Ground-state energy and relativistic corrections for positronium hydride

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Variational calculations of the ground state of positronium hydride (HPs) are reported, including various expectation values, electron-positron annihilation rates, and leading relativistic corrections to the total and dissociation energies. The calculations have been performed using a basis set of 4000 thoroughly optimized explicitly correlated Gaussian basis functions. The relative accuracy of the variational energy upper bound is estimated to be of the order of 2×10^{-10}, which is a significant improvement over previous nonrelativistic results.

I. INTRODUCTION

The interest in studies of small molecules where one or more nuclei are replaced with a positron was originally motivated by the pioneering works of Hylleraas and Ore [1] and Ore [2]. These works predicted the dynamical stability of the positronium molecule (Ps$_2$) and positronium hydride (HPs). Since then there has been a large number of theoretical works devoted to the study the properties of these two fundamental systems (for works on HPs see [3–19] and references therein), including the ground, metastable, and resonant states.

Along with the numerous theoretical studies, there has also been an array of experimental works attempting to produce and detect HPs. In 1992, Schrader *et al.* reported [20] the formation of positronium hydride in collisions between positrons and methane and gave an estimate of the binding energy, 1.1±0.2 eV. Recently, positronium physics and chemistry gained new impetus when the first experimental observation of the positronium molecule was reported [21,22]. At present it is being investigated whether more complicated positronium compounds, such as Ps$_n$ may exist. Moreover, it is believed that under certain conditions one may obtain a Bose-Einstein condensate, which will permit the creation of a powerful γ-ray laser. Due to its very short wavelength this laser could be used to probe objects as small as atomic nuclei [23].

Despite advances in experimental techniques and invention of new methods that allow a rapid creation of a large number of positrons in the laboratory [24,25], the experiments on atoms and molecules containing positrons remain a very challenging task. Thus, theoretical calculations are indispensable in elucidating the electronic structure and predicting the properties of such systems. In fact, just like the theoretical prediction of the existence of the Ps$_2$ molecule was followed by its experimental verification [21,22], there are planned experiments to confirm recent theoretical predictions of excited states of positronic systems [10,17,26].

Over the years the accuracy of the calculations has been getting progressively higher due to advances in computer hardware and development of more sophisticated computational approaches. At some point, in order to further improve theoretical predictions it becomes necessary to consider relativistic and QED effects. However, while the number of works where positronium hydride has been studied is quite large, essentially all of them have been performed at the nonrelativistic level of theory. The only work where relativistic effects in HPs have been considered is that of Yan and Ho [13].

One of the goals of the present study is to fill this gap and improve the results obtained in [13].

The positronium hydride belongs to a special class of Coulomb systems. It lies between the H$_2$ molecule and the fully nonadiabatic Ps$_2$ molecule, where both nuclei are replaced with e^+. Since the mass of one of the "nuclei" in HPs is the same as that of an electron, its motion cannot be considered slow. Therefore, the Born-Oppenheimer approximation cannot be used to separate the electronic and positronic degrees of freedom. Another distinct difference between HPs and H$_2$ is that the latter has a very large number of bound states, while for the positronium hydride only one excited state (of unnatural parity) have been predicted [17,18].

These positronic systems are also important testing grounds for various quantum mechanical methods. The highly accurate calculations available for these molecules can be used as benchmark test to compare the relative merit of different approaches. The connection between these molecules has also motivated various studies to explore the existence of similar systems. For example the stability of charged four particle systems containing two negatively and two positively charged particles has been studied in [27–33]. Recent success in the production of trapped antihydrogen atoms [34,35] has renewed interest in the interaction of matter with antimatter [36]. These problems can only be addressed by highly accurate quantum-mechanical calculations.

Accurate description of positronic systems is challenging for traditional quantum-chemical methods as the convergence of the wave function and energy is usually quite slow. In this work we employ the variational method in which the correlation in the motion of all particles is treated by expanding the wave function in terms of basis functions explicitly dependent on all interparticle coordinates.

II. FORMALISM

The nonrelativistic Hamiltonian of an N-particle Coulomb system in the laboratory reference frame reads (in atomic units)

$$H_{\text{NONREL}} = -\sum_{i=1}^{N} \frac{1}{2M_i} \nabla_{\mathbf{R}_i}^2 + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{R_{ij}}. \qquad (1)$$

Here $\mathbf{R}_i$, M_i, Q_i are the position, the mass, and the charge of the ith particle, $\nabla_{\mathbf{R}_i}$ is the gradient with respect to $\mathbf{R}_i$, and $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ are interparticle distances. In the case of positronium hydride $N = 4$. We will assume that the first particle in our

system is a proton (deuteron, triton, etc.), the second one is a positron, and the third and fourth particles are electrons. Thus, $M_1 = 1836.15267247, 3670.4829654, 5496.9215269, \infty$ (when the heavy nucleus is a proton, deuteron, triton, and $^\infty$H, respectively) and $M_2 = M_3 = M_4 = 1$. The numerical values of particle masses were taken from [37]). The charges of the particles are $Q_1 = Q_2 = 1$, $Q_3 = Q_4 = -1$.

In practice, instead of coordinates $\mathbf{R}_1, \ldots, \mathbf{R}_N$ it is convenient to use some set of "internal" coordinates, such as the Jacobi coordinates, or simply place the reference frame at one of the particles, e.g., particle 1, as is done in this work. This automatically separates out the motion of the center of mass. Our new coordinates are defined as follows [38–40]:

$$\mathbf{r}_1 = -\mathbf{R}_1 + \mathbf{R}_2, \ \mathbf{r}_2 = -\mathbf{R}_1 + \mathbf{R}_3, \ldots, \ \mathbf{r}_n = -\mathbf{R}_1 + \mathbf{R}_N, \quad (2)$$

where $n = N - 1$. We will also introduce the following notation: $q_i = Q_{i+1}, m_i = M_{i+1}, \mu_i = m_0 m_i / (m_0 + m_i)$, and $i = 0, \ldots, n$. In the new coordinates and notations the non-relativistic Hamiltonian can be written in a convenient matrix form:

$$H_{\text{nonrel}} = -\nabla'_{\mathbf{r}} \mathbf{M} \nabla_{\mathbf{r}} + \sum_{i=1}^{n} \frac{q_0 q_i}{r_i} + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{q_i q_j}{r_{ij}}. \quad (3)$$

Here the $3n \times 3n$ mass matrix $\mathbf{M} = M \otimes I_3$, where I_3 is the 3×3 identity matrix and $\otimes$ stands for the Kronecker product. The $n \times n$ matrix M is defined as follows: the diagonal elements are $1/(2\mu_1), 1/(2\mu_2), \ldots, 1/(2\mu_n)$, while the off-diagonal elements are $1/(2m_0)$. The prime symbol denotes vector or matrix transpose. $3n$-component position vector $\mathbf{r}$ and the gradient vector $\nabla_{\mathbf{r}}$ are

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_n \end{bmatrix}, \ \nabla_{\mathbf{r}} = \begin{bmatrix} \nabla_{\mathbf{r}_1} \\ \nabla_{\mathbf{r}_2} \\ \vdots \\ \nabla_{\mathbf{r}_n} \end{bmatrix}. \quad (4)$$

In order to solve the nonrelativistic problem with Hamiltonian (3) we use the variational method in which the wave function is expanded in terms of explicitly correlated Gaussian basis functions. It has been demonstrated by numerous previous applications in atomic, molecular, and nuclear physics (see, for example, [10–12,15,16,26,38,39,41–50] and references therein) that the method is capable of providing extremely accurate solutions for systems containing up to 6–8 particles.

