

An extension of Ore's positronium hydride wave function

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Abstract

An extension of Ore's wave function for positronium hydride (PsH), and computational results based on it are presented. To improve the flexibility of Ore's PsH wave function, the wave function is expanded using Gaussian functions, and a set of equations is derived for the expansion coefficients. The extended Ore's PsH wave function gives a positronium binding energy of 0.117 eV and a two-photon annihilation rate of 2.175 ns^{-1} . Ore's results are improved by 0.049 eV and 0.302 ns^{-1} . Inclusion of electron correlation effects further improves Ore's results. Application of the Ore-type wave function to many-electronic positronium-atom complexes is considered.

I. INTRODUCTION

The antiparticle of the electron, the positron (e^+), forms bound states with various electronic systems. The simplest bound state is positronium (Ps), which consists of one positron and one electron. The existence of Ps^- , Ps_2^+ , and Ps_2 has been predicted theoretically¹⁻⁴, and Ps^- and Ps_2 have been detected experimentally^{5,6}. The positron also forms bound states with atomic and molecular systems, referred to as positronium-atom and positronium-molecule complexes. Positronium-atom complexes have been extensively studied. In particular, positronium hydride (PsH) and positronium halides have been detected in experiments^{7,8} and have been studied theoretically⁹⁻¹⁷ by many researchers. The stability of other complexes has been also predicted¹⁸⁻²³.

The simplest stable positronium-atom complex is PsH, which consists of a hydrogen atom and positronium. PsH is a prototype of positronium-atom complexes, and plays a significant role in theoretical studies of positronium-atom complexes. The first theoretical calculation of PsH was by Ore in 1951²⁴. Ore wrote down a spin free PsH wave function of the ground state ($^2, ^1S$) as the product of the 1s eigenfunction of hydrogen atom ψ_{H} , positronium ψ_{Ps} , and

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ψ_{H} , which represents distribution of positronium from the proton :

$$\psi_{\text{Ore}} = S_{12} \psi_{\text{H}}(\mathbf{r}_1) \psi_{\text{H}}(\mathbf{r}_2) \psi_{\text{Ps}}(\mathbf{r}_{02}) \quad (1)$$

with

$$\psi_{\text{H}}(\mathbf{r}_1) = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} \exp(-r_1), \quad (2)$$

$$\psi_{\text{H}}(\mathbf{r}_2) = \left(\frac{k^3}{\pi}\right)^{\frac{1}{2}} \exp(-kr_2), \quad (3)$$

and

$$\psi_{\text{Ps}}(\mathbf{r}_{02}) = \left(\frac{1}{8}\right)^{\frac{1}{2}} \exp\left(-\frac{1}{2}r_{02}\right), \quad (4)$$

where 0 denotes the positron, 1 and 2 refer to the electrons, k is a variational parameter, and S_{12} is the symmetrizer with respect to exchange of 1 and 2. This is a valence-bond-like (VB-like) wave function. Ore obtained from the wave function the Ps binding energy of 0.068 eV and the two-photon annihilation rate of 2.045 ns^{-1} , and showed that PsH is energetically stable. Various theoretical methods have since been applied to PsH in order to refine Ore's result and develop computational methods which are applicable to many-electronic positronium-atom complexes. These methods include VB-like^{25, 26}, Hartree-Fock (HF)²⁷, configuration interaction (CI)²⁸⁻³², variational calculation with Hylleraas-type functions (Hylleraas)³³⁻³⁹, the combined Hylleraas-configuration-interaction method (Hylleraas-CI)⁴⁰, the coupled pair approximation (CPA) with Hylleraas-type functions⁴¹, the explicitly correlated Gaussian (ECG) expansion method^{42, 43}, and quantum Monte Carlo (QMC)⁴⁴⁻⁴⁶. At present, the ECG and Hylleraas methods give the most accurate energy and two-photon annihilation rate of PsH: their values are respectively 1.067 eV and 2.459 ns^{-1} . Although the ECG and Hylleraas methods yield the most accurate results for PsH, it is difficult to apply these methods to many-electronic positronium-atom complexes because of the many-electron integrals involved.

Ore's PsH wave function is very simple and has a clear physical rationale. Unfortunately, it suffers from two defects. One is the lack of flexibility of the wave function. The functions ψ_{H} and ψ_{Ps} in the wave function may deform so as to shield positive charge, like a valence bond wave function of the hydrogen molecule⁴⁷. The other defect is the absence of most electron correlation effects. Since the double-occupancy constraint of electrons is relaxed in Ore's PsH wave function, only a part of the radial electron correlation effect is included. The angular electron correlation effect is not included.

The present work extends Ore's PsH wave function, and refines the energy and two-photon annihilation rate of PsH given by Ore. Improvement in the flexibility of Ore's wave function may be highly significant. To this end, we expand ψ_{H} , ψ_{H} , and ψ_{Ps} using Gaussian functions, and derive a set of equations to determine variationally their expansion coefficients. Gaussian functions for ψ_{Ps} have a variable representing the positron-electron distance, i.e.

an explicitly correlated Gaussian function. Although the three-electron integrals over explicitly correlated Gaussian functions are required for the present calculations, these integrals are easily evaluated.

