

Towards an Accurate Wave Function for Positronium Hydride*

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A variational wave function for the ground state of positronium hydride is presented. The wave function is considerably more accurate than any previously reported. The only simplifications used are (a) only kinetic and Coulombic potential energy terms are included in the Hamiltonian, (b) the motion of the proton is ignored, and (c) the nucleus-positron distance is excluded from the wave function. The last assumption is the major source of error, but it enables us to evaluate all integrals exactly. Several trial wave functions are examined, the one giving the lowest energy being an open-shell exponential function times a 12-term power series through second-degree terms in the five remaining interparticle coordinates. Positronium hydride is found to be stable with respect to separation into hydrogen and positronium by at least 0.657 eV. The annihilation rate for two-photon events is found to be 2.095 nsec^{-1} for the trial wave function giving the lowest energy, and 2.265 nsec^{-1} for the trial wave function which most nearly satisfies the positron-electron cusp condition. A search for bound excited states of PsH and a bound state for the system $e^+\text{He}$ was unsuccessful.

1. INTRODUCTION

A number of reviews¹⁻²¹ indicate that positron annihilation may prove to be useful in chemical physics and chemistry, as it already is in solid-state physics. Specifically, it appears that the positron may serve as an accurate probe of the momentum distribution of electrons bound in atoms and molecules, providing certain technical difficulties can be overcome. One of these is the lack of a reliable method for calculating annihilation properties of atoms and molecules interacting with positrons. Without such a method nonempirical prediction and interpretation of annihilation properties is impossible. (Empirical correlation of annihilation properties with other properties of a molecule is of course presently possible.²²)

The annihilative lifetimes of the most unstable systems are $\sim 0.1 \text{ nsec}$, which corresponds to an uncertainty in the energy of $\sim 10^{-5} \text{ eV}$, a tiny fraction of chemical binding energies and even of thermal energies. Therefore it is reasonable to investigate the structure of positron-atom and positron-molecule complexes using an approximate method which ignores interactions coupling photon and positron-electron fields, and then to include the coupling as a perturbation, thus obtaining the annihilation parameters in first order. Consequently, systems of interest can be treated with nonrelativistic Schrödinger wave mechanics, and Chang Lee²³ and others have shown that all the significant annihilation properties can be calculated by evaluating integrals involving operators and eigenfunctions in configuration space.

A positron interacting with an atom or molecule is either bound to it or is scattering off it as either a free positron or a positronium atom. Annihilation from scattering states is always possible and probably dominates for most systems; but annihilation from bound states is evidently significant for many systems, and this mechanism must be included in any scheme of interpretation

which is complete and accurate. These two kinds of mechanisms require rather different treatments within the Schrödinger picture, but they have in common the need for accurate calculations on some simple systems. Such calculations are useful even if the methods employed are not extensible to more complex systems, for the results obtained then serve as standards of comparison for assaying the accuracy of other methods which are extensible. Experimental results are sparse.

The simplest system consisting of nuclei, electrons, and a positron is a positron plus a hydrogen atom. This system has been the object of serious calculations in several dozen publications (we estimate about 35). However, it does not have a bound state,²⁴⁻²⁸ so its utility as a standard comparison system is limited to methods which seek to understand annihilation of scattering positrons.

Our interest at present is in the mechanism for annihilation from states containing bound positrons,²⁹ so an accurate calculation on a bound system is needed. The simplest system which contains nuclei, electrons, and one positron and forms a bound state is positronium hydride, PsH, which is the subject of this paper. It has been considered by other authors in several calculations which are less extensive than those reported here.³⁰⁻³¹ It has not yet been observed.

Of course, the positronium atom Ps is an even simpler system and also has bound states, but the absence of nuclei and the lack of purely inter-electronic forces make it a poor comparison system for our purposes. However, some features of its simple structure have significant implications for our study. The trielectron $e_2^-e^+$ and quadrielectron or positronium molecule Ps_2 are also known to be bound,^{35,36} although neither has been observed.