The ground state of positronium hydride is a state with zero total orbital angular momentum. Therefore, it is desirable and convenient to employ basis functions of S symmetry in the calculations. The S Gaussians we use in this work have the following form:

$$\phi_k = \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}] = \exp[-\mathbf{r}'(L_k L'_k \otimes I_3)\mathbf{r}]. \quad (5)$$

In the above expression A_k is a symmetric, positive definite $n \times n$ matrix of exponential parameters that are unique for each basis function. Since the exponential parameters are subject to extensive optimization it is advantageous to choose matrix A_k as a Cholesky-factored product, $A_k = L_k L'_k$. Such a representation allows to avoid any constrains on the values of

the elements of L_k, while the elements of the original matrix A_k must obey the positive definiteness constrains.

In the case of a four-particle problem, explicitly correlated basis functions (5) can also be written in a more conventional form using the laboratory frame coordinates:

$$\phi_k = \exp\big[-\lambda_{12}^{(k)} R_{12}^2 - \lambda_{13}^{(k)} R_{13}^2 - \lambda_{14}^{(k)} R_{14}^2 - \lambda_{23}^{(k)} R_{23}^2 $$
$$- \lambda_{24}^{(k)} R_{24}^2 - \lambda_{34}^{(k)} R_{34}^2 \big], \quad (6)$$

where $\lambda_{ij}^{(k)}$ are certain parameters related to the elements of matrix L_k.

The total trial wave function of the system is a product of the spatial and spin parts and is antisymmetrized with respect to the permutations of the electrons. For the ground state of HPs it can be written as

$$\psi = \alpha_1 \alpha_2 (\alpha_3 \beta_4 - \beta_3 \alpha_4)(1 + P_{34}) \sum_{k=1}^{\mathcal{K}} \mathsf{c}_k \phi_k(\mathbf{r}; L_k). \quad (7)$$

Here $\mathcal{K}$ is the size of the basis, c_k are the coefficients of the expansion, numbers 1 through 4 refer to a particular particle and P_{34} is an operator that permutes spatial coordinates of electrons. α and β have their usual meaning of spin-up and spin-down state.

The minimization of the energy functional with respect to coefficients c_k in expansion (7) yields the generalized secular equation,

$$(\mathsf{H} - E_{\text{nonrel}} \mathsf{S})\mathsf{c} = 0, \quad (8)$$

where H and S are the $\mathcal{K} \times \mathcal{K}$ Hamiltonian and overlap matrices, respectively. Upon solving (8) one finds the set of optimal coefficients c_k and the upper bounds to the nonrelativistic energies. In this work we only deal with the lowest energy solution.

Since HPs is a small system with unity particle charges, the relativistic as well as quantum electrodynamics (QED) effects in this system are small in magnitude and can be accounted for in the framework of the perturbation theory in which the nonrelativistic solution serves as the zeroth-order approximation. The total energy of the system is sought as a series in powers of the fine structure constant, α:

$$E_{\text{TOT}} = E_{\text{NONREL}} + \alpha^2 E_{\text{REL}}^{(2)} + \alpha^3 E_{\text{QED}}^{(3)} + \ldots . \quad (9)$$

The successive corrections, $E_{\text{REL}}^{(2)}$, $E_{\text{QED}}^{(3)}$, and the higher order ones can be evaluated as the expectation values of some effective operators. In this work we consider only the leading relativistic corrections proportional to α^2. The total Hamiltonian is then

$$H_{\text{TOT}} = H_{\text{NONREL}} + \alpha^2 H_{\text{REL}}, \quad (10)$$

where the relativistic part, H_{REL}, consists of several terms,

$$H_{\text{REL}} = H_{\text{MV}} + H_{\text{D}} + H_{\text{OO}} + H_{\text{SS}} + H_{\text{A}}, \quad (11)$$

traditionally called the mass-velocity (MV), Darwin (D), orbit-orbit (OO), spin-spin (SS), and annihilation channel (A) corrections. In the general case, there is also the spin-orbit (SO) term present in the sum. However, its contribution vanishes for S states. The explicit expressions for the corresponding

operators in the laboratory coordinates are the following [51,52]:

$$H_{\mathrm{MV}} = -\frac{1}{8} \sum_{i=1}^{N} \frac{1}{M_i^3} \nabla_{\mathbf{R}_i}^4, \qquad (12)$$

$$H_{\mathrm{D}} = -\frac{\pi}{2} \sum_{j=1}^{N} \sum_{\substack{i \neq j \\ i \in \text{leptons}}}^{N} \frac{Q_i Q_j}{M_i^2} \delta(\mathbf{R}_{ij}), \qquad (13)$$

$$H_{\mathrm{OO}} = \frac{1}{2} \sum_{j=1}^{N} \sum_{i>j}^{N} \frac{Q_i Q_j}{M_i M_j} \frac{1}{R_{ij}}$$
$$\times \left(\nabla_{\mathbf{R}_i} \cdot \nabla_{\mathbf{R}_j} + \frac{1}{R_{ij}^2} \mathbf{R}_{ij} \cdot (\mathbf{R}_{ij} \cdot \nabla_{\mathbf{R}_i}) \nabla_{\mathbf{R}_j} \right), \quad (14)$$

$$H_{\mathrm{SS}} = -\frac{8\pi}{3} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{M_i M_j} \mathbf{S}_i \cdot \mathbf{S}_j \, \delta(\mathbf{R}_{ij}), \qquad (15)$$

$$H_{\mathrm{A}} = -2\pi \sum_{i=1}^{N} \sum_{\substack{j>i \\ i,j \in e^+ e^- \text{ pairs}}}^{N} \frac{Q_i Q_j}{M_i M_j} \left(\frac{3}{4} + \mathbf{S}_i \cdot \mathbf{S}_j \right) \delta(\mathbf{R}_{ij}). \qquad (16)$$

In the above expressions, $\delta(\mathbf{R}_{ij})$ stands for the three-dimensional Dirac δ function and $\mathbf{S}_i$ denotes the spin of the ith particle. Notation $i \in$ leptons in formula (13) means that index i runs over leptons only (in our case two electrons and a positron). In the general case it is also possible to include other types of particles (if there are any) in that expression. It is particularly straightforward for spin-1/2 fermions where the corresponding g factors need to be used. However, since all other particles have masses larger by several orders of magnitude than that of the electron, their contribution will be very tiny and much smaller than the QED corrections, which we do not consider in this work. For this reason we use the expression given in (13). In formula (16) the double sum runs over electron–positron pairs only, i.e., only those terms should be included where one of the indices i, j belongs to an electron and the other one to a positron.

