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Configuration Interaction Wavefunction for Positronium Hydride*

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A configuration interaction wavefunction is obtained for the pseudo-atom positronium hydride (consisting of one proton, one positron, and two electrons), using Slater orbitals centered on the proton as basis functions. A positive dissociation energy is calculated for the process PsH → Ps + H. Comparison is made with previous calculations of this energy, and its actual value is predicted to be 0.009 au. The two-quantum annihilation rate also is calculated.

Mit am Proton zentrierten Slaterfunktionen wird für das Pseudoatom Positroniumhydrid (aus einem Proton, einem Positron und zwei Elektronen) eine Wellenfunktion mit Konfigurationswechselwirkung aufgebaut. Für PsH → Ps + H errechnet sich eine positive Dissoziationsenergie. Ihr Wert wird mit früheren Berechnungen verglichen und zu 0,009 at. E. vorhergesagt. Auch die Geschwindigkeit der Zweiquantenzerstrahlung wird berechnet.

Sur base d'orbitales de Slater centrées sur le proton est obtenue une fonction d'onde, à interaction de configurations, pour le pseudo-atome d'hydride de positronium (un proton, un positron et deux électrons). Une énergie positive de dissociation se calcule pour PsH → Ps + H. On compare aux calculs précédents et prédit sa valeur à 0.009 unités atomiques. La vitesse de décomposition en deux quanta est aussi calculée.

1. Introduction

The possible existence of stable molecules in which a positron is attached to an ordinary molecule was first suggested by WHEELER [1]. Although semiquantitative calculations indicated that systems such as positronium chloride probably could exist [2], the first rigorous variational proof of the stability of a WHEELER compound was given by ORE for the system positronium hydride, PsH, comprising a proton, a positron, and two electrons [3].

The formation of positronium compounds has been postulated to explain anomalous positron decay in matter [4]. Indeed, experiments have been conducted which imply that useful information about organic compounds, such as ionization

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potentials and dissociation energies, will be obtainable from study of positron decay in these compounds [*5*].

Although several accurate wave-mechanical calculations have been carried out on systems composed of positrons and electrons alone [*6*], calculations are rarer for systems containing positrons plus atomic nuclei [*7*], and it is these systems which are of more interest to the chemist [*16*]. (The simplest neutral system containing at least one "heavy" particle is PsH.)

2. Wavefunctions and Energies

This pseudo-atom has been studied by ORE [*3*], and, more recently, by NEAMTAN, DAREWYCH, and OCZKOWSKI [*8*]. These calculations both employ Hylleraas-type trial functions including interparticle distances explicitly. This type of function is not readily extensible to many-electron systems, so it is of interest to obtain a wavefunction for PsH built from atomic orbitals centered on the proton.

We employ a linear combination of Slater determinants constructed from Slater-type orbitals of variationally-determined orbital exponents and principal quantum numbers [*9*],

$$[(2\zeta)^{2n+1}/(2n)!]^{1/2}\, r^{n-1}\, e^{-\zeta r}\, Y_{lm}(\theta, \varphi)\,. \tag{1}$$

Such a one-center configuration interaction procedure has been applied with success to many molecules, for example, H_2 and CH_4 [*9*, *10*].

To denote the three light particles, we let subscripts 1, 2, and 3 refer to electron 1, electron 2, and the positron, respectively. Since there are no more than two identical particles, the spins may be "factored-out", and a trial function singlet with respect to the electrons may be written in the form

$$\Psi = \sum_{i=1}^{9} C_i \Phi_i\,. \tag{2}$$

Here the individual Φ_i are properly symmetrized orbital product configurations, constructed from atomic orbitals of the form of Eq. (1), namely,

$$\begin{aligned}
\Phi_1 &= \frac{1}{\sqrt{2}}(ss' + s's)s''\,, & \Phi_2 &= \frac{1}{\sqrt{2}}(ss'' + s''s)s'\,, \\
\Phi_3 &= \frac{1}{\sqrt{2}}(ss' + s's)s'\,, & \Phi_4 &= \frac{1}{\sqrt{2}}(ss'' + s''s)s''\,, \\
\Phi_5 &= \frac{1}{\sqrt{6}}(s'''p + ps''')p''\,, & \Phi_6 &= \frac{1}{\sqrt{10}}(s'''d + ds''')d''\,, \\
\Phi_7 &= \frac{1}{\sqrt{14}}(s'''f + fs''')f\,, & \Phi_8 &= \frac{1}{\sqrt{3}}(p'p's'')\,, \\
\Phi_9 &= \frac{1}{\sqrt{5}}(d'd's'')\,,
\end{aligned} \tag{3}$$

where, for example, *pp* means the spherically symmetric combination $p_x p_x + p_y p_y + p_z p_z$, and all orbitals are centered on the proton; the first two orbitals in a product of three contain electrons; the third, the positron.