Some authors have suggested that annihilation in ionic crystals takes place mainly from a bound

system comprised of a positron and an anion. Indeed, several^{37,38} sets of observations show the lifetime for 2γ events in alkali halides is roughly independent of the cation but varies with the anion.³⁹ More recent experiments⁴⁰⁻⁴³ and calculations⁴⁴ show that the suggested mechanism does not afford a quantitative explanation of the observations, and indeed that structures like positronium halide may play no significant role in annihilation in alkali-halide crystals. Our interest in PsH springs from its use as a primitive example of a positron-molecule complex, and not from any supposed connection with annihilation in alkali-hydride crystals.

2. WAVE MECHANICS OF PsH

Assuming an infinite nuclear mass and ignoring relativistic effects and all but Coulombic interactions, we have the Hamiltonian

$$\mathcal{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_p^2) - \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_{1p}} + \frac{1}{r_{2p}} \right) + \left(\frac{1}{r_{12}} + \frac{1}{r_p} \right), \quad (2.1)$$

where we use atomic units,⁴⁵ $r_{ij} = |\vec{r}_i - \vec{r}_j|$, 1 and 2 refer to the electrons, p to the positron, and the nuclear index is suppressed.

A. Angular Momentum

The square of the total orbital angular momentum $\vec{L} = \vec{L}_1 + \vec{L}_2 + \vec{L}_p$ and its z component commute with \mathcal{H} and hence L and M_L are good quantum numbers in our approximation. A similar remark holds for the spin. Following Chang Lee's²³ discussion of spin angular momentum coupling for this system, we designate the spin functions for the two electrons as Σ_{ij} where i and j are the quantum numbers for the total electronic spin and its z component, the spin functions for the positron as $\sigma_{\pm 1/2}$, and the spin functions for all three light particles as χ_{MS}^S . Coupling the spins gives two doublets and one quartet

$$\chi_{\pm 1/2}^{1/2}(\text{para}) = \Sigma_{00}\sigma_{\pm 1/2}, \quad (2.2)$$

$$\chi_{\pm 1/2}^{1/2}(\text{ortho}) = (1/3)^{1/2}\Sigma_{10}\sigma_{\pm 1/2} - (2/3)^{1/2}\Sigma_{1\pm 1}\sigma_{\mp 1/2}, \quad (2.3)$$

$$\chi_{\pm 3/2}^{3/2}(\text{ortho}) = \Sigma_{1\pm 1}\sigma_{\pm 1/2}, \quad (2.4)$$

$$\chi_{\pm 1/2}^{3/2}(\text{ortho}) = (2/3)^{1/2}\Sigma_{10}\sigma_{\pm 1/2} + (1/3)^{1/2}\Sigma_{1\pm 1}\sigma_{\mp 1/2},$$

where we show the electronic parentage in parentheses. Because of the orthogonality of the two doublet spin functions, there is no mixing between them in any eigenfunction of our Hamiltonian (2.1), showing that the purely electronic spin quantum number S_e is also good in our approximation. Using

$$2S + 1, 2S_e + 1_L \quad (2.5)$$

as a term symbol, we see that the eigenfunctions have the forms

$$F_{M_L}^L(\vec{r}_1, \vec{r}_2, \vec{r}_p)\chi_{\pm 1/2}^{1/2}(\text{para}) \text{ for } 2, 1_L, (2.2')$$

$$G_{M_L}^L(\vec{r}_1, \vec{r}_2, \vec{r}_p)\chi_{\pm 1/2}^{1/2}(\text{ortho}) \text{ for } 2, 3_L, (2.3')$$

$$H_{M_L}^L(\vec{r}_1, \vec{r}_2, \vec{r}_p)\chi_{M_S}^{3/2}(\text{ortho}) \text{ for } 4, 3_L, (2.4')$$

respectively, where the functions F , G , and H depend upon spacial coordinates only, and are eigenfunctions of L^2 and L_z as indicated. Upon considering the electronic parent of each eigenfunction, we conclude that F is antisymmetric under the electron interchanger P_{12} , and G and H are symmetric. Since the spin parts are factorable in each eigenfunction, and since spin variables do not appear in the Hamiltonian, $2, 3_L$ and $4, 3_L$ states are degenerate. The degeneracy would be lifted by spin-spin interaction, which we do not consider here.