Upon transforming from the laboratory frame coordinates to the internal ones the expressions for the relativistic operators become (as before, we use lower case letters to refer to objects in the internal frame):

$$H_{\mathrm{mv}} = -\frac{1}{8} \left[\frac{1}{m_0^3} \left(\sum_{i=1}^{n} \nabla_{\mathbf{r}_i} \right)^4 + \sum_{i=1}^{n} \frac{1}{m_i^3} \nabla_{\mathbf{r}_i}^4 \right], \qquad (17)$$

$$H_{\mathrm{d}} = -\frac{\pi}{2} \left[\sum_{\substack{i=1 \\ i \in \text{leptons}}}^{n} \frac{q_0 q_i}{m_0^2} \delta(\mathbf{r}_i) + \sum_{\substack{i=1 \\ i \in \text{leptons}}}^{n} \frac{q_0 q_i}{m_i^2} \delta(\mathbf{r}_i) \right.$$
$$\left. + \sum_{j=1}^{n} \sum_{\substack{i \neq j \\ i \in \text{leptons}}}^{n} \frac{q_i q_j}{m_i^2} \delta(\mathbf{r}_{ij}) \right], \qquad (18)$$

$$H_{\mathrm{oo}} = -\frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{q_0 q_j}{m_0 m_j} \left[\frac{1}{r_j} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_j^3} \mathbf{r}_j'(\mathbf{r}_j \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right]$$
$$+ \frac{1}{2} \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{q_i q_j}{m_i m_j} \left[\frac{1}{r_{ij}} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_{ij}^3} \mathbf{r}_{ij}'(\mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right], \qquad (19)$$

$$H_{\mathrm{ss}} = -\frac{8\pi}{3} \sum_{i=1}^{n} \frac{q_0 q_i}{m_0 m_i} \mathbf{s}_0 \cdot \mathbf{s}_i \, \delta(\mathbf{r}_i)$$
$$- \frac{8\pi}{3} \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{q_i q_j}{m_i m_j} \mathbf{s}_i \cdot \mathbf{s}_j \, \delta(\mathbf{r}_{ij}), \qquad (20)$$

$$H_{\mathrm{a}} = -2\pi \sum_{\substack{i=1 \\ 0,i \in e^+ e^- \text{ pairs}}}^{n} \frac{q_0 q_i}{m_0 m_i} \left(\frac{3}{4} + \mathbf{s}_0 \cdot \mathbf{s}_i \right) \delta(\mathbf{r}_i)$$
$$- 2\pi \sum_{i=1}^{n} \sum_{\substack{j>i \\ i,j \in e^+ e^- \text{ pairs}}}^{n} \frac{q_i q_j}{m_i m_j} \left(\frac{3}{4} + \mathbf{s}_i \cdot \mathbf{s}_j \right) \delta(\mathbf{r}_{ij}). \qquad (21)$$

Here we have used the notation $\mathbf{s}_i \equiv \mathbf{S}_{i+1}$. Assuming our particular case of HPs and taking into account the indistinguishability of electrons the expectation values of the Darwin, spin-spin, and annihilation channel interactions can be written simply as

$$\langle H_{\mathrm{d}} \rangle = -\frac{\pi}{2} \langle \delta(\mathbf{r}_1) - 2\delta(\mathbf{r}_2) - 4\delta(\mathbf{r}_{12}) + 2\delta(\mathbf{r}_{23}) \rangle, \qquad (22)$$

$$\langle H_{\mathrm{ss}} \rangle = 2\pi \langle \delta(\mathbf{r}_{23}) \rangle, \qquad (23)$$

$$\langle H_{\mathrm{a}} \rangle = 3\pi \langle \delta(\mathbf{r}_{12}) \rangle. \qquad (24)$$

The details on evaluating matrix elements of various operators with basis functions (5) were presented elsewhere [40,42,53]. Here we will only mention a scheme that allows to significantly improve the convergence of expectation values that involve the Dirac δ functions. Such expectation values are needed not only in the calculations of the relativistic corrections to the energy, but also for the estimations of the decay rates, which will be considered later in this work. It is a known problem that expectation values of singular operators, such as the two-particle δ function, usually exhibit rather poor convergence in variational calculations when compared to the expectation values of "well-behaved" operators. The main reason for this is the fact that the expectation values of singular operators are very sensitive to the local properties of the trial wave function. When a singular operator's expectation value is evaluated, the integration occurs only in a small region of space (essentially in some subspace). Hence, the wave function is sampled only locally in such an integration. At the same time, it is known that while the energy (as well as the expectation values of "well-behaved," nonsingular operators) in the variational method is accurate to the second order, locally the wave function is accurate to the first order only. In other words, the local convergence of the wave function is significantly slower than the convergence of the energy (roughly speaking, one should expect twice fewer digits converged). This behavior is rather universal and independent of the basis set used. However, the

properties of a particular basis may amplify this problem even further. In the case of Gaussians, the inability to satisfy the Kato cusp conditions usually makes the slower convergence of the two-particle δ functions even worse. In order to alleviate the problem Drachman [54] proposed to replace the local δ function operator with a global operator, which, for the exact wave function, would give the same expectation value. Since this operator is global the convergence of its expectation value is noticeably better as has been demonstrated in [55], where some generalizations of the above idea were considered. In this work we adopted the following identity from [54], which holds for the exact wave function:

$$\langle\psi|\tilde{\delta}(\mathbf{R}_{ij})|\psi\rangle = \frac{1}{2\pi}\frac{M_i M_j}{M_i + M_j}\left[\langle\psi|\frac{2}{R_{ij}}(E - V)|\psi\rangle \right.$$
$$\left. - \sum_{k=1}^{N}\frac{1}{M_k}\langle\mathbf{\nabla}_{\mathbf{R}_k}\psi|\frac{1}{R_{ij}}|\mathbf{\nabla}_{\mathbf{R}_k}\psi\rangle\right]. \quad (25)$$

