Improved wave function for positronium hydride*

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An extension of an earlier calculation on positronium hydride PsH is presented. In the earlier work, the wave function was expressed as an exponential term $\exp(-Ar_1 - Br_2 - Cr_{1p} - Dr_{2p}) + \exp(-Br_1 - Ar_2 - Dr_{1p} - Cr_{2p})$, times a twelve-term polynomial in the interparticle coordinates: r_1, r_2, r_{1p}, r_{2p}, and r_{12} (the electrons are labeled 1 and 2; the positron is labeled as p). The coefficients in the polynomial were determined by the variational method. In the present work, the number of terms is increased; the coordinate r_p is included in the polynomial; the wave function is tested for the four cusp conditions; and an annihilation rate and the relaxation of the daughter system are calculated. The new binding energy, 0.794 eV, is greater than the earlier result by 0.137 eV. The annihilation rate is found to be 2.22 nsec^{-1}, with the $1s$ state being the most probable daughter-occupation state. The electron-positron, electron-nucleus, nucleus-positron, and electron-electron cusp values are, respectively, -0.4398, -1.065, -0.0102, and, 0.1126. The values of the repulsive cusps definitely show that the wave function has not yet converged to the exact function in all regions of three-particle space. A search for a bound excited state of PsH with the same symmetry of the ground state was unsuccessful.

I. INTRODUCTION

Several articles have recently been published concerning the nature of the positronium hydride (PsH) system. Utilizing an expansion in the interparticle coordinates, Lebeda and Schrader reported its ground state to be bound by 0.657 eV[1] and lately, Houston and Drachman have found this value to be at least 0.672 eV.[2] Both of these calculations used the Ritz variational principle and, hence, the calculated binding energies are lower bounds. The older literature on PsH[3-6] has been quite extensively reviewed.[1]

The Houston-Drachman function has the spatially symmetric form

$$F' = \phi' \sum_v c_v e^{-Ar_p} (e^{-Br_1} r_1^{Mv} r_{1p}^{Nv} + e^{-Br_2} r_2^{Mv} r_{2p}^{Nv}) r_p^{Lv}, \tag{1}$$

where

$$\phi' = e^{-z_1 r_1 - z_2 r_2} + e^{-z_2 r_1 - z_1 r_2}. \tag{2}$$

The expansion consisted of 56 terms. The subscripts 1 and 2 refer to the electrons, and p indicates the positron; the interparticle coordinate r_{ij} denotes the distance between the particles i and j.

The trial wave function of Lebeda and Schrader[1] had the spatial form

$$F = \phi \sum_u c_u (r_1^{Ju} r_2^{Ku} r_{1p}^{Lu} r_{2p}^{Mu} + r_1^{Ku} r_2^{Ju} r_{1p}^{Mu} r_{2p}^{Lu}) r_p^{Iu} r_{12}^{Nu}, \tag{3}$$

where

$$\phi = e^{-Ar_1 - Br_2 - Cr_{1p} - Dr_{2p}} + e^{-Br_1 - Ar_2 - Dr_{1p} - Cr_{2p}}. \tag{4}$$

The sum in Eq. (3) contained 12 terms. The function ϕ was used as the wave function by Neamtan, Darewych, and Oczkowski.[6] Its principal advantage is that all attractive particle pairs are represented in the wave function with decaying exponentials; therefore, short expansions of the form shown in Eq. (3) should yield quite accurate results. In the present work, a function of the Lebeda-Schrader form is again used, and is now extended to more terms.