We expect the ground state to be $2, 1_S$, although states with other symmetries, for example, $2, 3_P$ and $4, 3_P$, may also be bound.

B. Expansion in a Basis

Dropping the spin functions in the following, we now discuss the choice of a basis representation for F for use in the variational calculation described below. Many have remarked on the spherical symmetry of the Coulomb field,⁴⁶ one example of which is contained in Eq. (2.1). This implies that an arbitrary function of the six radial variables r_1 , r_2 , r_p , r_{12} , r_{1p} , and r_{2p} is an eigenfunction of L^2 with eigenvalue zero. It is also true that these six variables are not redundant, and completely specify the positions of the three light particles relative to each other and to the nucleus for S states. A suitable expansion, then, and the one used in this work, is

$$F = \psi^{(0)} \sum b(r_1^i r_2^j r_{1p}^k r_{2p}^l + r_1^j r_2^i r_{1p}^l r_{2p}^k) r_{12}^m r_p^n, \quad (2.6)$$

where the sum is over non-negative integral values of i , j , k , l , m , and n ; the b stands for parameters to be determined by minimizing the energy; and $\psi^{(0)}$ is a function which we now specify so that short expansions will give accurate results not only for the energy but also for the annihilation rate.

In regions of configuration space where two particles are close together, the Coulomb part of the Hamiltonian (2.1) is large in magnitude. If the two particles attract each other, the potential is large and negative, and the wave function is large [Fig. 1, curve (a)]. If the two particles repel each other, the potential is large and positive, and the wave function is small [Fig. 1, curves (b) and (c)]. Therefore, we should attempt

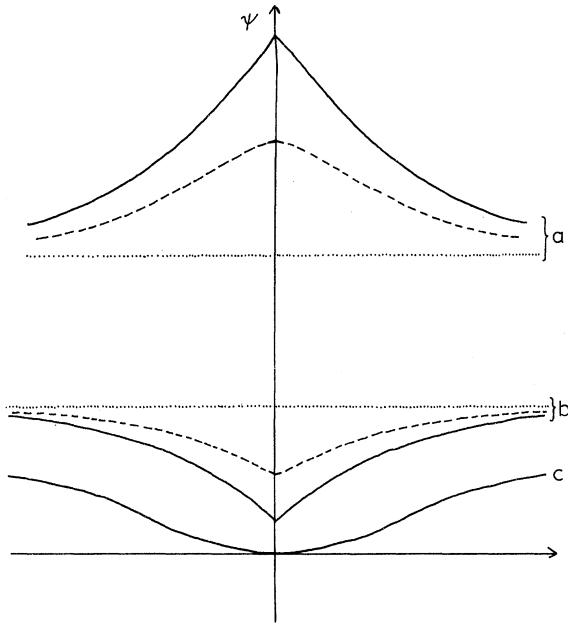


FIG. 1. (a) The Coulomb "hill" for attractive particles; (b) the Coulomb hole for nonidentical repulsive particles or for identical fermions with antiparallel spin; (c) the Coulomb hole for identical fermions with parallel spin, i.e., the Pauli hole. Plotted is an accurate wave function (solid curve), a partially correlated wave function (dashed curve), and an uncorrelated wave function (dotted line) versus interparticle distance in regions of space far from other particles and from nodes in the wave function.

to represent the wave function accurately in regions where attractive particles are close together, other regions of space being less important.