Here E is the total nonrelativistic energy corresponding to state ψ, and V is the potential energy operator. To distinguish the expectation values obtained using this identity from those computed directly, we use the tilde. In the internal coordinate frame, expression (25) acquires the following form:

$$\langle\psi|\tilde{\delta}(\mathbf{r}_{ij})|\psi\rangle = \frac{1}{2\pi}\frac{1}{\text{tr}[M J_{ij}]}\left[\langle\psi|\frac{2}{r_{ij}}(E - V)|\psi\rangle \right.$$
$$\left. - \langle\mathbf{\nabla}_{\mathbf{r}}\psi|\frac{1}{r_{ij}}\mathbf{M}|\mathbf{\nabla}_{\mathbf{r}}\psi\rangle\right], \quad (26)$$

where tr[...] stands for the trace, M is the mass matrix defined in (3), and J_{ij} is a $n \times n$ matrix whose only nonzero elements are the following four ones: $(J_{ij})_{ii} = (J_{ij})_{jj} = 1$, $(J_{ij})_{ij} = (J_{ij})_{ji} = -1$. For the case of the $\tilde{\delta}(\mathbf{r}_i)$ expectation value, one just needs to replace $J_{ij} \rightarrow J_{ii}$ (J_{ii} matrix is defined such that the only nonzero element of it is $(J_{ii})_{ii} = 1$) and $r_{ij} \rightarrow r_i$ in the right-hand side of the above formula.

Despite being a stable bound system in nonrelativistic quantum mechanics, in reality HPs undergoes a decay due to the electron–positron annihilation, similar to the one in the positronium atom, Ps. It is possible to determine the rate of the HPs decay by computing the average square of the amplitude of the wave function at the electron–positron coalescence points and relating this value to the well studied decay rate of the positronium atom, i.e., using the relation

$$\Gamma^{\text{HPs}} = N_{e^+} N_{e^-}\frac{\langle\delta_{e^+e^-}\rangle^{\text{HPs}}}{\langle\delta_{e^+e^-}\rangle^{\text{Ps}}}\Gamma^{\text{Ps}}, \quad (27)$$

where N_{e^+} and N_{e^-} are the numbers of positrons and electrons in the system. In general, the total decay rate of a system is the sum of k-photon annihilation rates,

$$\Gamma = \sum_{k=0}^{\infty} w_k \Gamma_{k\gamma}, \quad (28)$$

where w_k is the statistical weight of the spin state, which undergoes a particular k-photon annihilation. For the positronium atom both $\Gamma_{0\gamma}$ and $\Gamma_{1\gamma}$ are zeros, whereas for HPs they are extremely small in magnitude (the rate of 0γ and 1γ

processes is proportional to $\alpha^{12}c/a_0$ and $\alpha^8 c/a_0$, respectively; here c is the speed of light and a_0 is the Bohr radius). The dominating components are $\Gamma_{2\gamma} \propto \alpha^4 c/a_0$ and $\Gamma_{3\gamma} \propto \alpha^5 c/a_0$. The two-photon decay takes place when an electron–positron pair is in the singlet state (the statistical weight of which is $w = 1/4$), while the three-photon decay occurs in the triplet state ($w = 3/4$). The expressions for $\Gamma_{2\gamma}$ and $\Gamma_{3\gamma}$ in the positronium atom, including several leading radiative corrections, are known [56–58]. In this work, however, we must limit ourselves with the corrections proportional to $\alpha^2 \ln\frac{1}{\alpha}$ in $\Gamma_{2\gamma}^{\text{Ps}}$ and α^0 in $\Gamma_{3\gamma}^{\text{Ps}}$. This is because the expectation value of the electron–positron contact density in HPs available to us from calculations is purely nonrelativistic (i.e., does not include the leading correction of the order of α^2) and, therefore, the right-hand side in expression (27) can only be accurate up to terms greater than α^2. Using

$$\Gamma_{2\gamma}^{\text{Ps}} = 4\pi\frac{\alpha^4 c}{a_0}\langle\delta_{e^+e^-}\rangle^{\text{Ps}}\left[1 - \left(5 - \frac{\pi^2}{4}\right)\frac{\alpha}{\pi} + 2\alpha^2 \ln\frac{1}{\alpha} + \cdots\right], \quad (29)$$

$$\Gamma_{3\gamma}^{\text{Ps}} = \frac{16}{9}(\pi^2 - 9)\frac{\alpha^5 c}{a_0}\langle\delta_{e^+e^-}\rangle^{\text{Ps}}[1 + \cdots], \quad (30)$$

and the known value $\langle\delta_{e^+e^-}\rangle^{\text{Ps}} = 1/(8\pi)$ the expression for the total electron–positron annihilation rate in HPs becomes

$$\Gamma^{\text{HPs}} = 2\pi\frac{\alpha^4 c}{a_0}\langle\delta_{e^+e^-}\rangle^{\text{HPs}}\left[1 + \left(\frac{19\pi}{12} - \frac{17}{\pi}\right)\alpha + 2\alpha^2 \ln\frac{1}{\alpha}\right]. \quad (31)$$

III. COMPUTATIONAL DETAILS

The choice of nonlinear variational parameters plays a crucial role in calculations that involve explicitly correlated basis functions. It is a particularly important subject when Gaussian functions are used. In fact, in calculations that require high accuracy it is the optimization of nonlinear parameters that consumes most of the computer time. Several approaches have been proposed to to deal with high computational demands [39,41,42,59–64]. In this work we have used an approach that combines a stochastic selection of the parameters [41,42,59] with a direct optimization that uses the analytic energy gradient [39,40,64]. In the present calculations the basis set was grown from zero to 4000 functions. During this process, the basis was reoptimized a large number of times (essentially after adding each new subset of ten basis functions). In order to ensure high-numerical stability of the calculations we did not allow any severe linear dependencies among basis functions. This was done through monitoring overlaps of basis functions. Those changes of the nonlinear parameters that resulted in excessively high absolute value of an overlap (i.e., those that yielded $\mathsf{S}_{kl} > 1 - t$, where t is some small threshold, which we set to be around 0.01) were automatically rejected. Such monitoring is a computationally inexpensive procedure and at the same time it is quite efficient. Our experience suggests that most of linear dependencies in the calculations of systems such as HPs appear as linear dependencies between two basis functions.