To test the accuracy of short expansions, Kato's cusp condition at particle coalescence[7] may be utilized. This condition states that the exact wave function U must satisfy

$$\left(\frac{\partial \ln U}{\partial r_{ij}}\right)_{r_{ij}=0} = q_i q_j \mu_{ij} = v_{ij}, \tag{5}$$

where u_{ij} is the reduced mass of the coalescing particles, and q_i and q_j are the charges. Taking the average of Eq. (5) for a trial function F suggests the form

$$v_{ij} = \left\langle F \left| \delta(\vec{r}_{ij}) \frac{\partial}{\partial r_{ij}} \right| F \right\rangle \Big/ \langle F | \delta(\vec{r}_{ij}) | F \rangle. \tag{6}$$

It has been shown[8] that the satisfaction of these averaged cusp conditions, although a useful guide, does not guarantee accuracy in a calculated energy. There is, however, a clear relationship between

TABLE I. Comparison of the ground-state energies, annihilation rates, and electron-positron cusp values for three wave functions of PsH.

	Lebeda-Schrader (Ref. 1)	Houston-Drachman (Ref. 2)	Present work
Number of terms	12	56	17
Ground-state energy (a.u.)	−0.7742	−0.7748	−0.7792
Binding energy (eV)	0.657	0.672	0.794
Annihilation rate ($nsec^{-1}$)	2.10	2.46	2.22
Electron-positron cusp	−0.4070	−0.4766	−0.4398

accurate cusp values (v_{ij}) and the expectation values of the operator $\delta(\vec{r}_{ij})$.[8] Since the annihilation rate[1]

$$P = 100.94\langle F|\delta(\vec{r}_{1p})|F\rangle \text{ nsec}^{-1} \quad (7)$$

is dependent upon the same δ operator, it seems sensible to judge the accuracy of a calculated annihilation rate by the respective cusp value [Eq. (6)].

The result of the Lebeda-Schrader energy calculations for their 12-term function is summarized in Table I. The ground-state energy was determined to be −0.7742 a.u., showing the PsH to be bound by 0.657 eV. The first excited state has an energy of −0.7432 a.u., which is deficient by 0.184 eV from being a bound state.

Subsequently, the relaxation of the residue or daughter system was investigated by Schrader and Petersen,[9] using Neamtan's wave function [Eq. (4)]. The probability that the ith state of the daughter is occupied after annihilation is given by

$$P_i = N^{-1}\int d\vec{r}_2 \left| \int d\vec{r}_1 \phi_i^*(\vec{r}_1) F(\vec{r}_1, \vec{r}_2, \vec{r}_2)\right|^2, \quad (8)$$

where $\phi_i(\vec{r}_1)$ is the ith eigenstate of the daughter (H atom), $F(\vec{r}_1, \vec{r}_2, \vec{r}_2)$ is the coalesced parent (PsH) wave function [from $F(\vec{r}_1, \vec{r}_2, \vec{r}_p)$], and N is the norm of $F(\vec{r}_1, \vec{r}_2, \vec{r}_2)$. Probabilities reported for the daughter states are listed in Table II.

II. PRESENT CALCULATION

The present work extends the Lebeda-Schrader and Petersen-Schrader work in several ways: the number of terms in the wave function is increased; the coordinate r_p is included; and the daughter relaxation is calculated for the full wave function. Lack of the coordinate r_p in the Lebeda-Schrader function resulted in too much positron density at the nucleus.[9] In view of the fact that preliminary calculations[1] showed r_p to be more effective than r_{12} in lowering the computed excited-state energy, it was hoped that a bound excited state would result in the present work. This hope was not realized, however.

The electron-positron cusp condition is an important constraint on the exact wave function. An accurate value of the annihilation rate calculated from an approximate function therefore depends upon its cusp value at electron-positron coalescence. Other cusp values may also be significant. For example, the electrons will be drawn near the positron by Coulombic forces and thus will quite probably be closer to each other than they are in the hydride ion. Hence, it was felt that satisfaction of the electron-electron cusp condition might also be significant in calculating the annihilation rate. In this work, values for all possible conditions are calculated in order to determine the merit of our wave function.