Kato⁴⁷ showed that the exact wave function Φ for a system of particles interacting through Coulombic forces exhibits a certain point property where pairs of particles collide. It is

$$\left(\frac{\partial \ln \Phi}{\partial r_{ij}} \right)_{r_{ij}=0} = q_i q_j \mu_{ij} = \nu_{ij} \quad (2.7)$$

which is referred to as the cusp condition or coalescence condition. q_i and q_j are the charges of particles i and j and μ_{ij} is their reduced mass. Equation (2.7) must be modified if there is non-zero relative orbital angular momentum between the two particles⁴⁸ or if the spin is not factorable from the wave function.⁴⁹ Neither of these problems concerns us here.

Requiring our approximate wave function F to satisfy Eq. (2.7) does not guarantee it to be accurate for small r_{ij} , of course. However, calculations with a large variety of approximate wave functions for the helium ground state show that, with the exception of obviously pathological functions, there is a strong positive correlation between the accuracy of calculated cusp values ν_{ij} and the expectation values of the operator $\delta(\vec{r}_i - \vec{r}_j)$.⁵⁰ In our approximation the annihilation

properties themselves are point properties, and their calculation involves integrals containing delta functions between annihilating partners, which are attractive (see Sec. 4.A). Thus, it makes good sense to require our approximate F to satisfy the cusp conditions (2.7), at least approximately and at least for the attractive particle pairs.

We may proceed in any of a number of ways: We may perform a constrained variation of the energy by adding cusp conditions to the variational functional with Lagrange multipliers⁵¹⁻⁵³; we may calculate a first-order correction to a given F by taking an operator involving $\delta(\vec{r}_i - \vec{r}_j)$ and/or $\partial/\partial r_{ij}$ as the perturbation⁵⁴⁻⁵⁶; and so forth.⁵⁷⁻⁶⁰

Our approach is simpler than any of these and is probably fairly accurate. We simply use a functional form for F which enables us to satisfy the important cusp conditions exactly by a particular choice of parameters. Then the free variation of the Hamiltonian expectation value will presumably result in a good representation of F where attractive particles collide. Relatively large errors elsewhere will not affect the over-all accuracy of F much since it is small in such regions.

Equation (2.7) says that in regions where particles i and j are close together and far away from other particles which are themselves well separated and far away from nodes of the wave function, $\Phi \sim 1 + \nu_{ij} r_{ij} \sim \exp(\nu_{ij} r_{ij})$ but for a multiplicative slowly varying function of the other interparticle coordinates. The attractive pairs in our system are the electron-nucleus and electron-positron pairs for which ν_{ij} is -1 and $-\frac{1}{2}$, respectively. Hence $\exp(-r_1 - r_2 - r_{1p}/2 - r_{2p}/2)$ might serve as a reasonable $\psi^{(0)}$ in Eq. (2.6). The forms of $\psi^{(0)}$ used here are the open- and closed-shell generalizations of this, namely

$$\psi_c^{(0)} = \exp[-\alpha(r_1 + r_2) - \beta(r_{1p} + r_{2p})], \quad (2.8a)$$

$$\psi_o^{(0)} = \exp(-\alpha r_1 - \beta r_2 - \gamma r_{1p} - \delta r_{2p}) + \exp(-\beta r_1 - \alpha r_2 - \delta r_{1p} - \gamma r_{2p}). \quad (2.8b)$$

