponding matrix elements and expectation values must be regularized before computations.

The negative positronium ion Ps^- and the negative hydrogen ion $^\infty H^-$ are the Coulomb three-body system with unit charges. Such systems/ions have only one bound state (=ground

1^1S-state). The non-relativistic Hamiltonian H of an arbitrary Coulomb three-body system/ion with unit charges takes the form (in atomic units $\hbar = 1$, $|e| = 1$, $m_e = 1$)

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M}\nabla_3^2 - \frac{1}{r_{32}} - \frac{1}{r_{31}} + \frac{1}{r_{21}}, \tag{1}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = r_{ji}$ are the three interparticle distances (=relative coordinates), $(ij) =$ (21), (31), (32) and $\mathbf{r}_i$ are the three Cartesian coordinates of the three particles. Also, in this equation and everywhere below in this study the subscripts 1 and 2 stand for the two electrons e^-, while the subscript 3 means the positron e^+ in the Ps^- ion ($M = 1$) and infinitely heavy nucleus ($M = \infty$) in the $^\infty H^-$ ion. Our first goal is to determine the total energies and wavefunctions of the ground $1^1S(L = 0)$-bound states in the Ps^- and $^\infty H^-$ negative ions. In other words, we need to obtain the highly accurate solutions of the corresponding Schrödinger equation $H\Psi = E\Psi$, where $E < 0$ and bound state wavefunction Ψ has the unit norm. In this study, we shall assume that the non-relativistic Schrödinger equation is exact. All required relativistic and QED corrections to that equation and its solutions can be computed later by using the formulae of perturbation theory and applying the highly accurate wavefunction Ψ determined during the solutions of the non-relativistic Schrödinger equation.

To approximate three-body wavefunctions Ψ and compute various bound state properties in this work we apply the exponential variational expansion in perimetric and/or relative coordinates. For the ground 1^1S-state in the Ps^- and $^\infty H^-$ ions this expansion of the trial wavefunction takes the form [4]

$$\Psi = \frac{1}{2}(1 + \hat{P}_{21}) \sum_{i=1}^{N} C_i \exp(-\tilde{\alpha}_i r_{32} - \tilde{\beta}_i r_{31} - \tilde{\gamma}_i r_{21})$$
$$= \frac{1}{2}(1 + \hat{P}_{21}) \sum_{i=1}^{N} C_i \exp(-\alpha_i u_1 - \beta_i u_2 - \gamma_i u_3), \tag{2}$$

where C_i are linear (or variational) parameters and $\alpha_i(\tilde{\alpha}_i)$, $\beta_i(\tilde{\beta}_i)$ and $\gamma_i(\tilde{\gamma}_i)$ are nonlinear parameters. The operator $\hat{P}_{21}$ is the permutation of the two identical (1 and 2) particles (electrons) in the Ps^- and $^\infty H^-$ ions. Note that Ψ, equation (2), is, in fact, only the spatial part of the total wavefunction. The corresponding spin part of the total wavefunction is anti-symmetric and it is written in the form $\chi_s = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$, where α and β are the spin-up and spin-down functions.

The three relative coordinates in equation (2) r_{32}, r_{31} and r_{21} are simply and uniformly related to the perimetric coordinates u_1, u_2 and u_3, where $u_i = \frac{1}{2}(r_{ij} + r_{ik} - r_{jk})$ and $i \neq j \neq k = (1, 2, 3)$. The inverse relations take the form $r_{ij} = u_i + u_j$ and Jacobian of the $(r_{32}, r_{31}, r_{21}) \to (u_1, u_2, u_3)$ transformation equals 2. Note that the three perimetric coordinates are independent, always positive and each of them varies between 0 and $+\infty$. These properties of the perimetric coordinates simplify drastically the optimization of the nonlinear parameters α_i, β_i and γ_i in equation (2). In fact, for optimization of the nonlinear parameters in the trial wavefunctions, equation (2), we apply our approach developed a few years ago and modified recently in [4]. All computations in this work have been performed with the use of software written and tested by David H Bailey [5, 6].