In the calculations we used standard double precision (64-bit) arithmetic until the basis size reached approximately

TABLE I. Nonrelativistic energies and relativistic corrections for isotopologues of HPs. The tilde sign indicates that the expectation values of the corresponding operators were evaluated using relation (26). Values in parentheses represent estimates of the remaining uncertainty due to the finite size of the basis set used. At the bottom of the table we also show the nonrelativistic energies and relativistic corrections for isolated hydrogen-like atoms. All values are in atomic units.

system	basis size	$\langle H_{\mathrm{nonrel}} \rangle$	$\langle H_{\mathrm{mv}} \rangle$	$\langle \tilde{H}_{\mathrm{d}} \rangle$	$\langle H_{\mathrm{oo}} \rangle$	$\langle \tilde{H}_{\mathrm{ss}} \rangle$	$\langle \tilde{H}_{\mathrm{a}} \rangle$	$\langle H_{\mathrm{nonrel}} + \alpha^2 H_{\mathrm{rel}} \rangle$
HPs	500	−0.788 870 347 543	−0.756 135 34	0.693 847 98	−0.134 960 75	0.027 397 34	0.230 856 76	−0.788 867 098 892
	1000	−0.788 870 685 002	−0.756 414 09	0.693 848 28	−0.134 960 84	0.027 398 37	0.230 857 02	−0.788 867 451 115
	2000	−0.788 870 709 195	−0.756 592 79	0.693 848 34	−0.134 960 89	0.027 398 46	0.230 857 01	−0.788 867 484 819
	3000	−0.788 870 711 910	−0.756 632 66	0.693 848 34	−0.134 960 88	0.027 398 47	0.230 857 02	−0.788 867 489 656
	4000	−0.788 870 712 244(200)	−0.756 648 84	0.693 848 34	−0.134 960 88	0.027 398 47	0.230 857 02	−0.788 867 490 851(1000)
DPs	4000	−0.789 033 601 257(200)	−0.757 397 90	0.694 319 68	−0.134 683 43	0.027 427 46	0.230 875 38	−0.789 030 377 357(1000)
TPs	4000	−0.789 087 802 858(200)	−0.757 647 28	0.694 476 57	−0.134 591 04	0.027 437 12	0.230 881 49	−0.789 084 578 123(1000)
$^{\infty}$HPs	4000	−0.789 196 766 900(200)	−0.758 148 80	0.694 792 04	−0.134 405 21	0.027 456 53	0.230 893 78	−0.789 193 540 488(1000)
Ps(^1S)		−0.250 000 000 000	−0.078 125 00	0.125 000 00	−0.125 000 00	−0.250 000 00	0.000 000 00	−0.250 017 473 101
Ps(^3S)		−0.250 000 000 000	−0.078 125 00	0.125 000 00	−0.125 000 00	0.083 333 33	0.250 000 00	−0.249 986 409 811
H		−0.499 727 839 712	−0.623 640 31	0.499 183 96	−0.000 543 73			−0.499 734 496 135
D		−0.499 863 815 247	−0.624 319 35	0.499 591 56	−0.000 272 22			−0.499 870 471 667
T		−0.499 909 056 541	−0.624 545 41	0.499 727 22	−0.000 181 82			−0.499 915 712 961
$^{\infty}$H		−0.500 000 000 000	−0.625 000 00	0.500 000 00	0.000 000 00			−0.500 006 656 419

2500 functions. After that we switched to extended precision (80-bit). This was done to enable more efficient optimization of nonlinear parameters, which is very sensitive to the accuracy of the eigenvalues and eigenvectors obtained. Arithmetic operations with 80-bit precision, just like those performed with 64-bit precision, are hardware-accelerated in any x86-compatible CPU found in most commodity computers today. While there is a certain performance penalty associated with the 80-bit precision, using it does not result in an enormous slow down of the calculations.

The optimization of nonlinear parameters in this work was performed only for the lightest isotopologue, HPs. Since the wave functions of DPs, TPs, and $^{\infty}$HPs are very close to that of HPs, the change can be effectively accounted for by readjusting the linear coefficients of the basis functions, i.e., by computing a new Hamiltonian matrix and solving an eigenvalue problem (which needs to be done only once) using the same basis set. Due to the smallness of the change of the wave function, such a time-saving simplification has essentially no effect on the accuracy of the calculations.

The vast majority of the computational time in the variational calculations of this study is spent on two tasks: the evaluation of the Hamiltonian and overlap matrix elements and the solution of the generalized eigenvalue problem (8). The first task can be easily and very effectively parallelized. The second one also allows a certain degree of parallelization (although the scalability is somewhat worse). Therefore, efficient algorithms that utilize parallelism in either shared memory or distributed memory environments can be developed. In our case all calculations have been carried out using 4–16 processes communicating via Message Passing Interface (MPI) protocol.

Due to the very extensive optimization of the nonlinear parameters, the generation of the basis set used in this work required several months of continuous computing. We stopped when the basis length reached 4000. However, if it becomes necessary in the future, the calculations can be easily resumed.

IV. RESULTS AND DISCUSSION

In Table I we show the convergence of the nonrelativistic energy of HPs in terms of the number of basis functions. We also present the energies obtained with the final basis set for other isotopologues of the positronium hydride: DPs, TPs, and $^{\infty}$HPs. According to our estimates (which are based on studying the convergence patterns and extrapolating to the limit of an infinite basis set size) the accuracy of the nonrelativistic calculations in this work exceeds the previous best result [16] by nearly an order of magnitude in spite of a smaller number of basis functions used. In fact, the energy corresponding to the largest basis set of 5000 explicitly correlated Gaussians generated in work [16] was reached with only 2150 basis functions in this work. The better convergence is a result of a significantly more extensive optimization of the nonlinear parameters. It should be noted that the difference in the optimization quality becomes particularly pronounced when the basis size is large enough (several thousand functions), while for small basis sets the extra computational effort does not seem to be justified.

In addition to the nonrelativistic energies, in Table I we also show all components of the relativistic corrections and the total relativistic energies. When computing the latter quantity we used $\alpha = 0.0072973525376$ for the value of the fine structure constant [37]. In general, the computed relativistic corrections agree with those obtained by Yan and Ho [13] using the Hylleraas-type basis. However, we have found that the value of the mass-velocity correction in work [13] is likely to contain an error. In the case of $^{\infty}$HPs (we use this isotopologue for comparison because not all of the recoil relativistic effects were calculated in [13]) we obtained -4.03725×10^{-5} a.u. for the expectation value of H_{mv} multiplied by α^2, while Yan and Ho reported $-2.60410(30) \times 10^{-5}$ a.u. We believe our value is correct as with our computer code we have evaluated $\langle H_{\mathrm{mv}} \rangle$ in the case of several other atomic and molecular systems (including those containing positrons) for which independent results are available in the literature, and found no discrepancies in any of those cases.