Following the addition to the expansion of a quadratic term previously omitted, terms involving r_p were added until all possible linear and quadratic terms were included except r_p^2 and $r_p r_{12}$. These were omitted because of a programming error for r_p^2, and excessive time requirements for $r_p r_{12}$. One cubic term $(r_{1p}r_1 + r_{2p}r_2)r_{12}$ was included on the

TABLE II. Comparison of the probabilities for occupation of the daughter states.

	Petersen-Schrader (Ref. 9)	Houston-Drachman[a] (Ref. 2)	Present work[b]
1s	0.9770	0.9869	0.9705
2s	0.0030	0.0014	0.0071
3s	0.0003	0.0002	0.0007
2p	0.0084	0.0032	0.0020

[a] For this calculation, Eq. (1) has φ in the form $e^{-\alpha r_1 - \beta r_2}$ where $z = 1.032$, $A = 0.527\mathfrak{C}$, and $B = -0.3760$.

[b] Parameters used in Eq. (4) are $A = 0.2212$, $B = 1.026$, $C = 0.4724$, and $D = 0.08479$.

TABLE III. Results of the energy calculations for the scaled wave functions.

N						13	14	15	16	17
Ground-state energy (a.u.)						−0.7743	−0.7744	−0.7748	−0.7782	−0.7792
Binding energy (eV)						0.662	0.663	0.673	0.768	0.794
Scale factor						0.8490	0.8521	0.8618	0.8689	0.8721
First-excited-state energy (a.u.)						−0.7433	−0.7434	−0.7434	−0.7436	−0.7471
I	J	K	L	M	N					
0	0	0	0	0	0	0.5000	0.5000	0.5000	0.5000	0.5000
0	0	0	0	0	1	0.0792	0.0785	0.0835	0.0906	0.1326
0	1	0	0	0	0	−0.1820	−0.1806	−0.1800	−0.1936	−0.2086
0	0	0	1	0	0	−0.0467	−0.0444	−0.0335	−0.0465	−0.0266
0	0	0	0	0	2	0.0036	0.0034	0.0058	0.0072	0.0141
0	2	0	0	0	0	0.0112	0.0112	0.0114	0.0110	0.0151
0	0	0	2	0	0	0.0018	0.0019	0.0017	0.0052	0.0068
0	1	1	0	0	0	0.0118	0.0118	0.0128	0.0125	0.0176
0	0	0	1	1	0	0.0004	0.0004	0.0007	0.0044	0.0054
0	1	0	0	0	1	−0.0179	−0.0176	−0.0229	−0.0274	−0.0496
0	0	0	1	0	1	−0.0043	−0.0042	−0.0052	−0.0061	−0.0132
0	1	0	1	0	0	0.0049	0.0046	0.0044	0.0043	−0.0004
0	0	1	1	0	0	0.0022	0.0022	−0.0001	0.0002	−0.0009
1	0	0	0	0	0		−0.0023	−0.0156	−0.0046	−0.0194
1	0	1	0	0	0			0.0043	0.0108	0.0180
1	0	0	0	1	0				−0.0075	−0.0095
0	1	0	1	0	1					0.0008

basis of its probable ability to lower the ground-state energy.

The results of the energy calculations for the 17-term expansion are detailed in Table III. The lowest ground-state energy computed was −0.7792 a.u., revealing the PsH system to be bound by 0.794 eV. The first-excited-state energy is given as −0.7471 a.u., which is, 0.078 eV short of binding.

Applying Eq. (7), an annihilation rate for the new wave function was determined to be 2.22 nsec^{-1} (Table IV).

The cusp values at electron-positron, electron-nucleus, positron-nucleus, and electron-electron coalescence were computed and are summarized in Table IV.

The Peterson-Schrader program was available for calculations of the daughter relaxation states and was employed after changes to accomodate the 17-term expansion. Table II lists the probabilities obtained from Neamtan's wave function, the Houston-Drachman function, and the scaled 17-term wave function.