The highly accurate wavefunction Ψ obtained during the optimization process can be used to determine a large number of bound state properties $\langle\hat{X}\rangle$. In general, if $\hat{X}$ is an arbitrary regular operator defined in the non-relativistic three-body systems, then its expectation value $\langle\hat{X}\rangle$ can be considered as the corresponding quantum property. In fact, in our earlier works we have extensively discussed the computation of many regular properties for the Ps^- and $^\infty H^-$ ions. The total variational energies of the ground 1^1S-states in the Ps^- and $^\infty H^-$ ions can be

Table 1. The total energies (E) in atomic units for the ground states of the Ps^- and $^\infty H^-$ ions. N designates the number of basis functions used.

$N(A)$	$E(Ps^-)$	$N(A)$	$E(^\infty H^-)$
3000	−0.262 005 070 232 980 107 769 9731	2800	−0.527 751 016 544 377 196 588 192
3300	−0.262 005 070 232 980 107 770 2890	3000	−0.527 751 016 544 377 196 588 632
3500	−0.262 005 070 232 980 107 770 3449	3300	−0.527 751 016 544 377 196 589 134
3700	−0.262 005 070 232 980 107 770 3662	3500	−0.527 751 016 544 377 196 589 410
3800	−0.262 005 070 232 980 107 770 3723	3700	−0.527 751 016 544 377 196 589 586
3800[a]	−0.262 005 070 232 980 107 770 3745	3700[a]	−0.527 751 016 544 377 196 589 733

[a] After additional optimization of the 'fast' nonlinear parameters at this dimension (our current procedure is described in detail in second part of [4]).

found in table 1 (all values are in atomic units). The numerical values of many bound state properties are presented in table 2 (for the Ps^- ion), table 3 and table 4 (for the $^\infty H^-$ ion). The physical meaning for almost all of these expectation values in these tables is quite clear from the notations used, and here we can make only a few following remarks. In tables 2–4, the notations δ_{31}, δ_{21} and δ_{321} stand for the two- and three-particle delta-functions, respectively. Here and below $\delta_{ij} = \delta(\mathbf{r}_{ij})$ and $\delta_{321} = \delta(\mathbf{r}_{32}) \cdot \delta(\mathbf{r}_{31})$. The convergence of all delta-functions in the Ps^- ion is shown in table 3. The results from table 3 are of great interest for evaluating the corresponding annihilation rates, since the $\delta_{31} = \delta(\mathbf{r}_{31})$ value determines, e.g., the two-photon annihilation rate, while $\langle\delta(\mathbf{r}_{321})\rangle = \langle\delta(\mathbf{r}_{32}) \cdot \delta(\mathbf{r}_{31})\rangle$ value is needed to compute the one-photon annihilation rate $\Gamma_{1\gamma}$ (for more detail see, e.g., [1]).

The two-particle cusp ratios (or two-particle cusp, for short) are determined in a traditional manner [7]:

$$\nu_{ij} = \frac{\left\langle \delta(\mathbf{r}_{ij}) \frac{\partial}{\partial r_{ij}} \right\rangle}{\langle \delta(\mathbf{r}_{ij}) \rangle}, \tag{3}$$

where $\delta(\mathbf{r}_{ij})$ is the appropriate two-particle δ-function and $(ij) = (21)$ and (31). The exact (=predicted) value of the two-particle cusp ν_{ij} in any Coulomb system equals [8, 9]

$$\nu_{ij} = q_i q_j \frac{m_i m_j}{m_i + m_j}, \tag{4}$$

where q_i and q_j are the electric charges and m_i and m_j are the masses of these particles. As follows from the last formula the electron–electron cusp in an arbitrary system (and any state in this system) always equals 0.5 au (exactly).