We also attempt to include the rest of electron correlation effect. Usually, CI, CPA, perturbation theory, and so on are used to do this. Most of these methods involve complicated wave functions. Ore's PsH wave function is characterized by its simple form. To keep the simple form of the wave function, we apply an effective potential taking into account the electron-electron Coulomb hole. Such potentials have been proposed by Clementi and co-workers⁴⁸ and Panas and Snis^{49,50}. This work uses the latter potential.

The Ore-type wave function, i.e. the VB-like wave function of a positron and an atom, is applicable to many-electronic positronium-atom complexes. We also extend the Ore-type wave function to many-electronic positronium-atom complexes. The matrix elements over determinantal Ore-type wave functions are formulated.

Below, Section II sets out the theoretical method and computational details of the extended Ore's PsH wave function. Section III discusses our results and gives the matrix elements over determinantal Ore-type wave functions for many-electronic positronium-atom complexes. Section IV summarizes this work.

II. THEORY AND COMPUTATION

We expand ψ_H , ψ'_H , and ψ_{Ps} using Gaussian functions as follows :

$$\psi_H(\mathbf{r}_1) = \sum_{i=1}^{N_H} C_i f_i(\mathbf{r}_1), \quad (5)$$

$$\psi'_H(\mathbf{r}_2) = \sum_{i=1}^{N_H} C'_i f_i(\mathbf{r}_2), \quad (6)$$

$$\psi_{Ps}(\mathbf{r}_{02}) = \sum_{i=1}^{N_{Ps}} D_i g_i(\mathbf{r}_{02}), \quad (7)$$

where $f_i(\mathbf{r}_\mu) = \exp(-\alpha_i r_\mu^2)$ ($\mu = 1, 2$ and $i = 1, \dots, N_H$) and $g_i(\mathbf{r}_{02}) = \exp(-\beta_i r_{02}^2)$ ($i = 1, \dots, N_{Ps}$). Cartesian Gaussian functions $x^{l_x} y^{l_y} z^{l_z} \exp(-\alpha_i r^2)$ are used when the electronic orbital has nonzero angular momentum. The coefficients $\{C_i\}$, $\{C'_i\}$, and $\{D_i\}$ are variationally determined. A set of equations for this is derived by minimizing the functional

$$\mathcal{L} = E - \lambda_H (\langle \psi_H | \psi_H \rangle - 1) - \lambda'_H (\langle \psi'_H | \psi'_H \rangle - 1) - \lambda_{Ps} (\langle \psi_{Ps} | \psi_{Ps} \rangle - 1) \quad (8)$$

with respect to ψ_H , ψ'_H , and ψ_{Ps} . Here, λ_H , λ'_H , and λ_{Ps} are Lagrange multipliers, and $E = H/S$; S is the overlap matrix $\langle \psi_{Ore} | \psi_{Ore} \rangle$ and H is the matrix $\langle \psi_{Ore} | \mathcal{H} | \psi_{Ore} \rangle$ with the Hamiltonian

$$\mathcal{H} = -\frac{1}{2}(\alpha_0 + \alpha_1 + \alpha_2) + \mathbf{r}_0^{-1} - \mathbf{r}_1^{-1} - \mathbf{r}_2^{-1} - \mathbf{r}_{01}^{-1} - \mathbf{r}_{02}^{-1} + \mathbf{r}_{12}^{-1}. \quad (9)$$

By setting the first variation in \mathcal{L} equal to zero, the following equations are obtained :

$$\sum_{j=1}^{N_H} f_i(\mathbf{r}_1) \sum_{j=1}^{N_H} f_j(\mathbf{r}_2) \sum_{P_S} (r_{02}) | \mathcal{H} - E | S_{12} f_j(\mathbf{r}_1) \sum_{j=1}^{N_H} f_j(\mathbf{r}_2) \sum_{P_S} (r_{02}) C_j = \sum_{j=1}^{N_H} f_i | f_j | C_j, \quad (10)$$

$$\sum_{j=1}^{N_H} f_i(\mathbf{r}_1) f_j(\mathbf{r}_2) \sum_{P_S} (r_{02}) | \mathcal{H} - E | S_{12} \sum_{j=1}^{N_H} f_j(\mathbf{r}_1) f_j(\mathbf{r}_2) \sum_{P_S} (r_{02}) C'_j = \sum_{j=1}^{N_H} f_i | f_j | C'_j, \quad (11)$$

$$\sum_{j=1}^{N_{P_S}} f_i(\mathbf{r}_1) \sum_{j=1}^{N_{P_S}} f_j(\mathbf{r}_2) g_j(r_{02}) | \mathcal{H} - E | S_{12} \sum_{j=1}^{N_{P_S}} f_j(\mathbf{r}_1) \sum_{j=1}^{N_{P_S}} f_j(\mathbf{r}_2) g_j(r_{02}) D_j = \sum_{j=1}^{N_{P_S}} g_i | g_j | D_j, \quad (12)$$

where $\sum_{j=1}^{N_H} = S$, $\sum_{j=1}^{N_{P_S}} = S'$, and $\sum_{P_S} = S_{P_S}$, i.e. new Lagrange multipliers. The exact values of these Lagrange multipliers are zero. These equations are similar to the generalized valence bond (GVB) equations proposed by Goddard⁵¹. They must be solved by the self-consistent field (SCF) procedure. We refer to this as the Ore-SCF method.