TABLE II. Binding energies (in eV) for isotopologues of HPs obtained both in nonrelativistic calculations and after the inclusion of the relativistic corrections with the largest basis of 4000 functions. Values in parentheses represent estimates of the remaining uncertainty due to the finite size of the basis set used.

system	nonrel.	rel.
HPs	1.065 131 730(4)	1.064 387 474(50)
DPs	1.065 864 083(4)	1.065 119 758(50)
TPs	1.066 107 905(4)	1.065 363 558(50)
∞HPs	1.066 598 270(4)	1.065 853 877(50)

At the bottom of Table I we provide the values of the total energies and relativistic corrections for isolated hydrogen-like atoms. Combined in appropriate pairs these can be used to compare them with the corresponding values for the HPs isotopologues.

The knowledge of the total binding energies of the HPs isotopologues as well as its subsystems (H and Ps atoms) allows the determination of the binding energies. The cor-responding data is given in Table II. The inclusion of the relativistic corrections has a very small effect on the binding energies (less than 0.1% change). This effect is almost 10x larger in magnitude than the shift of the total energy due to the inclusion of the relativistic corrections. Therefore, most of the change in the binding energy is due to the relativistic effects in separated H and Ps atoms. The relativistic effects in HPs and in the isolated H and Ps atoms do not cancel out significantly as takes place in some weakly bound molecules. Indeed, while the positronium hydride structure is consistent with that of a molecule (rather than an atom), the binding and the interaction of the electrons cannot be considered weak.

In Table III we present the expectation values of various quantities. These include the powers of the interparticle distances, two-particle Dirac δ functions $\delta(\mathbf{r}_{ij}) \equiv \delta(x_i - x_j)\delta(y_i - y_j)\delta(z_i - z_j)$, products of two Dirac δ functions $\delta(\mathbf{r}_{ij})\delta(\mathbf{r}_{lm})$ and $\delta(\mathbf{r}_{ij})\delta(\mathbf{r}_{jk})$ (the latter determine the three-particle coalescence probabilities), and the product of three Dirac δ functions, $\delta(\mathbf{r}_{ij})\delta(\mathbf{r}_{jk})\delta(\mathbf{r}_{kl})$, which in the case of a four-particle system, such as HPs, is equal to the value of the wave function square at the origin. For convenience of the

TABLE III. Expectation values of various powers of interparticle distances and the Dirac δ functions. For the expectation values of a single δ function we show the results obtained in both the direct calculations and using relation (26). The latter ones are marked with a tilde. Indices a and b in some double δ functions emphasize that the two electrons are different. All values are in atomic units.

system	basis size	$\langle 1/r_{H^+e^+}^2 \rangle$	$\langle 1/r_{e^+e^-}^2 \rangle$	$\langle 1/r_{H^+e^-}^2 \rangle$	$\langle 1/r_{e^-e^-}^2 \rangle$	$\langle 1/r_{H^+e^+} \rangle$	$\langle 1/r_{e^+e^-} \rangle$	$\langle 1/r_{H^+e^-} \rangle$	$\langle 1/r_{e^-e^-} \rangle$
HPs	500	0.172 014 772	0.349 071 114	1.205 649 513	0.213 648 294	0.347 301 925	0.418 428 418	0.729 258 284	0.370 330 922
	1 000	0.172 013 641	0.349 072 614	1.205 651 819	0.213 646 523	0.347 301 530	0.418 428 480	0.729 258 149	0.370 330 394
	2 000	0.172 013 540	0.349 072 759	1.205 652 123	0.213 646 371	0.347 301 497	0.418 428 492	0.729 258 147	0.370 330 354
	3000	0.172 013 541	0.349 072 777	1.205 652 143	0.213 646 366	0.347 301 507	0.418 428 498	0.729 258 147	0.370 330 361
	4 000	0.172 013 540	0.349 072 780	1.205 652 147	0.213 646 365	0.347 301 507	0.418 428 498	0.729 258 148	0.370 330 360
DPs	4 000	0.172 088 169	0.349 108 392	1.206 359 185	0.213 777 865	0.347 381 564	0.418 462 267	0.729 483 359	0.370 442 488
TPs	4 000	0.172 113 007	0.349 120 245	1.206 594 493	0.213 821 637	0.347 408 203	0.418 473 504	0.729 558 301	0.370 479 803
∞HPs	4 000	0.172 162 946	0.349 144 077	1.207 067 607	0.213 909 656	0.347 461 760	0.418 496 096	0.729 708 964	0.370 554 828

system	basis size	$\langle r_{H^+e^+} \rangle$	$\langle r_{e^+e^-} \rangle$	$\langle r_{H^+e^-} \rangle$	$\langle r_{e^-e^-} \rangle$	$\langle r_{H^+e^+}^2 \rangle$	$\langle r_{e^+e^-}^2 \rangle$	$\langle r_{H^+e^-}^2 \rangle$	$\langle r_{e^-e^-}^2 \rangle$
HPs	500	3.663 490 430	3.481 169 368	2.313 152 927	3.577 005 779	16.271 935 302	15.593 396 345	7.824 650 807	15.895 655 820
	1 000	3.663 501 879	3.481 175 784	2.313 161 069	3.577 021 997	16.272 155 569	15.593 537 619	7.824 794 250	15.895 938 518
	2 000	3.663 503 158	3.481 176 236	2.313 161 605	3.577 023 204	16.272 180 014	15.593 548 866	7.824 804 450	15.895 960 551
	3 000	3.663 502 763	3.481 176 137	2.313 161 605	3.577 023 087	16.27 217 5247	15.593 547 926	7.824 805 150	15.895 959 702
	4 000	3.663 502 768	3.481 176 138	2.313 161 609	3.577 023 097	16.272 175 401	15.593 548 008	7.824 805 250	15.895 959 906
DPs	4 000	3.662 564 472	3.480 724 774	2.312 344 283	3.575 906 378	16.263 361 341	15.588 915 940	7.818 931 308	15.885 726 099
TPs	4 000	3.662 252 357	3.480 574 621	2.312 072 405	3.575 534 891	16.260 430 064	15.587 375 303	7.816 977 838	15.882 322 508
∞HPs	4 000	3.661 625 055	3.480 272 821	2.311 525 968	3.574 788 230	16.254 539 620	15.584 279 135	7.813 052 338	15.875 482 712