The expectation values of the two interparticle cosine functions are determined as follows:

$$\tau_{ij} = \langle \cos(\mathbf{r}_{ik} \hat{} \mathbf{r}_{jk}) \rangle = \left\langle \frac{\mathbf{r}_{ik} \cdot \mathbf{r}_{jk}}{r_{ik} \cdot r_{jk}} \right\rangle = \tau_{ji} \tag{5}$$

where $(i, j, k) = (1, 2, 3)$ and all cyclic permutations, while the notation $\mathbf{r}_{ik} \hat{} \mathbf{r}_{jk}$ means the angle between the $\mathbf{r}_{ik}$ and $\mathbf{r}_{jk}$ vectors. For an arbitrary three-body system the sum of the three cosine expectation values τ_{21}, τ_{31}, τ_{32} can be written in the form

$$\tau_{21} + \tau_{31} + \tau_{32} = 1 + 4 \cdot \langle f \rangle \tag{6}$$

where the quantity $\langle f \rangle$ from the last equation is expressed in terms of the relative coordinates r_{32}, r_{31}, r_{21} and perimetric coordinates u_1, u_2, u_3 as follows:

$$\begin{aligned} \langle f \rangle &= \frac{1}{2} \langle \Psi | \frac{u_1}{r_{32}} \frac{u_2}{r_{31}} \frac{u_3}{r_{21}} | \Psi \rangle = \frac{1}{2} \int_0^\infty \int_0^\infty \int_{|r_{32}-r_{31}|}^{r_{32}+r_{31}} |\Psi(r_{32}, r_{31}, r_{21})|^2 u_1 u_2 u_3 \, \mathrm{d}r_{32} \, \mathrm{d}r_{31} \, \mathrm{d}r_{21} \\ &= \int_0^\infty \int_0^\infty \int_0^\infty |\Psi(u_1, u_2, u_3)|^2 u_1 u_2 u_3 \, \mathrm{d}u_1 \, \mathrm{d}u_2 \, \mathrm{d}u_3. \end{aligned} \tag{7}$$

Table 2. The expectation values $\langle X_{ij}\rangle$ in atomic units of some properties for the ground state of the Ps^- ion. The notations 1 and 2 designate the electrons, while 3 stands for the positron (e^+).