Our arguments for taking $\psi^{(0)}$ to be of the form given by Eq. (2.8b) can be stated also in simple physical terms. The dissociation products $\text{Ps} + \text{H}$ are 6.1 eV more favorable than the alternative products $e^+ + \text{H}^-$. Therefore, the dominant contribution in the exact (unknown) ground-state wave function for PsH is the coupled structure: virtual ground-state positronium, and virtual ground-state hydrogen atom. In this light it seems clear that representing F as the product

$$F \sim \varphi(r_1) \varphi(r_2) f(r_p) \quad (2.9)$$

corresponds to the unfavored dissociation products and will lead to gross inaccuracies, particularly in the positronic density

$$\rho_p(\vec{r}_p) = \int d\vec{r}_1 \int d\vec{r}_2 |F(\vec{r}_1, \vec{r}_2, \vec{r}_p)|^2 \quad (2.10)$$

and therefore in the annihilation properties as well. While the Euler-Lagrange equations resulting from the ansatz (2.9) are particularly simple,^{32,33} being just the Hartree equations, the physical situation indicates the approximation is unrealistic.

Similarly, if a bound excited state of PsH exists, an important contribution to the eigenfunction is probably virtual excited positronium, and virtual ground-state hydrogen atom. Excited states corresponding to the ansatz (2.9) presume that the positron is somehow excited relative to the nucleus. The basis set implied in Eq. (2.6), where $\psi^{(0)}$ is given by Eq. (2.8a) or (2.8b), contains all these contributions. If an excited bound state exists, it is properly sought in the second lowest root of the secular equation resulting from the variation of the linear parameters in the trial wave function.

3. ENERGY AND WAVE FUNCTION

A. Ground State of PsH

Two sets of calculations of the wave function are presented here, one using $\psi_c^{(0)}$ [Eq. (2.8a)], the closed-shell form, as $\psi^{(0)}$ in Eq. (2.6), and one using $\psi_o^{(0)}$, the open-shell form. Parameters for $\psi_o^{(0)}$ are taken from the work of Neamtan *et al.*³¹ and for $\psi_c^{(0)}$ we used $\alpha = 1$ and $\beta = \frac{1}{2}$. The coordinates are scaled as described below so that the virial theorem is satisfied.

Judging from the work of Green *et al.*⁶¹ and others on the helium ground state, one expects the most significant terms in the expansion [Eq. (2.6)] to be linear terms in the coordinates not present in the exponential factor, namely r_{12} and r_p . Unfortunately, the difficulty in evaluating the integrals (see Appendix) if arbitrary powers of both these coordinates are included is prohibitive, and one of them is omitted from the expansion. A series of simple calculations summarized in Table I indicates that r_{12} is significantly more efficacious than r_p in lowering the total energy of the system, so r_p is omitted.

The expansion was then built up stepwise by in-

cluding first the constant term plus all possible linear terms, then the constant plus linear plus quadratic terms, and so forth, always with the coordinate r_p omitted. Because of speed and memory limitations of the IBM-7044 at the University of Iowa Computer Center, the expansion could not be extended beyond cubic terms for the closed-shell function and quadratic terms for the open-shell function. The closed-shell calculation was extended slightly beyond quadratic terms in an attempt to obtain an energy comparable to the best open-shell results. Results are given in Tables II and III.

With the nonlinear parameters α , etc., in Eq. (2.8) fixed at each stage in the expansion, the energy minimization reduces to the solution of the familiar secular equation

$$\det(\mathcal{H}_{pq} - ES_{pq}) = 0, \quad (3.1)$$

where p and q denote terms in the expansion in Eq. (2.6), and \mathcal{H}_{pq} and S_{pq} are matrix elements of the Hamiltonian and unity, respectively. At each stage the virial theorem is satisfied in the manner described by Hylleraas.⁶² If one replaces the arguments of a trial function $\tilde{r}_1, \tilde{r}_2, \tilde{r}_p$ by $\lambda\tilde{r}_1, \lambda\tilde{r}_2, \lambda\tilde{r}_p$ then \mathcal{H}_{pq} can be written

$$\mathcal{H}_{pq} = \lambda^2 T_{pq} + \lambda V_{pq}, \quad (3.2)$$

where T_{pq} and V_{pq} are the values of the kinetic and potential energy matrix elements calculated for $\lambda = 1$. The virial theorem is satisfied by giving λ the value which minimizes the desired root E of Eq. (3.1). This value for λ is calculated by iteration, but the quantities T_{pq} and V_{pq} need be calculated only once.