system	basis size	$\langle \delta_{H^+e^+} \rangle$	$\langle \delta_{e^+e^-} \rangle$	$\langle \delta_{H^+e^-} \rangle$	$\langle \delta_{e^-e^-} \rangle$	$\langle \tilde{\delta}_{H^+e^+} \rangle$	$\langle \tilde{\delta}_{e^+e^-} \rangle$	$\langle \tilde{\delta}_{H^+e^-} \rangle$	$\langle \tilde{\delta}_{e^-e^-} \rangle$
HPs	500	0.001 638 389	0.024 458 439	0.176 894 912	0.004 382 960	0.001 622 696	0.024 494 663	0.177 041 115	0.004 360 422
	1 000	0.001 626 822	0.024 485 106	0.176 973 054	0.004 366 761	0.001 622 883	0.024 494 690	0.177 041 413	0.004 360 586
	2 000	0.001 623 949	0.024 489 921	0.177 023 446	0.004 362 226	0.001 622 902	0.024 494 690	0.177 041 456	0.004 360 600
	3 000	0.001 623 365	0.024 493 123	0.177 033 069	0.004 361 278	0.001 622 903	0.024 494 690	0.177 041 458	0.004 360 602
	4 000	0.001 623 154	0.024 493 465	0.177 037 452	0.004 361 160	0.001 622 903	0.024 494 690	0.177 041 458	0.004 360 602
DPs	4 000	0.001 623 996	0.024 495 414	0.177 188 620	0.004 365 776	0.001 623 745	0.024 496 639	0.177 192 629	0.004 365 216
TPs	4 000	0.001 624 277	0.024 496 062	0.177 238 938	0.004 367 312	0.001 624 026	0.024 497 287	0.177 242 948	0.004 366 753
∞HPs	4 000	0.001 624 841	0.024 497 366	0.177 340 118	0.004 370 403	0.001 624 589	0.024 498 591	0.177 344 131	0.004 369 843

system	basis size	$\langle \delta_{H^+e^+} \delta_{H^+e^+} \rangle$	$\langle \delta_{H^+e^+} \delta_{e_a^- e_b^-} \rangle$	$\langle \delta_{H^+e_a^-} \delta_{e^+e_b^-} \rangle$	$\langle \delta_{H^+e_a^-} \delta_{H^+e_b^-} \rangle$	$\langle \delta_{e^+e_a^-} \delta_{e^+e_b^-} \rangle$	$\langle \delta_{H^+e^+} \delta_{H^+e_a^-} \delta_{e^+e_b^-} \rangle$
HPs	500	8.7403×10^{-4}	3.1225×10^{-5}	6.2365×10^{-3}	7.5321×10^{-3}	3.7460×10^{-4}	1.9180×10^{-4}
	1000	8.5986×10^{-4}	3.1582×10^{-5}	6.3212×10^{-3}	7.5334×10^{-3}	3.7147×10^{-4}	1.9038×10^{-4}
	2000	8.5038×10^{-4}	3.1749×10^{-5}	6.3509×10^{-3}	7.5404×10^{-3}	3.6961×10^{-4}	1.8898×10^{-4}
	3000	8.4933×10^{-4}	3.1856×10^{-5}	6.3597×10^{-3}	7.5406×10^{-3}	3.6907×10^{-4}	1.8782×10^{-4}
	4000	8.4725×10^{-4}	3.1909×10^{-5}	6.3646×10^{-3}	7.5432×10^{-3}	3.6887×10^{-4}	1.8738×10^{-4}
DPs	4000	8.4819×10^{-4}	3.1947×10^{-5}	6.3701×10^{-3}	7.5589×10^{-3}	3.6918×10^{-4}	1.8772×10^{-4}
TPs	4000	8.4850×10^{-4}	3.1960×10^{-5}	6.3719×10^{-3}	7.5641×10^{-3}	3.6928×10^{-4}	1.8783×10^{-4}
∞HPs	4000	8.4913×10^{-4}	3.1985×10^{-5}	6.3756×10^{-3}	7.5746×10^{-3}	3.6948×10^{-4}	1.8806×10^{-4}

reader, in Table III instead of pseudoparticle indices (1, 2, or 3) we use subscripts indicating the actual particles, for example $\mathbf{r}_{H^+e^+} \equiv \mathbf{r}_1$ or $\mathbf{r}_{e^+e^-} \equiv \mathbf{r}_{23}$. As one can see from the data in Table III, the convergence of the nonsingular operators such as powers of the interparticle distances is similar (just slightly worse) to that of the nonrelativistic energy. The situation is different for the singular operators. The expectation values of the Dirac δ functions computed directly, as expected, show a substantially lower level of convergence. The convergence gets worse for the products of two Dirac δ functions; and for the product of three δ functions the accuracy probably does not exceed three decimal figures. As was explained in Sec. II, in addition to the fact that, unlike the energy, the wave function in the variational method is accurate only to the first order, we face the problem of a somewhat poor description of the cusp region by the Gaussian-type basis. In contrast to the direct evaluation of the expectation values of the pair δ functions, the use of relation (26) noticeably improves the convergence. Unfortunately, such a transformation is likely to be possible only for the expectation values of $\delta(\mathbf{r}_{ij})$. More singular operators, such as the products of two and more δ functions will probably require some matrix elements that are too difficult to evaluate.

Next, we use the expectation values of the pair Dirac δ functions with formula (31) to determine the rates of the electron–positron annihilation in HPs isotopologues. The computed values are shown in Table IV. The numeric uncertainties (due to the finiteness of the basis set used) of these values are very small and do not appear in the significant figures shown in Table IV. Much larger is the uncertainty due to the missing α^2 and higher-order terms

TABLE IV. Electron–positron annihilation rates (in $\sec^{-1}$) for HPs isotopologues.

system	Γ
HPs	$2.465\,156 \times 10^9$
DPs	$2.465\,352 \times 10^9$
TPs	$2.465\,418 \times 10^9$
∞HPs	$2.465\,549 \times 10^9$

in formula (31), which we roughly estimate to be of the order of $0.0003 \times 10^9\ \mathrm{s}^{-1}$.

In summary, high-accuracy variational calculations of the ground state of positronium hydride and its isotopologues have been performed using a variational expansion in terms of explicitly correlated Gaussian basis functions. A new upper bound to the nonrelativistic energy has been obtained and leading relativistic corrections have been computed. In this work we have improved the accuracy of binding energies, various expectation values, and electron–positron annihilation rates. We also corrected and expanded the results of the only previous study that considered relativistic effects in HPs.