$\langle X_{ij}\rangle$	Ps^-	$\langle X_{ij}\rangle$	Ps^-
$\left\langle r_{21}^{-2}\right\rangle$	0.036 022 058 454 537 165	$\left\langle r_{21}^{-1}\right\rangle$	0.155 631 905 652 480 397 419
$\left\langle r_{31}^{-2}\right\rangle$	0.279 326 542 224 949 154	$\left\langle r_{31}^{-1}\right\rangle$	0.339 821 023 059 220 306 479
$\langle r_{21}\rangle$	8.548 580 655 099 186 1115	$\left\langle r_{21}^{2}\right\rangle$	93.178 633 847 981 329 006
$\langle r_{31}\rangle$	5.489 633 252 359 449 9333	$\left\langle r_{31}^{2}\right\rangle$	48.418 937 226 237 955 413
$\left\langle r_{21}^{3}\right\rangle$	1265.580 447 878 144 1205	$\left\langle r_{21}^{4}\right\rangle$	21054.453 389 258 358 095
$\left\langle r_{31}^{3}\right\rangle$	607.295 629 623 278 442 20	$\left\langle r_{31}^{4}\right\rangle$	9930.638 679 796 004 1546
$\langle(r_{31}\cdot r_{32})^{-1}\rangle$	0.090 935 346 529 989 3985	$\langle \mathbf{r}_{31}\cdot\mathbf{r}_{32}\rangle$	1.829 620 302 247 290 92
$\langle(r_{31}\cdot r_{21})^{-1}\rangle$	0.060 697 690 288 581 9557	$\langle \mathbf{r}_{31}\cdot\mathbf{r}_{21}\rangle$	46.589 316 923 990 664 503
$\langle(r_{32}\cdot r_{31}\cdot r_{21})^{-1}\rangle$	0.022 034 238 016 335 30	$\frac{1}{2}\left(\left\langle\frac{r_{32}^2}{r_{31}^3}\right\rangle-\left\langle\frac{r_{21}^2}{r_{31}^3}\right\rangle\right)$	−0.123 432 091 105 261 593
$\left\langle\frac{\mathbf{r}_{31}\cdot\mathbf{r}_{32}}{r_{31}^3}\right\rangle$	0.046 478 420 424 385 602	$\left\langle\frac{\mathbf{r}_{31}\cdot\mathbf{r}_{21}}{r_{31}^3}\right\rangle$	0.293 342 602 634 871 746
$\left\langle-\frac{1}{2}\nabla_1^2\right\rangle$	0.066 619 294 535 890 008 5246	$\langle \mathbf{p}_1\cdot\mathbf{p}_2\rangle$	0.004 472 107 910 579 926 329 722
$\left\langle-\frac{1}{2}\nabla_3^2\right\rangle$	0.128 766 481 161 200 090 720	$\langle \mathbf{p}_1\cdot\mathbf{p}_3\rangle$	0.128 766 481 161 200 090 7195
τ_{31}	0.591 981 701 148 902 233 258	$\langle\delta_{31}\rangle$	$2.073\,319\,800\,5178\times10^{-2}$
τ_{21}	0.019 769 632 817 132 001 755	$\langle\delta_{21}\rangle$	$1.709\,967\,563\,57\times10^{-4}$
$\langle f\rangle$	0.050 933 258 778 734 117 0676	$\langle\delta_{321}\rangle$	$3.588\,914\,61\times10^{-5}$
ν_{31}	−0.500 000 000 001 21	ν_{21}	0.499 999 999 891 34
ν_{31}^{a}	−0.5	ν_{21}^{a}	0.5
$\left\langle r_{21}^{-3}\right\rangle_R$	0.011 310 500 730 58	$\left\langle r_{31}^{-3}\right\rangle_R$	−0.253 484 174 704 05
$\left\langle r_{21}^{-3}\right\rangle$	0.013 459 309 344 903	$\left\langle r_{31}^{-3}\right\rangle$	0.007 056 875 449 733
$\left\langle r_{21}^{-4}\right\rangle_R$	0.000 304 810 115 8	$\left\langle r_{21}^{-5}\right\rangle_R$	−0.001 442 518 415 8
$\left\langle r_{31}^{-4}\right\rangle_R$	0.135 769 697 986	$\left\langle r_{31}^{-5}\right\rangle_R$	−0.050 344 707 775
$\langle f_{21}\rangle$	−0.003 223 212 861	$\langle F_{21}\rangle$	0.000 480 586 806
$\langle f_{31}\rangle$	0.134 914 310 854	$\langle F_{31}\rangle$	0.246 790 335 899
$\left\langle r_{21}^{-4}\right\rangle$	−0.002 918 402 745	$\left\langle r_{21}^{-5}\right\rangle$	−0.000 961 931 610
$\left\langle r_{31}^{-4}\right\rangle$	0.270 684 008 84	$\left\langle r_{31}^{-5}\right\rangle$	0.196 445 628 12

[a] The exact value from equation (4).

Table 3. Convergence of the delta-function expectation values in in atomic units for the ground states of the Ps^- ion. N designates the number of basis functions used.

N	$\langle\delta_{31}\rangle\equiv\langle\delta_{+-}\rangle$	$\langle\delta_{21}\rangle\equiv\langle\delta_{--}\rangle$	$\langle\delta_{321}\rangle\equiv\langle\delta_{+--}\rangle$
3000	$2.073\,319\,800\,519\,7\times10^{-2}$	$1.709\,967\,563\,53\times10^{-4}$	$3.588\,915\,97\times10^{-5}$
3300	$2.073\,319\,800\,518\,5\times10^{-2}$	$1.709\,967\,563\,45\times10^{-4}$	$3.588\,916\,25\times10^{-5}$
3500	$2.073\,319\,800\,519\,0\times10^{-2}$	$1.709\,967\,563\,54\times10^{-4}$	$3.588\,916\,47\times10^{-5}$
3700	$2.073\,319\,800\,517\,9\times10^{-2}$	$1.709\,967\,563\,45\times10^{-4}$	$3.588\,917\,25\times10^{-5}$
3800	$2.073\,319\,800\,518\,7\times10^{-2}$	$1.709\,967\,563\,40\times10^{-4}$	$3.588\,917\,36\times10^{-5}$
3800[a]	$2.073\,319\,800\,518\,1\times10^{-2}$	$1.709\,967\,563\,39\times10^{-4}$	$3.588\,917\,35\times10^{-5}$
V[b]	$2.073\,319\,800\,518\,0(15)\times10^{-2}$	$1.709\,967\,563\,40(10)\times10^{-4}$	$3.588\,917\,5(4)\times10^{-5}$

[a] After additional optimization of the 'fast' nonlinear parameters at this dimension (for more details, see the second part of [4]).
[b] Numerical values currently used for numerical evaluation of various annihilation rates (see, e.g., [19]).