To include electron correlation effects, this work attempts to use an effective potential taking into account the electron-electron Coulomb hole proposed by Panas and Snis^{49,50}. They replaced r_{12}^{-1} by $v(r_{12})$:

$$v(r_{12}) = 2 \int_0^{\frac{1}{2}} ds \exp(-s^2 r_{12}^2), \quad (13)$$

where $\frac{1}{2}$ is a cut-off parameter. $\int_0^{\frac{1}{2}}$ depends on Gaussian functions of electron-electron interaction integrals

$$\int d\mathbf{r}_1 \int d\mathbf{r}_2 v(r_{12}) \exp(-\frac{1}{2} r_1^2 - \frac{1}{2} r_2^2), \quad (14)$$

and $\int_0^{\frac{1}{2}}$ is the following form :

$$= \left[\frac{1 + \frac{1}{2}}{2} + \left[\left(\frac{1 + \frac{1}{2}}{2} \right)^2 + \frac{1}{f^2} \right]^{\frac{1}{2}} \right]^{\frac{1}{2}}, \quad (15)$$

where f is a scale factor; its recommended value is 2.

In the present Ore-SCF calculations, the non-linear parameters $\{ \alpha_i \}$ and $\{ \beta_i \}$ of the Gaussian sets are individually generated by the relation

$$\alpha_i = \beta_i \cosh \frac{i}{N} \quad (i = 1, \dots, N), \quad (16)$$

where α_i and β_i are parameters and N is the number of Gaussian functions. This is a simple extension of the even-tempering method⁵². The relation (16) generates a set of non-linear parameters which can adequately express orbitals not only at outer region but also near the origin.

The two-photon annihilation rate Γ is calculated by

$$\Gamma = n_e^{-3} \int | \psi(\mathbf{r}_0 - \mathbf{r}_1) |^2, \quad (17)$$

where n_e is the number of electrons, α is the fine structure constant, $\delta(\mathbf{r}_0 - \mathbf{r}_1)$ is the Dirac delta function, and ψ is a normalized wave function.

III. RESULTS AND DISCUSSION

A. PsH calculations

We first examine convergence of the total energy and two-photon annihilation rate of Ps for N_{Ps} . Table I summarizes the total energies and two-photon annihilation rates of Ps, together with their deviations from the exact values. The total energy of Ps rapidly converges versus N_{Ps} . The total energy calculated with a 10-term Gaussian set is almost the same as the exact value. Convergence of the two-photon annihilation rate is relatively slow, however, because the Gaussian function is cusplless. The two-photon annihilation rate calculated with a 20-term Gaussian set is the same as the exact value of 2.008 ns^{-1} .

Table II summarizes the total energies and two-photon annihilation rates of PsH obtained from Ore-SCF calculations for some values of N_H and N_{Ps} . We denote the total energy and the two-photon annihilation rate calculated with N_H - and N_{Ps} -term Gaussian sets as $E_{PsH}(N_H, N_{Ps})$ and $\Gamma_{PsH}(N_H, N_{Ps})$, respectively. Our best Ore-SCF results for PsH are a total energy of -0.754304 hartree and a two-photon annihilation of 2.157 ns^{-1} , which are respectively E_{PsH}

TABLE I. Total energies E_{Ps} and two-photon annihilation rates Γ_{Ps} of Ps. E_{Ps} and Γ_{Ps} denote deviations from the exact values. The exact E_{Ps} and Γ_{Ps} are -0.25 hartree and 2.008 ns^{-1} .

N_{Ps}	E_{Ps} (hartree)	E_{Ps} (hartree)	Γ_{Ps} (ns^{-1})	Γ_{Ps} (ns^{-1})
2	-0.242906	0.007094	1.107	0.901
4	-0.249576	0.000424	1.658	0.350
6	-0.249960	0.000040	1.853	0.155
8	-0.249995	0.000005	1.933	0.075
10	-0.249999	0.000001	1.961	0.047
12	-0.250000	0.000000	1.977	0.031
14	-0.250000	0.000000	1.995	0.013
16	-0.250000	0.000000	2.003	0.005
18	-0.250000	0.000000	2.006	0.002
20	-0.250000	0.000000	2.008	0.000

TABLE II. Total energies E_{PsH} and two-photon annihilation rates Γ_{PsH} of PsH for N_H and N_{Ps} .