The nonrelativistic Hamiltonian for the problem, taking the mass of the proton to be infinite, is, in atomic units

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \tfrac{1}{2}\nabla_3^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_{12}} - \frac{1}{r_{13}} - \frac{1}{r_{23}} \tag{4}$$

Table 1. *Matrix Elements*

i	j	H_{ij}(integral n) (au)	H_{ij}(non-integral n) (au)	S_{ij}(integral n)	S_{ij}(non-integral n)
1	1	−1.1917083	−1.1917507	1.8581807	1.8471553
2	1	−0.8507441	−0.8220350	1.1135393	1.0901129
	2	−0.4823664	−0.5412482	1.3140130	1.3058620
3	1	−1.1017199	−1.0777664	1.5369742	1.5149315
	2	−0.6459026	−0.6961063	1.3462538	1.3291741
	3	−0.8909969	−0.9641403	1.8581807	1.8471553
4	1	−0.9530887	−0.9408592	1.3462538	1.3291741
	2	−0.7365267	−0.7173764	1.0868717	1.0709936
	3	−0.8507441	−0.8220350	1.1135393	1.0901129
	4	−0.8345161	−0.8341879	1.3140130	1.3058620
5	1	−0.1630837	−0.1639303	0.0	0.0
	2	−0.1401937	−0.1410787	0.0	0.0
	3	−0.1622472	−0.1663348	0.0	0.0
	4	−0.1494370	−0.1479547	0.0	0.0
	5	−0.2550938	−0.2490016	1.0	1.0
6	1	−0.0857632	−0.0855362	0.0	0.0
	2	−0.0724537	−0.0733005	0.0	0.0
	3	−0.0773649	−0.0796805	0.0	0.0
	4	−0.0850047	−0.0837978	0.0	0.0
	5	−0.1381657	−0.1397018	0.0	0.0
	6	0.1879429	0.1996040	1.0	1.0
7	1	−0.0549104	−0.0547868	0.0	0.0
	2	−0.0466157	−0.0470213	0.0	0.0
	3	−0.0472602	−0.0486821	0.0	0.0
	4	−0.0570376	−0.0561197	0.0	0.0
	5	−0.0866974	−0.0875560	0.0	0.0
	6	−0.1537353	−0.1554878	0.0	0.0
	7	0.8364747	0.8581837	1.0	1.0
8	1	0.2224241	0.2259574	0.0	0.0
	2	0.1135123	0.1114773	0.0	0.0
	3	0.1839757	0.1853174	0.0	0.0
	4	0.1372348	0.1359242	0.0	0.0
	5	−0.0675220	−0.0664572	0.0	0.0
	6	0.0	0.0	0.0	0.0
	7	0.0	0.0	0.0	0.0
	8	0.6423166	0.6567456	1.0	1.0
9	1	0.1152731	0.1173168	0.0	0.0
	2	0.0625589	0.0613392	0.0	0.0
	3	0.0953469	0.0962166	0.0	0.0
	4	0.0756328	0.0747909	0.0	0.0
	5	0.0	0.0	0.0	0.0
	6	−0.0244559	−0.0238468	0.0	0.0
	7	0.0	0.0	0.0	0.0
	8	0.2094675	0.2185144	0.0	0.0
	9	2.0356486	2.0476687	1.0	1.0

where r_i is the distance between the proton and particle i and r_{ij} the ij interparticle distance.

The integrals occuring in the matrix elements H_{ij} and S_{ij} are evaluated by techniques similar to those described by Joy and Parr [*9*]. The matrix elements for the variationally-optimum functions are given in Tab. 1 and the corresponding linear coefficients C_i in Tab. 2. "Non-integral n" refers to the function with all parameters optimum and "integral n" refers to the function with the principal quantum numbers the integers closest to the variationally-determined ones.

Table 2. *Wavefunctions*

i	Configuration Type	C_i(integral n)[a]	C_i(non-integral n)[b]
1	$ss's''$	0.222359	0.214241
2	$ss''s'$	−0.088950	−0.105456
3	$ss's'$	0.209089	0.232915
4	$ss''s''$	0.451214	0.455137
5	$s'''pp''$	0.285967	0.284142
6	$s'''dd''$	0.122406	0.121062
7	$s'''ff$	0.055065	0.054319
8	$p'p's''$	−0.083681	−0.084297
9	$d'd's''$	−0.019253	−0.019233
Energy (e^2/a_0)		−0.748792	−0.750128

[a] Parameter values, $(n, n/\zeta)$ couples: $s(1,0.92158)$, $s'(1,1.4504)$, $s''(3,3.0956)$, $s'''(1,1.0617)$, $p(3,2.6988)$, $p'(2,1.6177)$, $p''(3,2.8981)$, $d(4,2.9611)$, $d'(3,1.7940)$, $d''(5,3.0865)$, $f(6,3.1205)$.

[b] Parameter values: $s(0.9710, 0.90433)$, $s'(1.1916, 1.5210)$, $s''(2.8673, 3.1299)$, $s'''(0.9661, 1.0589)$, $p(2.739, 2.6614)$, $p'(2.326, 1.6229)$, $p''(3.344, 2.8946)$, $d(4.337, 2.9470)$, $d'(3.418, 1.7960)$, $d''(4.782, 3.0646)$, $f(6.071, 3.1005)$.