[1] E. A. Hylleraas and A. Ore, Phys. Rev. **71**, 493 (1947).
[2] A. Ore, Phys. Rev. **83**, 665 (1951).
[3] C. F. Lebeda and D. M. Schrader, Phys. Rev. **178**, 24 (1969).
[4] Y. K. Ho, Phys. Rev. A **34**, 609 (1986).
[5] T. Yoshida and G. Miyako, Phys. Rev. A **54**, 4571 (1996).
[6] A. M. Frolov and V. H. Smith, Phys. Rev. A **55**, 2662 (1997).
[7] A. M. Frolov and V. H. Smith, Phys. Rev. A **56**, 2417 (1997).
[8] D. Bressanini, M. Mella, and G. Morosi, Phys. Rev. A **57**, 1678 (1998).
[9] N. Jiang and D. M. Schrader, J. Chem. Phys. **109**, 9430 (1998).
[10] J. Usukura, K. Varga, and Y. Suzuki, Phys. Rev. A **58**, 1918 (1998).
[11] K. Strasburger and H. Chojnacki, J. Chem. Phys. **108**, 3218 (1998).
[12] K. Varga, Phys. Rev. Lett. **83**, 5471 (1999).
[13] Z.-C. Yan and Y. K. Ho, Phys. Rev. A **60**, 5098 (1999).
[14] S. L. Saito, J. Chem. Phys. **118**, 1714 (2003).
[15] J. Mitroy, Phys. Rev. A **73**, 054502 (2006).
[16] S. Bubin and L. Adamowicz, Phys. Rev. A **74**, 052502 (2006).
[17] M. W. J. Bromley, J. Mitroy, and K. Varga, Phys. Rev. A **75**, 062505 (2007).
[18] J. Mitroy and M. W. J. Bromley, Phys. Rev. Lett. **98**, 063401 (2007).
[19] Z.-C. Yan and Y. K. Ho, Phys. Rev. A **78**, 012711 (2008).
[20] D. M. Schrader, F. M. Jacobsen, N.-P. Frandsen, and U. Mikkelsen, Phys. Rev. Lett. **69**, 57 (1992).
[21] D. B. Cassidy and A. P. Mills, Nature (London) **449**, 195 (2007).
[22] D. B. Cassidy, S. H. M. Deng, and A. P. Mills, Phys. Rev. A **76**, 062511 (2007).
[23] C. Surko, Nature (London) **449**, 153 (2007).
[24] C. Gahn, G. D. Tsakiris, G. Pretzler, K. J. Witte, C. Delfin, C.-G. Wahlström, and D. Habs, Appl. Phys. Lett. **77**, 2662 (2000).
[25] H. Chen, S. C. Wilks, J. D. Bonlie, E. P. Liang, J. Myatt, D. F. Price, D. D. Meyerhofer, and P. Beiersdorfer, Phys. Rev. Lett. **102**, 105001 (2009).
[26] K. Varga, J. Usukura, and Y. Suzuki, Phys. Rev. Lett. **80**, 1876 (1998).
[27] D. Bressanini, M. Mella, and G. Morosi, Phys. Rev. A **55**, 200 (1997).
[28] E. Armour, J.-M. Richard, and K. Varga, Phys. Rep. **413**, 1 (2005).
[29] T. Rebane, Phys. At. Nucl. **72**, 55 (2009).
[30] J.-M. Richard, Phys. Rev. A **49**, 3573 (1994).
[31] J. Mitroy and S. A. Novikov, Phys. Rev. A **70**, 032511 (2004).
[32] K. Varga, S. Fleck, and J. M. Richard, Europhys. Lett. **37**, 183 (1997).

[33] K. Strasburger, J. Phys. B **37**, 4483 (2004).

[34] M. Amoretti *et al.*, Nature (London) **419**, 456 (2002).

[35] G. Gabrielse *et al.*, (ATRAP Collaboration), Phys. Rev. Lett. **89**, 213401 (2002).

[36] D. K. Gridnev and C. Greiner, Phys. Rev. Lett. **94**, 223402 (2005).

[37] CODATA 2006 Recommended values of the fundamental physical constants, available at [http://physics.nist.gov/cuu].

[38] M. Cafiero, S. Bubin, and L. Adamowicz, Phys. Chem. Chem. Phys. **5**, 1491 (2003).

[39] S. Bubin, M. Cafiero, and L. Adamowicz, Adv. Chem. Phys. **131**, 377 (2005).

[40] S. Bubin and L. Adamowicz, J. Chem. Phys. **124**, 224317 (2006).

[41] K. Varga and Y. Suzuki, Phys. Rev. C **52**, 2885 (1995).

[42] Y. Suzuki and K. Varga, *Stochastic Variational Approach to Quantum-Mechanical Few-Body Problems*, Lecture Notes in Physics (Springer-Verlag, Berlin, 1998).

[43] J. Komasa, W. Cencek, and J. Rychlewski, Phys. Rev. A **52**, 4500 (1995).

[44] J. Mitroy, Phys. Rev. A **70**, 024502 (2004).

[45] S. Bubin and L. Adamowicz, J. Chem. Phys. **121**, 6249 (2004).

[46] S. Bubin, M. Stanke, D. Kędziera, and L. Adamowicz, Phys. Rev. A **75**, 062504 (2007).

[47] M. Stanke, D. Kędziera, S. Bubin, and L. Adamowicz, Phys. Rev. Lett. **99**, 043001 (2007).

[48] W. Cencek and K. Szalewicz, Int. J. Quantum Chem. **108**, 2191 (2008).

[49] M. Puchalski and A. Czarnecki, Phys. Rev. Lett. **101**, 183001 (2008).

[50] S. Bubin and L. Adamowicz, Phys. Rev. A **83**, 022505 (2011).

[51] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).

[52] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Kvantovaya Elektrodinamika (Quantum Electrodynamics)* (Nauka, Moscow, 1989), in Russian.

[53] S. Bubin, M. Stanke, D. Kędziera, and L. Adamowicz, Phys. Rev. A **76**, 022512 (2007).

[54] R. J. Drachman, J. Phys. B **14**, 2733 (1981).

[55] K. Pachucki, W. Cencek, and J. Komasa, J. Chem. Phys. **122**, 184101 (2005).

[56] G. S. Adkins, R. N. Fell, and J. Sapirstein, Phys. Rev. Lett. **84**, 5086 (2000).

[57] A. Czarnecki, K. Melnikov, and A. Yelkhovsky, Phys. Rev. A **61**, 052502 (2000).

[58] B. A. Kniehl, A. V. Kotikov, and O. L. Veretin, Phys. Rev. A **80**, 052501 (2009).

[59] V. I. Kukulin and V. M. Krasnopol'sky, J. Phys. G **3**, 795 (1977).

[60] S. A. Alexander, H. J. Monkhorst, and K. Szalewicz, J. Chem. Phys. **85**, 5821 (1986).

[61] S. A. Alexander, H. J. Monkhorst, and K. Szalewicz, J. Chem. Phys. **87**, 3976 (1987).

[62] P. M. Kozlowski and L. Adamowicz, J. Chem. Phys. **95**, 6681 (1991).

[63] P. M. Kozlowski and L. Adamowicz, J. Chem. Phys. **96**, 9013 (1992).

[64] D. B. Kinghorn, Int. J. Quantum Chem. **57**, 141 (1996).