The lowest energy obtained for any of these calculations is -0.7742 a. u. which indicates binding of Ps and H of 0.657 eV. The most accurate previous wave function, that of Neamtan *et al.*³¹ yielded -0.7584 a. u., indicating binding by 0.228 eV.

TABLE I. Preliminary calculations.

Wave function	b	E_0 (au) ^a	E_1 (au) ^a
		Closed Shell [Eq. (2.8a)] ^b	
$\psi_c^{(0)}(1 + br_{12})$	0.4882	-0.7307	+0.0967
$\psi_c^{(0)}(1 + br_p)$	0.8912	-0.6975	-0.3953
$\psi_c^{(0)}(1 + br_{12}^2)$	0.6682	-0.7244	-0.1913
$\psi_c^{(0)}(1 + br_p^2)$	1.1468	-0.6974	-0.4778
		Open shell [Eq. (2.8b)] ^c	
$\psi_o^{(0)}(1 + br_{12})$	0.6862	-0.7631	-0.6050
$\psi_o^{(0)}(1 + br_p)$	1.1939	-0.7595	-0.6727
$\psi_o^{(0)}(1 + br_{12}^2)$	0.8175	-0.7613	-0.6876
$\psi_o^{(0)}(1 + br_p^2)$	1.1468	-0.7608	-0.6974

^a E_0 and E_1 are the two roots of the secular equation.

^bThe values of α and β (before scaling) are $\alpha = 1$ and $\beta = \frac{1}{2}$.

^c α, β, γ , and δ are the values calculated by Neamtan *et al.* (Ref. 31). All coordinates were scaled so that the virial theorem is satisfied for the ground state.

TABLE II. Closed-shell results. $\alpha=1$, $\beta=\frac{1}{2}$ before scaling.

Label	1	2	3	4
E_0 (au)	-0.6968	-0.7429	-0.7722	-0.7724
Binding energy (eV)	-1.45	-0.193	+0.604	+0.610
Scale factor	0.6108	0.6518	0.6604	0.6584
Norm of ψ^a	17.580	33.884	70.546	57.238
$i j k l m n$	b coefficients ^b			
0 0 0 0 0 0	0.5	0.5	0.5	0.5
0 0 0 0 1 0		0.2300	0.1317	0.1232
0 1 0 0 0 0		-0.2697	-0.1553	-0.1936
0 0 0 1 0 0		0.0661	0.0679	0.0125
0 0 0 0 2 0			-0.0103	-0.0092
0 2 0 0 0 0			0.3071	0.2749
0 0 0 2 0 0			0.1119	0.1351
1 1 0 0 0 0			-0.2042	-0.1552
0 0 1 1 0 0			-0.0847	-0.0860
0 1 0 0 1 0			-0.0484	-0.0397
0 0 0 1 1 0			0.0868	0.0737
0 1 0 1 0 0			-0.2971	-0.2641
0 1 1 0 0 0			0.1503	0.1381
0 3 0 0 0 0				0.0002
0 0 0 3 0 0				-0.0048
1 1 0 1 0 0				-0.0144
0 1 1 1 0 0				0.0081

^aNorm of $\psi = \int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_p \psi^2$, where the coordinates in ψ have not been scaled.

^b $b = \frac{1}{2}$ for $ijklmn = 000000$ so the leading term in the expansion (2.6) is unity.

B. Bound Excited States of PsH

The second lowest root of the secular equation was obtained for all the calculations performed. The lowest second root in any case was that obtained from the 12-term open-shell function in

Table III. Its value is -0.7432 a.u. which falls short of binding by 0.184 eV. The virial theorem was satisfied by separate scaling of this root. This result should not be taken as strong evidence that a bound excited state does not exist, however. The wave function is independent of the coordinate

TABLE III. Open-shell results. Exponential parameters α , β , γ , and δ are those of Neamtan *et al.* (Ref. 31).