III. DISCUSSION OF RESULTS

As seen in Table III, the addition of the five new terms to the wave function results in an increase in the binding energy of the ground state of PsH by 21% over Lebeda and Schrader's previous value (0.657 eV) and by 18% over the Houston-Drachman value (0.672 eV). The inefficiency of the latter expansion may be attributed partly to the omission of the r_{12} coordinate [see Eq. (1)].

The first-excited-state energy was lowered as expected with the use of the r_p coordinate, but not sufficiently for binding. The wave function for a bound first excited state, if it exists, might have a symmetry different from that of the present expansion. It must not be overlooked, moreover, that only three terms involving the r_p coordinate were added to the function. With the use of more such terms, a bound excited state might yet be

TABLE IV. Results of the cusp value and annihilation-rate calculations.

N	12	13	14	15	16	17
Electron-positron cusp	−0.4070	−0.4029	−0.4010	−0.3948	−0.4287	−0.4398
Electron-nucleus cusp	−1.017	−1.010	−1.011	−1.021	−1.037	−1.065
Nucleus-positron cusp	0.0	0.0	−0.0069	−0.0218	0.0036	−0.0102
Electron-electron cusp	0.1863	0.1867	0.1876	0.1655	0.1623	0.1126
Annihilation rate (nsec^{-1})	2.10	2.10	2.10	2.09	2.19	2.22
Lifetimes (nsec)	0.477	0.477	0.477	0.478	0.4562	0.4503

found with the present symmetry.

Practical considerations dictated that no more terms be added to the expansion at the present. With the use of the nucleus-positron coordinate, many integrals containing the square of the exponential factor [Eq. (4)] and $r_p^i r_{12}^{\pm 1}$ or $r_{12}^i r_p^{\pm 1}$ (i being a positive integer) arose, which greatly increased the computation time. With the exception of the thirteenth term, the calculation of each term's matrix elements required an average of 100 hours of computer time. Some of this time was necessitated by the chaining of the subprograms so that the computations could be performed on the local IBM-7040, but most was required for the integration.

The cusp values indicate that the 17-term function reported here, while a significant improvement over the 12-term function, has not yet converged to the exact wave function in all regions of three-particle space. The cusp conditions for the attractive pairs, the electron-positron (−0.4398) and the electron-nucleus values (−1.065), are close to their respective, theoretical values (−0.5000 and −1.000). The nucleus-positron (−0.0102) and the electron-electron cusps (0.1126) are, however, far from their respective theoretical values (1.000 and 0.5000). The nucleus-positron correlation is particularly poor, as indicated by the instability in the cusps, as shown in Table IV. These facts suggest that more terms with r_{12} and r_p must be added to the wave function before it can be considered to be accurate everywhere.

The lifetime of the system from this expansion, 0.450 nsec, is longer than that obtained by Houston and Drachman (0.407 nsec), and also falls slightly outside the range 0.426 ± 0.020 nsec suggested by observations on a series of alkali hydride crystals.[10] Since Houston and Drachman's electron-positron cusp value (−0.4766) agrees more closely with the theoretical value, their annihilation rate may be better, provided that electron-electron correlation is not important to the annihilation process. Several terms containing r_p and r_{12} added to the 17-term function would appear to resolve this question in the future. The "experimental" value of Gainotti *et al.*[10] should be interpreted with caution, owing to uncertainties in the assumptions underlying their extrapolation.

The probabilities for the daughter states secured from this function agree generally with the values of Houston and Drachman as well as those of Petersen and Schrader (Table II). The most probable occupation state for the daughter (H atom) is the 1*s* state.

It should be noted that the scale factor of each expansion is less than 1 (Table III). This implies that the exponential parameters of Eq. (5) need to be reoptimized, since an exact wave function would have a scale factor equal to 1. The method of steepest descents might be employed to determine the best exponential values. Because this method would require many recalculations of the matrix elements for various changes in the parameters, this improvement in the function is not practical at present on the local computer.

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