N_H	$N_{Ps} = 8$		$N_{Ps} = 10$		$N_{Ps} = 20$	
	E_{PsH} (hartree)	Γ_{PsH} (ns^{-1})	E_{PsH} (hartree)	Γ_{PsH} (ns^{-1})	E_{PsH} (hartree)	Γ_{PsH} (ns^{-1})
8	-0.754052	2.085	-0.754056	2.114	-0.754057	2.163
10	-0.754249	2.081	-0.754253	2.110	-0.754254	2.158
12	-0.754288	2.080	-0.754292	2.109	-0.754293	2.157
14	-0.754296	2.080	-0.754300	2.109	-0.754301	2.157
16	-0.754298	2.080	-0.754302	2.109	-0.754303	2.157
20	-0.754299	2.080	-0.754303	2.109	-0.754304	2.157

(20, 20) and $E_{\text{PsH}}(20, 20)$. At each N_{Ps} , the total energy converges slowly to $E_{\text{PsH}}(20, N_{\text{Ps}})$ versus N_{H} . $E_{\text{PsH}}(8, N_{\text{Ps}})$ is higher than $E_{\text{PsH}}(20, N_{\text{Ps}})$ by 247 μ hartree. The two-photon annihilation rate converges rapidly to $\Gamma_{\text{PsH}}(20, N_{\text{Ps}})$ versus N_{H} , and is constant for $N_{\text{H}} > 10$. Convergence of the total energy of PsH for N_{Ps} is rapid. This is similar to the case of Ps. $E_{\text{PsH}}(20, 10)$ is very close to our best total energy $E_{\text{PsH}}(20, 20)$; the energy difference is ~ 1 μ hartree. On the other hand, the difference between $E_{\text{PsH}}(20, 10)$ and $E_{\text{PsH}}(20, 20)$ is large. It is clear that the total energy depends on N_{H} rather than N_{Ps} , and that the two-photon annihilation rate depends strongly on N_{Ps} . A Gaussian set of $N_{\text{Ps}} = 20$ should be employed in order to calculate an accurate two-photon annihilation rate.

We now compare our best Ore-SCF results with other works. Table III summarizes the total energies, Ps binding energies, and two-photon annihilation rates of PsH together with other works. Our Ps binding energy and two-photon annihilation rate are improved by 0.049 eV and 0.112 ns^{-1} over Ore's results. This is due to the high flexibility of our wave function. However, the energy lowering is very small in comparison with the energy difference from the most accurate energy given by the ECG and Hylleraas calculations^{38, 39, 42}. This may be due to the lack of electron correlation effects.

The results obtained from replacement of r_{12}^{-1} by $v(r_{12})$ are also listed in Table III. This calculation method is designated Ore-SCF+corr. Electron correlation effects are included with $f = 2$ and 1.15032. The latter f value is optimized to reproduce the total energy of H^- . The results are further improved by inclusion of electron correlation effects. The two-photon annihilation rate approaches the most accurate value. The total energy is far from the most accurate value, however. A further extension to include electron correlation effects is needed.

We propose a wave function which can take account of angular electron correlation effects,

$$\Psi = \Psi_{\text{Ore}} + \sum_{l=1} C_l S_{12} [\psi_l(r_1) \psi_l(r_2)]^{(0)} \Psi_{\text{Ps}}(r_{02}), \quad (18)$$

where ψ_l and ψ_l are mutually non-orthogonal correlating orbitals with angular momentum l , $[\psi_l \psi_l]^{(0)}$ is an electron part coupled to the S state, and C_l 's are coefficients. This wave

TABLE III. Comparison with other works of total energies E_{PsH} , Ps binding energies BE, and two-photon annihilation rates Γ_{PsH} of PsH for $N_{\text{H}} = 20$ and $N_{\text{Ps}} = 20$.

Method	Reference	E_{PsH} (hartree)	BE (eV)	Γ_{PsH} (ns^{-1})
Ore-SCF	This work	- 0.754304	0.117	2.157
Ore-SCF + corr ($f = 2$)	This work	- 0.759318	0.254	2.234
Ore-SCF + corr ($f = 1.15032$)	This work	- 0.770202	0.550	2.353
Ore	Refs. 24 and 25	- 0.75251	0.068	2.045
Hylleraas	Refs. 38 and 39	- 0.789197	1.067	2.459
ECG	Ref. 42	- 0.789197	1.067	2.459
Experiment	Refs. 7 and 57		1.1 ± 0.2	2.35

function is determined by variational optimization not only of ψ_H , ψ'_H , and ψ_{Ps} , but also of $\{\psi_i\}$, $\{\psi'_i\}$, and $\{C_i\}$. In other words, this is a multiconfiguration SCF method with non-orthogonal orbitals. The wave function may be solved by the super-CI procedure⁵³. The results will be given elsewhere.