Label	5	6	7
E_0 (au)	-0.7584	-0.7679	-0.7742
Binding energy (eV)	0.228	0.487	0.657
Scale factor	1	0.9135	0.8643
Norm of ψ^a	2.050×10^4	9.486×10^3	3.935×10^3
$i j k l m n$	b coefficients ^b		
0 0 0 0 0 0	0.5	0.5	0.5
0 0 0 0 1 0		0.0446	0.0894
0 1 0 0 0 0		-0.0869	-0.2050
0 0 0 1 0 0		-0.0278	-0.0494
0 0 0 0 2 0			0.0044
0 2 0 0 0 0			0.0154
0 0 0 2 0 0			0.0029
1 1 0 0 0 0			0.0163
0 0 1 1 0 0			0.0002
0 1 0 0 1 0			-0.0232
0 0 0 1 1 0			-0.0044
0 1 0 1 0 0			0.0056

^aNorm of $\psi = \int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_p \psi^2$, where the coordinates in ψ have not been scaled.

^bThe term for $ijklmn = 011000$ was inadvertently left out of the basis set. $b = \frac{1}{2}$ for $ijklmn = 000000$ so that the leading term in the expansion (2.6) is unity.

r_p and the calculations reported in Table I indicate that this coordinate has a more significant influence on the second root than on the first. We conclude that if PsH has a bound excited $^2,^1S$ state, its wave function probably contains a small but significant contribution in which the positron is excited with respect to the nucleus, as well as excited virtual positronium contributions.

Finally we note that all the roots of our secular equations belong to $^2,^1S$. It is quite possible that a state with some other symmetry has an energy level below -0.75 a. u.

C. Is e^+He a Bound System?

For the wave function of this system Khare, Wallace, Bach, and Chodos⁶³ wrote

$$\psi = e^{-\alpha r_1 - \beta r_2 - \gamma r_1 p} (1 + c \vec{r}_1 \cdot \vec{r}_{1p}) \quad (3.3)$$

$$+ e^{-\beta r_1 - \alpha r_2 - \gamma r_2 p} (1 + c \vec{r}_2 \cdot \vec{r}_{2p}).$$

Optimal values of the variational parameters yield an energy of -2.89587 a. u. which is 0.215 eV above that of the unbound system $He + e^+$ (the helium ground-state energy is -2.903724 a. u.). These authors compared their result with the He energy obtained with the trial wave function

$$e^{-\alpha' r_1 - \beta' r_2} + e^{-\beta' r_1 - \alpha' r_2} \quad (3.4)$$

which is 2.8754 a. u. for optimal values of α' and β' and concluded that the positron is bound by 0.0205 a. u. or 0.558 eV. This procedure is not strictly valid since the difference between two upper bounds is not itself a bound and may contain errors difficult to estimate. In particular, we would like to point out that the proper comparison with the function (3.3) is with

$$e^{-\alpha'' r_1 - \beta'' r_2} (1 + c'' r_1^2) + e^{-\beta'' r_1 - \alpha'' r_2} (1 + c'' r_2^2) \quad (3.5)$$

which is obtained from (3.3) by omitting \vec{r}_p . This is so because the form of Eq. (3.3) admits to the trial function some purely interelectronic correlations not present in (3.4). The energy for helium with a trial function of the form (3.5) is not in the literature, so the proper comparison cannot be made. However, the energy of helium in the radial limit (infinite expansion in powers of r_1 and r_2 only, omitting r_{12}) is well characterized⁶⁴ and is known to be within 0.0003 eV of -2.87902 a. u., which is still above the energy for e^+He as reported by Khare *et al.* by 0.460 eV. Thus we cannot definitely show on the basis of these numbers whether the system is bound or not.