Table 4. The expectation values $\langle X_{ij}\rangle$ in atomic units of some properties for the ground state of the $^{\infty}H^{-}$ ion. The notations 1 and 2 designate the electrons, while 3 stands for the infinitely heavy proton.

$\langle X_{ij}\rangle$	$^{\infty}H^{-}$	$\langle X_{ij}\rangle$	$^{\infty}H^{-}$
$\left\langle r_{21}^{-2}\right\rangle$	0.155 104 152 562 425 371	$\left\langle r_{21}^{-1}\right\rangle$	0.311 021 502 214 300 051 53
$\left\langle r_{31}^{-2}\right\rangle$	1.116 662 824 525 419 316	$\left\langle r_{31}^{-1}\right\rangle$	0.683 261 767 651 527 222 35
$\langle r_{21}\rangle$	4.412 694 497 991 727 721 17	$\left\langle r_{21}^{2}\right\rangle$	25.202 025 291 240 331 899 2
$\langle r_{31}\rangle$	2.710 178 278 444 420 365 35	$\left\langle r_{31}^{2}\right\rangle$	11.913 699 678 051 262 275 1
$\left\langle r_{21}^{3}\right\rangle$	180.605 600 230 174 774 8	$\left\langle r_{21}^{4}\right\rangle$	1590.094 603 939 485 288
$\left\langle r_{31}^{3}\right\rangle$	76.023 097 049 027 179 10	$\left\langle r_{31}^{4}\right\rangle$	645.144 542 412 219 368 1
$\langle(r_{31}\cdot r_{32})^{-1}\rangle$	0.382 627 890 340 205 41	$\langle\mathbf{r}_{31}\cdot\mathbf{r}_{32}\rangle$	−0.687 312 967 568 903 674 475
$\langle(r_{31}\cdot r_{21})^{-1}\rangle$	0.253 077 567 064 566 870	$\langle\mathbf{r}_{31}\cdot\mathbf{r}_{21}\rangle$	12.601 012 645 620 165 950
$\langle(r_{32}\cdot r_{31}\cdot r_{21})^{-1}\rangle$	0.200 823 439 629 182 4	$\frac{1}{2}\left(\left\langle\frac{r_{32}^2}{r_{31}^3}\right\rangle-\left\langle\frac{r_{21}^2}{r_{31}^3}\right\rangle\right)$	−0.464 261 853 080 556 472
$\left\langle\frac{\mathbf{r}_{31}\cdot\mathbf{r}_{32}}{r_{31}^3}\right\rangle$	−0.122 630 969 254 792 88	$\left\langle\frac{\mathbf{r}_{31}\cdot\mathbf{r}_{21}}{r_{31}^3}\right\rangle$	0.805 892 736 906 320 083
$\left\langle-\frac{1}{2}\nabla_1^2\right\rangle$	0.263 875 508 272 188 598 249	$\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle$	0.032 879 781 852 304 721 667
$\left\langle-\frac{1}{2}\nabla_3^2\right\rangle$	0.560 630 798 396 681 918 249	$\langle\mathbf{p}_1\cdot\mathbf{p}_3\rangle$	−0.560 630 798 396 681 918 226
τ_{31}	0.649 871 581 192 088 166 936	$\langle\delta_{31}\rangle$	0.164 552 872 847 13
τ_{21}	−0.105 147 693 565 977 901 039	$\langle\delta_{21}\rangle$	$2.737\,992\,126\,229\,4\times10^{-3}$
$\langle f\rangle$	0.048 648 867 204 549 608 30	$\langle\delta_{321}\rangle$	$5.039\,712\,8\times10^{-3}$
ν_{31}	−1.000 000 000 014 54	ν_{21}	0.499 999 998 1281
ν_{31}^{a}	−1.0	ν_{21}^{a}	0.5
$\left\langle r_{21}^{-3}\right\rangle_R$	0.064 307 887 272 1	$\left\langle r_{31}^{-3}\right\rangle_R$	−3.435 594 850 5463
$\left\langle r_{21}^{-3}\right\rangle$	0.098 714 511 0695	$\left\langle r_{31}^{-3}\right\rangle$	−1.367 762 464 6890
$\left\langle r_{21}^{-4}\right\rangle_R$	−0.051 066 886 311	$\left\langle r_{21}^{-5}\right\rangle_R$	−0.029289745749
$\left\langle r_{31}^{-4}\right\rangle_R$	5.042 273 284 752	$\left\langle r_{31}^{-5}\right\rangle_R$	−4.665 299 747 870
$\langle f_{21}\rangle$	−0.051 609 927 896	$\langle F_{21}\rangle$	−0.019 857 873 894
$\langle f_{31}\rangle$	3.323 815 587 264	$\langle F_{31}\rangle$	7.911 272 546 863
$\left\langle r_{21}^{-4}\right\rangle$	−0.102 676 814 206	$\left\langle r_{21}^{-5}\right\rangle$	−0.049 147 619 644
$\left\langle r_{31}^{-4}\right\rangle$	8.366 088 872 02	$\left\langle r_{31}^{-5}\right\rangle$	3.245 972 798 99