B. A further extension

We now consider application of Ore-type wave function to many-electronic positronium-atom complexes. We derive matrix elements over an N-electron determinantal Ore-type wave function

$$\psi_p(\mathbf{x}_0, \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (N!)^{-\frac{1}{2}} \mathcal{A} \psi_p(\mathbf{x}_{01}) \psi_a(\mathbf{x}_2) \psi_b(\mathbf{x}_3) \dots, \quad (19)$$

where \mathbf{x} is a space-spin coordinate, $\psi_p(\mathbf{x}_{01}) = \psi_p(\mathbf{x}_1) \psi_{Ps}(\mathbf{x}_{01})$, $\{\psi_a\}$ are mutually orthogonal electron spin-orbitals except for ψ_p . Here, \mathcal{A} is the unnormalized antisymmetrizer for N electrons :

$$\mathcal{A} = \sum_P (-1)^p P, \quad (20)$$

where P is a permutation operator and p is the parity of the permutation. The Hamiltonian of N-electronic positronium-atom complexes in atomic units is

$$\mathcal{H} = \sum_{i=1}^N h(i) + \sum_{i<j}^N r_{ij}^{-1} + h_+(\mathbf{0}) - \sum_{i=1}^N r_{0i}^{-1}, \quad (21)$$

where

$$h(i) = -\frac{1}{2} \nabla_i^2 - Zr_i^{-1}, \quad (22)$$

$$h_+(\mathbf{0}) = -\frac{1}{2} \nabla_0^2 + Zr_0^{-1}, \quad (23)$$

and Z is the nuclear charge. We have to derive the overlap, one-electron, one-positron, positron-electron, and electron-electron matrix elements. The matrix elements of any N-electron operator O over ψ_p and ψ_q are respectively written as

$${}_p\langle O \rangle_q = \int d\mathbf{x}_0 \int d\mathbf{x}_1 \dots \int d\mathbf{x}_N [{}_p\psi(\mathbf{x}_{01}) \psi_a(\mathbf{x}_2) \dots] O [{}_q\mathcal{A} \psi_p(\mathbf{x}_{01}) \psi_a(\mathbf{x}_2) \dots]. \quad (24)$$

This formula is obtained using the fact that \mathcal{A} is commutable with O, and O is symmetric for electron permutation. Each matrix element can be derived with the help of diagrams, similar to the diagrams of Bonham^{54, 55}. The diagrams for overlap, one-positron, one-electron, positron-electron, and electron-electron matrix elements are shown in FIG. 1-5. A diagram of this sort consists of a circle, solid circles, and two solid lines, which respectively express a positronic coordinate, electronic coordinates, and two positron-electron distances (r_{0i}). A vertex and broken line in FIG. 2 and 3 represents a one-body operator. A broken line in FIG. 4 and 5 represents a two-body Coulomb interaction.

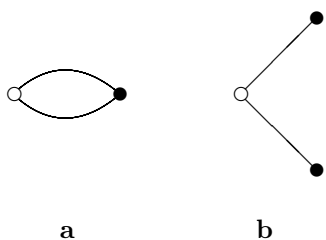


FIG. 1. Diagrams for overlap matrix element

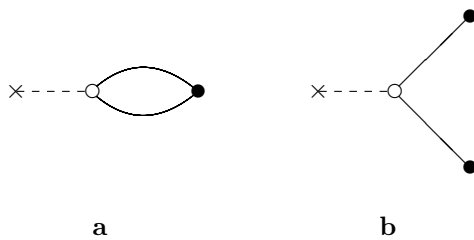


FIG. 2. Diagrams for one-positron matrix element

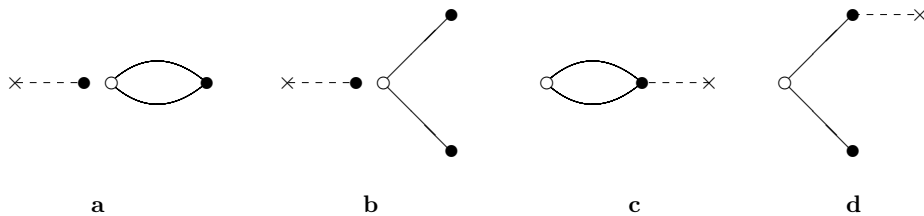


FIG. 3. Diagrams for one-electron matrix element

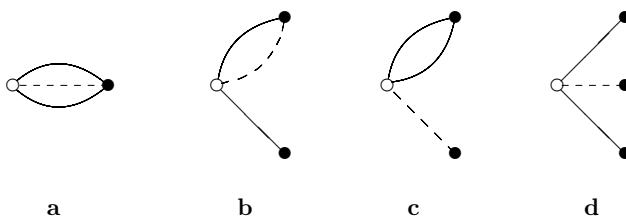


FIG. 4. Diagrams for positron-electron interaction matrix element

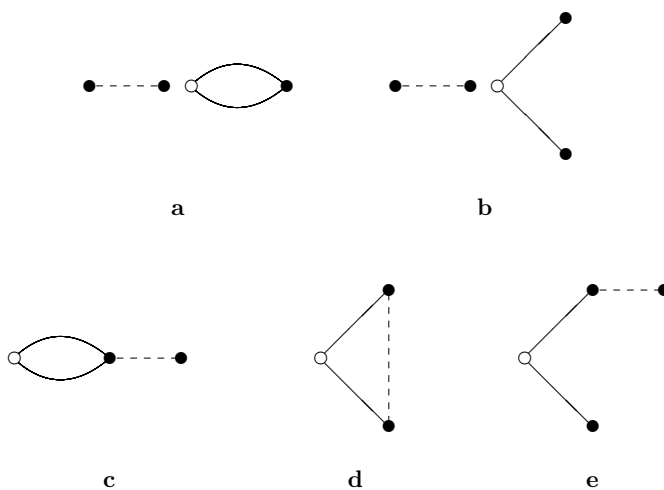


FIG. 5. Diagrams for electron-electron interaction matrix element

Overlap matrix elements are easily derived. The diagrams a and b in FIG. 1 are respectively two- and three-electron integrals, and the resulting formula is

$${}_p \langle | \rangle_q = {}_p \langle | \rangle_q - \sum_a {}_p \langle a | \rangle_a \langle a | \rangle_q. \quad (25)$$