The calculated energy of PsH is −0.750128 au with non-integral n, −0.748792 au with integral n. Since the energy of the hydrogen atom, −0.5 au, plus the energy of the positronium atom, −0.25 au, is −0.75 au, the additional flexibility of non-integral quantum numbers in this calculation makes the difference between binding and not binding.

3. Comparison with other Calculations

There appear to be only two previous calculations on PsH, Ore's original work [*3*] and the more recent investigation by Neamtan et al. [*8*]. Using the present scheme for numbering the particles, we may write Ore's function,

$$\exp(-\alpha r_1 - \beta r_2 - \gamma r_{23}) + \exp(-\alpha r_2 - \beta r_1 - \gamma r_{13}) , \tag{5}$$

and that of Neamtan et al.,

$$\exp(-\alpha r_1 - \beta r_2 - \gamma r_{23} - \delta r_{13}) + \exp(-\alpha r_2 - \beta r_1 - \gamma r_{13} - \delta r_{23}) . \tag{6}$$

These functions have the form

$$ss'f(2, 3) + s'sf(1, 3) , \tag{7}$$

and

$$ss'f(2, 3)\, g(1, 3) + s'sf(1, 3)\, g(2, 3) , \tag{8}$$

where s and s' denote Slater 1s functions centered on the proton, and f and g are positron-electron correlating functions. The energy of both functions is better than that of Eq. (2): Eq. (5) gives an energy of -0.7525 au, while Eq. (6) gives -0.7584 au.

It is probable that the description of the electron-electron correlation given by Eqs. (7) and (8) is poorer than that given by Eq. (2), since Eqs. (7) and (8) contain only the ss'-type description for interelectronic motion (aside from the coupling of this motion through the positron). In the "united atom limit", PsH becomes helium, and there the ss' description gives an energy of -2.8757 au [*11*], compared with the four-term configuration interaction energy of -2.8980 au [*12*] and the exact PEKERIS result -2.9037 au [*13*]. In the more diffuse two-electron analogue, the hydride ion, the ss' energy is -0.51330 au [*11*], compared with the four-term configuration interaction result -0.52544 au [*12*] and the accurate -0.52775 au [*14*].

From these considerations it may be concluded that the main deficiency in Eq. (2) is in the description of the electron-positron correlation. Eqs. (7) and (8) have cusps where the outer electron and the positron coincide. If extended to a larger number of harmonics, Eq. (2) could approximate this behavior quite closely. Tab. 3 lists estimated energy contributions of the various harmonics in the true wavefunction. The actual total energy of PsH is probably very close to -0.759 au.

Table 3. *Energy contributions by term type*

Term[a]	Energy increment (au)
– –[b]	0.6833
sss[c]	0.0066
spp	0.0378
sdd	0.0126
sff	0.0050
sll[d]	0.0021
pps	0.0105
dds	0.0010
lls[e]	0.0001
Total (extrapolated) energy of PsH	0.7590

[a] The first two orbitals describe the angular behavior of the electron functions; the third, the positron.

[b] Energy of the four functions of pure S-type in Eq. (2) of text.

[c] Estimated for further functions of type *sss*.

[d] Estimated for terms of type *sgg*, *shh*, etc.

[e] Estimated for terms of type *ffs*, *ggs*, etc.

4. Annihilation Rate

Conservation laws imply that an annihilating positron-electron pair produces either two or three photons according as the spins of the Ps^+e^- pair are antiparallel or parallel, respectively. Since experiments show that the half-life for three-photon emission is at least an order of magnitude larger than that for two-photon emission, it may be considered, to a fairly good approximation, that only the two-photon process can occur. (In fact, the experimental apparatus may be constructed so as to record only two-photon events.)

According to FERRELL [*15*] and NEAMTAN et al. [*8*] the rate γ of decay from PsH, relative to positronium itself, Ps^+e^-, is

$$\gamma = \frac{\gamma_{\mathrm{PsH}}}{\gamma_{\mathrm{Ps}}} = \frac{1}{2}\left[\frac{2\varrho_{\mathrm{PsH}}}{\varrho_{\mathrm{Ps}}}\right], \tag{9}$$

where $\varrho_{\mathrm{PsH}} = \int \Psi^* \delta(r_1 - r_3)\, \Psi dv_1 dv_2 dv_3$ is the probability of electron 1 and the positron being at the same position in space regardless of the position of electron 2, and ϱ_{Ps} is the probability of the electron being at the position of the positron in Ps. The value of γ_{Ps} is known to be 8.0 nsec^{-1} [*17*]. The factor $\frac{1}{4}$ appears because the probability of an electron-positron pair in PsH being in a singlet state is $\frac{1}{4}$; the factor 2 appears because there are two electrons.

The present calculation gives for the ratio of rates 0.78 for the integer function and 0.83 for the non-integer function. The calculation of NEAMTAN et al. gives 0.247, presumably closer to the correct value because of the better description of the positron-electron motion. (Yet, improvement of the description of electron-electron correlation in their function would be expected to increase the value of the ratio.)

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