[a] The exact value from equation (4).

For symmetric (e.g., for two-electron) systems one also finds that in equation (6) $\tau_{32}=\tau_{31}$. The expectation value $\langle f\rangle$ can be calculated directly or by applying τ_{ij}. The coincidence of these two values of $\langle f\rangle$ is an additional test to prove the correctness of our results.

Tables 2 and 4 also include the principal values (=non-singular parts) of some singular expectation values. The singular expectation values reported in this study include the $\left\langle\frac{1}{r_{ij}^3}\right\rangle$, $\left\langle\frac{1}{r_{ij}^4}\right\rangle$, $\left\langle\frac{1}{r_{ij}^5}\right\rangle$, $\left\langle\frac{\mathbf{r}_{31}\cdot\mathbf{r}_{32}}{r_{31}^3}\right\rangle$ and $\left\langle\frac{\mathbf{r}_{31}\cdot\mathbf{r}_{22}}{r_{31}^3}\right\rangle$ expectation values. Here and everywhere below $(ij)=(21)$ and (31). The computation of the principal parts of these singular integrals is described in detail in our previous works (see, e.g., [11]). Here we just present the final formulae used in computations. The principal parts of the $\left\langle r_{ij}^{-3}\right\rangle$, $\left\langle r_{ij}^{-4}\right\rangle$ and $\left\langle r_{ij}^{-5}\right\rangle$ expectation values have been computed with the use of the following formulae:

$$\left\langle\frac{1}{r_{ij}^3}\right\rangle=4\pi\langle\delta(\mathbf{r}_{ij})\rangle+\left\langle\frac{1}{r_{ij}^3}\right\rangle_R \tag{8}$$

Table 5. The best values of the total energies (E) in atomic units for the ground states of the Ps^- and H^- ions obtained in earlier variational computations.

	$E(Ps^-)$		$E(^\infty H^-)$
E^a	−0.262 005 070 232 980 107 770 374 5	E^b	−0.527 751 016 544 377 196 589 733
E^c	−0.262 005 070 232 980 107 766 6	E^c	−0.527 751 016 544 377 196 586 5
E^d	−0.262 005 070 232 980 107 696	E^d	−0.527 751 016 544 377 196 503
E^e	−0.262 005 070 232 965	E^e	−0.527 751 016 544 253
E^f	−0.262 005 070 232 94	–	–

[a,b] This work.
[c] Reference [2].
[d] Reference [19].
[e] Reference [1].
[f] Reference [18].