Here we simply write integrals by omitting positronic and electronic coordinates; functions in the bra and the ket are arranged in order of electronic coordinate number :

$${}_p \langle a | \rangle_a \langle a | \rangle_q = {}_p \langle (01) \rangle_a \langle (2) | \rangle_a \langle (1) \rangle_q \langle (02) \rangle. \quad (26)$$

In FIG. 2, a vertex with broken line represents an one-positron operator $h_+(0)$. The diagrams a and b in FIG. 2 respectively refer to two-electron and three-electron integrals with $h_+(0)$. The matrix element of $h_+(0)$ is

$${}_p \langle h_+(0) | \rangle_q = {}_p \langle h_+ | \rangle_q - \sum_a {}_p \langle a | h_+ | \rangle_a \langle a | \rangle_q. \quad (27)$$

The matrix element of a one-electron operator $h(i)$ is derived from four-type diagrams in FIG. 3. The diagrams a and b in FIG. 3 are the products of a one-electron integral of $h(i)$ and an overlap integral. The resulting matrix element formula is

$$\begin{aligned} {}_p \left\langle \prod_{i=1} h(i) \right\rangle_q &= \sum_a \langle a | h | \rangle_a \left[{}_p \langle | \rangle_q - \sum_b {}_p \langle b | \rangle_b \langle b | \rangle_q \right] \\ &+ \sum_{a,b} \langle a | h | \rangle_b \langle b | \rangle_a \langle a | \rangle_q \\ &+ {}_p \langle h | \rangle_q - \sum_a {}_p \langle a | h(1) + h(2) | \rangle_a \langle a | \rangle_q. \end{aligned} \quad (28)$$

The matrix element of operator h_{01}^{-1} is expressed by four-type diagrams as shown in FIG. 4. This operator is a positron-electron interaction with sign reversed. The diagram d in FIG. 4 is a four-electron integral. The resulting matrix element is

$$\begin{aligned} {}_p \left\langle \prod_{i=1} r_{0i}^{-1} \right\rangle_q &= {}_p \langle r_{01}^{-1} | \rangle_q + \sum_a {}_p \langle a | r_{02}^{-1} | \rangle_q \langle a | \rangle_a \\ &- \sum_a {}_p \langle a | r_{01}^{-1} + r_{02}^{-1} | \rangle_a \langle a | \rangle_q \\ &+ \sum_{a,b} {}_p \langle a | b | r_{02}^{-1} (1 - P_{12}) | \rangle_a \langle b | \rangle_q. \end{aligned} \quad (29)$$

where P_{12} is the permutation of electron 1 and 2. The electron-electron interaction matrix element is complicated due to electron exchange, and is expressed by five-type diagrams as shown in FIG. 5. The diagrams a and b in FIG. 5 are the products of a two-electron interaction integral and an overlap integral. The diagram e expresses a four-electron integral. The resulting electron-electron interaction matrix element is

$$\begin{aligned}
\left| \begin{matrix} p \\ i < j \end{matrix} \mathbf{r}_{ij}^{-1} \right|_q &= \begin{matrix} a & b \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} a & b \end{matrix}} \left[\begin{matrix} p \\ p \mid q - c \end{matrix} \begin{matrix} p & c \\ c & q \end{matrix} \right] \\
&+ \begin{matrix} a & b \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} c & b \end{matrix}} \begin{matrix} p & c \\ a & q \end{matrix} \\
&+ \begin{matrix} a & b \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} a & c \end{matrix}} \begin{matrix} p & c \\ b & q \end{matrix} \\
&+ \begin{matrix} p & a \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} p & a \end{matrix}} \\
&+ \begin{matrix} p & a & b \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} a & b & q \end{matrix}} \\
&+ \begin{matrix} p & a & b \end{matrix} \left| \mathbf{r}_{23}^{-1}(1 - P_{23}) \right|_{\begin{matrix} a & b & q \end{matrix}} . \tag{30}
\end{aligned}$$

We also give the overlap and Hamiltonian matrix elements between $\begin{matrix} p \end{matrix}$ and single, double, and triple electron excited determinants of $\begin{matrix} p, & q, a, & q, a, b, & q, a, b, c \end{matrix}$ and $\begin{matrix} rst \\ q, a, b, c \end{matrix}$. Here, $\begin{matrix} rst \\ q, a, b, c \end{matrix}$ is any electron excited determinant in which electrons have been excited from $\begin{matrix} a, & b, & c, \dots \end{matrix}$ to $\begin{matrix} r, & s, & t, \dots \end{matrix}$. These matrix elements have non-vanishing terms.

The matrix elements between $\begin{matrix} p \end{matrix}$ and $\begin{matrix} q, a \end{matrix}$ are as follows:

$$\left| \begin{matrix} p \\ q, a \end{matrix} \right|_{q, a}^r = - \begin{matrix} p & a \end{matrix} \left| \begin{matrix} r & q \end{matrix} \right|, \tag{31}$$

$$\left| \begin{matrix} p \\ h_+(0) \end{matrix} \right|_{q, a}^r = - \begin{matrix} p & a \end{matrix} \left| \begin{matrix} h_+ & r & q \end{matrix} \right|, \tag{32}$$

$$\begin{aligned}
\left| \begin{matrix} p \\ i=1 \end{matrix} h(i) \right|_{q, a}^r &= \begin{matrix} a \mid h \mid r \end{matrix} \left[\begin{matrix} p \mid q - b \end{matrix} \begin{matrix} p & b \\ b & q \end{matrix} \right] \\
&- \begin{matrix} b \mid h \mid b \end{matrix} \begin{matrix} p & a \\ r & q \end{matrix} \\
&- \begin{matrix} p & a \end{matrix} \left| \begin{matrix} h(1) + h(2) \end{matrix} \right|_{\begin{matrix} r & q \end{matrix}}, \tag{33}
\end{aligned}$$

$$\begin{aligned}
\left| \begin{matrix} p \\ i=1 \end{matrix} \mathbf{r}_{0i}^{-1} \right|_{q, a}^r &= \begin{matrix} p & a \end{matrix} \left| \mathbf{r}_{02}^{-1} \right|_{\begin{matrix} q & r \end{matrix}} - \begin{matrix} p & a \end{matrix} \left| \mathbf{r}_{01}^{-1} + \mathbf{r}_{02}^{-1} \right|_{\begin{matrix} r & q \end{matrix}} \\
&+ \begin{matrix} p & b & a \end{matrix} \left| \mathbf{r}_{02}^{-1}(1 - P_{12}) \right|_{\begin{matrix} b & r & q \end{matrix}}, \tag{34}
\end{aligned}$$

and

$$\begin{aligned}
\left| \begin{matrix} p \\ i < j \end{matrix} \mathbf{r}_{ij}^{-1} \right|_{q, a}^r &= \begin{matrix} a & b \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} r & b \end{matrix}} \left[\begin{matrix} p \mid q - c \end{matrix} \begin{matrix} p & c \\ c & q \end{matrix} \right] \\
&+ \begin{matrix} a & b \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} c & b \end{matrix}} \begin{matrix} p & c \\ r & q \end{matrix} \\
&+ \begin{matrix} a & b \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} r & c \end{matrix}} \begin{matrix} p & c \\ b & q \end{matrix} \\
&+ \begin{matrix} p & a \end{matrix} \left| \mathbf{r}_{12}^{-1}(1 - P_{12}) \right|_{\begin{matrix} q & r \end{matrix}}
\end{aligned}$$

$$\begin{aligned}
& + \int_{\mathbf{b}} \langle \mathbf{p} | \mathbf{a} | \mathbf{b} | \mathbf{r}_{12}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{r} | \mathbf{b} | \mathbf{q} \\
& + \int_{\mathbf{b}} \langle \mathbf{p} | \mathbf{a} | \mathbf{b} | \mathbf{r}_{23}^{-1} (1 - \mathbf{P}_{23}) | \mathbf{r} | \mathbf{b} | \mathbf{q} \\
& - \int_{\mathbf{b}} \langle \mathbf{p} | \mathbf{a} | \mathbf{b} | \mathbf{r}_{23}^{-1} (1 - \mathbf{P}_{23}) | \mathbf{b} | \mathbf{r} | \mathbf{q} .
\end{aligned} \tag{35}$$

The matrix elements between $|\mathbf{p}\rangle$ and $|\mathbf{q}, \mathbf{ab}\rangle^{\text{rs}}$ have non-vanishing terms except for the matrix elements $\langle \mathbf{p} | \mathbf{h}(\mathbf{i}) | \mathbf{q}, \mathbf{ab}\rangle^{\text{rs}}$ and $\langle \mathbf{p} | \mathbf{h}_*(0) | \mathbf{q}, \mathbf{ab}\rangle^{\text{rs}}$. The resulting matrix elements are as follows:

$$\begin{aligned}
\langle \mathbf{p} | \mathbf{h}(\mathbf{i}) | \mathbf{q}, \mathbf{ab}\rangle^{\text{rs}} &= \langle \mathbf{a} | \mathbf{h} | \mathbf{s} | \mathbf{p} | \mathbf{b} | \mathbf{r} | \mathbf{q} - \langle \mathbf{a} | \mathbf{h} | \mathbf{r} | \mathbf{p} | \mathbf{b} | \mathbf{s} | \mathbf{q} \\
& + \langle \mathbf{b} | \mathbf{h} | \mathbf{r} | \mathbf{p} | \mathbf{a} | \mathbf{s} | \mathbf{q} - \langle \mathbf{b} | \mathbf{h} | \mathbf{s} | \mathbf{p} | \mathbf{a} | \mathbf{r} | \mathbf{q} ,
\end{aligned} \tag{36}$$