$$\left\langle \frac{1}{r_{ij}^4} \right\rangle = \langle f_{ij} \rangle + \left\langle \frac{1}{r_{ij}^4} \right\rangle_R = -6\pi \left\langle \delta(\mathbf{r}_{ij}) \frac{\partial}{\partial r_{ij}} \right\rangle + \left\langle \frac{1}{r_{ij}^4} \right\rangle_R \tag{9}$$

$$\left\langle \frac{1}{r_{ij}^5} \right\rangle = \langle F_{ij} \rangle + \left\langle \frac{1}{r_{ij}^5} \right\rangle_R = 2\pi \left[\left\langle \delta(\mathbf{r}_{ij}) \frac{\partial^2}{\partial r_{ij}^2} \right\rangle - \frac{1}{3} \left\langle \delta(\mathbf{r}_{ij}) \frac{\partial^2}{\partial r_{kj} \partial r_{ki}} \right\rangle \right] + \left\langle \frac{1}{r_{ij}^5} \right\rangle_R , \tag{10}$$

where $\left\langle \frac{1}{r_{ij}^n} \right\rangle_R = \left\langle r_{ij}^{-n} \right\rangle_R$ designates the regular part of the $\left\langle r_{ij}^{-n} \right\rangle$ expectation value. The explicit formulae for the regular parts of the $\left\langle \frac{1}{r_{ij}^3} \right\rangle$, $\left\langle \frac{1}{r_{ij}^4} \right\rangle$ and $\left\langle \frac{1}{r_{ij}^5} \right\rangle$ expectation values are presented in [11]. The difference between the principal and regular parts of any expectation value is called the finite term contribution (or finite contributions) [11]. For the regular expectation values all finite contributions equal zero identically. In equations (8)–(10), the $\langle \delta(\mathbf{r}_{ij}) \hat{A}(r_{ij}, r_{ki}, r_{kj}) \rangle$ expectation value means the $\langle \delta(\mathbf{r}_{ij}) \hat{A}(r_{ij}, r_{ki}, r_{kj})(\Psi^* \Psi) \rangle$ expectation value. All expectation values mentioned in these formulae, including the finite-term contributions $\langle f_{ij} \rangle$ and $\langle F_{ij} \rangle$, can be found in tables 2 and 4.

Note that for the $^\infty H^-$ ion, the electron–electron expectation value $\left\langle r_{21}^{-3} \right\rangle$ corresponds to the so-called Araki–Sucher term which contributes to the lowest order QED correction [12, 13]. Another contribution to that correction comes from the Bethe logarithm [14]. The expectation values $\left\langle r_{ij}^{-5} \right\rangle$ are needed to compute the matrix elements of the potential $V \sim r^{-5}$. Such expectation values are needed, e.g., to compute the Wichmann–Kroll corrections on the vacuum polarization [15].

The explicit formula for the $\left\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{32}}{r_{31}^3} \right\rangle$ expectation value takes the form

$$\left\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{32}}{r_{31}^3} \right\rangle = \frac{1}{2} \left\langle \frac{1}{r_{31}} \right\rangle + \frac{1}{2} \left[\left\langle \frac{r_{32}^2}{r_{31}^3} \right\rangle - \left\langle \frac{r_{21}^2}{r_{31}^3} \right\rangle \right]. \tag{11}$$

The first expectation value on the right-hand side of this expression is regular (it can be found, e.g., in the expectation value of the Coulomb $\frac{1}{r_{31}}$ potential). The second and third expectation values on the right-hand side of this equation are individually singular. But each of them contains exactly the same singularity, which can be written in the form $\simeq A \cdot (\ln \varepsilon + \gamma_E)$ (at $\varepsilon \to 0$), where ε is a small (positive) parameter, while γ_E is the Euler constant ($\gamma_E = 0.577\,215\ldots$) and A is a numerical constant (for more detail, see, e.g., [11] and references therein). Since the two terms with singularities have the opposite signs, these two singularities cancel each other completely from the final expression. The complete cancellation of singularities means that the right-hand side of equation (11) is regular and its computation does

not present any problem. The method of regularization based on the complete compensation of singular parts arising from different terms in one formula was proposed almost 200 years ago by Italian mathematician Frullani [16]. In general, the singular expectation value which can be regularized with the use of this method is called Frullanian. Note that the $\left\langle \frac{\mathbf{r}_{31}\cdot\mathbf{r}_{21}}{r_{31}^3}\right\rangle$ expectation value is also Frullanian, while the $\left\langle \frac{\mathbf{r}_{32}\cdot\mathbf{r}_{21}}{r_{31}^3}\right\rangle$ expectation value is not (it is singular). In the last case, the two singularities from different terms are added to each other (instead of cancellation). Such a case can be designated as anti-Frullanian. The regular expectation value $\left\langle \frac{\mathbf{r}_{31}\cdot\mathbf{r}_{21}}{r_{31}^3}\right\rangle$ can be computed either directly, or with the use of the following formula:

$$\left\langle \frac{\mathbf{r}_{31}\cdot\mathbf{r}_{21}}{r_{31}^3}\right\rangle = \left\langle \frac{1}{r_{31}}\right\rangle - \left\langle \frac{\mathbf{r}_{31}\cdot\mathbf{r}_{32}}{r_{31}^3}\right\rangle. \tag{12}$$

Tables 2 and 4 contain the $\frac{1}{2}\left(\left\langle \frac{r_{32}^2}{r_{31}^3}\right\rangle - \left\langle \frac{r_{21}^2}{r_{31}^3}\right\rangle\right)$, $\left\langle \frac{\mathbf{r}_{31}\cdot\mathbf{r}_{21}}{r_{31}^3}\right\rangle$ and $\left\langle \frac{\mathbf{r}_{31}\cdot\mathbf{r}_{32}}{r_{31}^3}\right\rangle$ expectation values.

Thus in this work we have determined the bound state properties of the ground $1^1S(L=0)$-state in the Ps^- and $^\infty H^-$ ions to a benchmark accuracy. Our variational results obtained for the ground state energies are the best-to-date. The energies determined in a number of earlier computations can be found in table 5. Our results also include some singular properties, i.e. the properties which are represented by the singular expectation values. In particular, we have computed the $\left\langle r_{ij}^{-3}\right\rangle$, $\left\langle r_{ij}^{-4}\right\rangle$, $\left\langle r_{ij}^{-5}\right\rangle$, $\left\langle \frac{\mathbf{r}_{31}\cdot\mathbf{r}_{21}}{r_{31}^3}\right\rangle$ and $\left\langle \frac{\mathbf{r}_{31}\cdot\mathbf{r}_{32}}{r_{31}^3}\right\rangle$ singular expectation values. Analogous computations of the singular expectation values for the 1^1S- and 2^3S-states of the helium atoms (^{3}He, ^{4}He and $^\infty$He atoms) have been performed in [17].

References

[1] Frolov A M 1998 *Phys. Rev.* A **57** 2436
[2] Drake G W F, Cassar M and Nistor R A 2002 *Phys. Rev.* A **65** 054501
[3] Ho Y K 1993 *Phys. Rev.* A **48** 4780
[4] Frolov A M 2001 *Phys. Rev.* E **64** 036704
Frolov A M 2006 *Phys. Rev.* E **74** 027702
[5] Bailey D H 1995 *ACM Trans. Math. Softw.* **21** 379
[6] Bailey D H 2000 *Comput. Sci. Eng.* **2** 24
[7] Kato T 1957 *Commun. Pure Appl. Math.* **10** 151
[8] Pack R T and Brown W B 1966 *J. Chem. Phys.* **45** 556
[9] Chong D P and Schrader D M 1969 *Mol. Phys.* **16** 137
[10] Fock V A 1930 *Z. Phys.* **63** 855
[11] Frolov A M 2005 *J. Phys. B: At. Mol. Opt. Phys.* **38** 2723
[12] Araki H 1957 *Prog. Theor. Phys.* **17** 619
[13] Sucher J 1958 *Phys. Rev.* **109** 1010
[14] Bethe H A and Salpeter E E 1957 *Quantum Mechanics of One- and Two-Electron Atoms* (Berlin: Springer)
[15] Wichmann E H and Kroll N M 1956 *Phys. Rev.* **101** 843
[16] Frullani G 1828 *Memorie della Societa Italiana delle Socienze* **20** 448
[17] Frolov A M 2007 *J. Chem. Phys.* **126** 104302
[18] Ho Y K 1990 *Phys. Lett.* A **144** 237
[19] Frolov A M and Smith V H Jr 2003 *J. Phys.* B **36** 2911