$$\langle \mathbf{p} | \mathbf{r}_{0i}^{-1} | \mathbf{q}, \mathbf{ab}\rangle^{\text{rs}} = \langle \mathbf{p} | \mathbf{a} | \mathbf{b} | \mathbf{r}_{02}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{r} | \mathbf{s} | \mathbf{q} + \langle \mathbf{p} | \mathbf{b} | \mathbf{a} | \mathbf{r}_{02}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{s} | \mathbf{r} | \mathbf{q} , \tag{37}$$

and

$$\begin{aligned}
\langle \mathbf{p} | \mathbf{r}_{ij}^{-1} | \mathbf{q}, \mathbf{ab}\rangle^{\text{rs}} &= \langle \mathbf{a} | \mathbf{b} | \mathbf{r}_{12}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{r} | \mathbf{s} | \left[\langle \mathbf{p} | \mathbf{q} - \langle \mathbf{c} | \mathbf{p} | \mathbf{c} | \mathbf{q} \right] \\
& + \int_{\mathbf{c}} \langle \mathbf{a} | \mathbf{b} | \mathbf{r}_{12}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{c} | \mathbf{s} | \langle \mathbf{p} | \mathbf{c} | \mathbf{r} | \mathbf{q} \\
& + \int_{\mathbf{c}} \langle \mathbf{a} | \mathbf{b} | \mathbf{r}_{12}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{r} | \mathbf{c} | \langle \mathbf{p} | \mathbf{c} | \mathbf{s} | \mathbf{q} \\
& + \langle \mathbf{p} | \mathbf{a} | \mathbf{b} | \mathbf{r}_{12}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{r} | \mathbf{s} | \mathbf{q} \\
& + \langle \mathbf{p} | \mathbf{a} | \mathbf{b} | \mathbf{r}_{23}^{-1} (1 - \mathbf{P}_{23}) | \mathbf{r} | \mathbf{s} | \mathbf{q} \\
& - \langle \mathbf{p} | \mathbf{a} | \mathbf{b} | \mathbf{r}_{23}^{-1} (1 - \mathbf{P}_{23}) | \mathbf{s} | \mathbf{r} | \mathbf{q} .
\end{aligned} \tag{38}$$

Matrix elements between $|\mathbf{p}\rangle$ and $|\mathbf{q}, \mathbf{abc}\rangle^{\text{rst}}$ are nonzero only for electron-electron interaction, and the formula is

$$\begin{aligned}
\langle \mathbf{p} | \mathbf{r}_{ij}^{-1} | \mathbf{q}, \mathbf{abc}\rangle^{\text{rst}} &= \langle \mathbf{a} | \mathbf{b} | \mathbf{r}_{12}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{s} | \mathbf{r} | \langle \mathbf{p} | \mathbf{c} | \mathbf{t} | \mathbf{q} \\
& + \langle \mathbf{a} | \mathbf{b} | \mathbf{r}_{12}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{t} | \mathbf{s} | \langle \mathbf{p} | \mathbf{c} | \mathbf{r} | \mathbf{q} \\
& + \langle \mathbf{a} | \mathbf{b} | \mathbf{r}_{12}^{-1} (1 - \mathbf{P}_{12}) | \mathbf{r} | \mathbf{t} | \langle \mathbf{p} | \mathbf{c} | \mathbf{s} | \mathbf{q} .
\end{aligned} \tag{39}$$

The matrix elements are complicated in form, and have up to four-electron integrals. It is easy to calculate four-electron integrals over explicitly correlated Cartesian Gaussian functions⁵⁶.

IV. SUMMARY

We have extended Ore's PsH wave function so as to improve its flexibility. This was accom-

plished by expansion of ψ_H , $\psi_{H'}$, and ψ_{Ps} using Gaussian functions. A set of equations to determine these expansion coefficients variationally was derived. The extended Ore's PsH wave function yielded a Ps binding energy of 0.117 eV and a two-photon annihilation rate of 2.157 ns⁻¹. The values are improved by 0.049 eV and 0.302 ns⁻¹. The rest of the effect of electron correlation was also incorporated by using the effective potential proposed by Panas and Snis. As a result, a Ps binding energy of 0.254 eV and a two-photon annihilation rate of 2.234 ns⁻¹ were obtained.

We further applied the Ore-type wave function to many-electronic positronium-atom complexes. The matrix elements over the determinantal many-electronic Ore-type wave functions were derived with the help of diagrams. The resulting matrix elements have complicated form, and include four-electron integrals. The four-electron integrals over explicitly correlated Cartesian Gaussian functions can easily be evaluated by the use of our computational method. Further work for many-electronic complexes is in progress.

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