However, a valid comparison can be made from the work of Oczkowski,⁶⁵ who minimized the energy of e^+He for the trial wave function of the form (2.8b)

$$\psi = \exp(-\alpha r_1 - \beta r_2 - \gamma r_1 p - \delta r_2 p) + \exp(-\beta r_1 - \alpha r_2 - \delta r_1 p - \gamma r_2 p), \quad (3.6)$$

and found the lowest energy was -2.8754 a. u. for $\gamma = \delta = 0$ and values of α and β equal to α' and β' in (3.4). The structure corresponding to these parameter values is, of course, a free positron and a helium atom.

We performed a number of calculations with closed-shell expansions, including one with 13 terms, with the ratio α/β [Eq. (2.8a)] held fixed at 2 and obtained -2.8092 a. u. as the best (scaled) energy. On the other hand, by varying α and β independently with only a two-term expansion [the constant term and a term in $(r_1 + r_2)$] gave $E = -2.8475$ a. u. for $\lambda\beta = 0.007$. The variation was not carried to completion because E and $\lambda\beta$ were both decreasing, indicating no binding. We feel these results provide a good indication that e^+He is not bound.

A more convincing indication that e^+He is unbound was given recently by Gertler, Snodgrass, and Spruch.⁶⁶ These authors exhibit a necessary condition based upon the adiabatic potential for a positron scattering off a helium atom. The proof depends upon a knowledge of the exact adiabatic potential, which in this case is the energy of the molecular ion HeH^+ . The exact potential is unknown so the proof is not strictly rigorous. However, a very accurate variational estimation of the energy of HeH^+ is available,⁶⁷ and based upon this potential Gertler *et al.* conclude that a positive particle will not bind to a helium atom if its mass is less than 2.38 times the electronic mass.

In view of the results of Oczkowski,⁶⁵ Gertler, Snodgrass, and Spruch,⁶⁶ and ourselves, it is difficult to understand the numbers reported by Khare *et al.*⁶³

4. ANNIHILATION RATE

A. Results for the Calculation

Several^{17,23,31,44} have shown that for one-positron many-electron systems in which the electrons constitute a closed-shell structure, the annihilation probability for two-photon events can be written

$$P = \pi \alpha^3 \langle \psi | \sum_i \delta(\vec{r}_i - \vec{r}_p) | \psi \rangle, \quad (4.1)$$

where the sum $i = 1, \dots, n$ goes over the electrons, ψ is the wave function, α is the fine-structure constant, and the units of P are (atomic units of time)⁻¹. One a. u. of time is 2.4189×10^{-17} sec,⁴⁵ so P is

$$P = 50.47n \langle \psi | \delta(\vec{r}_1 - \vec{r}_p) | \psi \rangle \text{ nsec}^{-1} \quad (4.2)$$

for n electrons, owing to the symmetry of $|\psi|^2$ and $\sum_i \delta(\vec{r}_i - \vec{r}_p)$ under P_{12} . Equation (4.1) implies²³ that the annihilation event involves only the annihilating partners; i. e., that other particles present play only spectator roles and begin to rearrange themselves into eigenstates of the $(n-1)$ -electron system only after annihilation is completed. Recent theoretical results⁶⁸ indicate that in a degenerate electron gas annihilation events in which a spectator electron is excited may be significant. This mechanism is due to degeneracies not present in our system and need

not concern us here. Events which produce a number of photons different from two are also ignored. These events are known to be much less probable.

Equation (4.2) gives the annihilation rate for PsH as

$$P = 100.94 \langle \psi | \delta(\vec{r}_1 - \vec{r}_p) | \psi \rangle \text{ nsec}^{-1}, \quad (4.3)$$

where ψ is assumed to be properly scaled and normalized. Results are listed in Table IV for both the annihilation rate and the electron-positron cusp value calculated for each of the wave functions reported in this work. The cusp value [Eq. (2.7)] is taken to be⁵⁰

$$\nu_{1p} = \frac{\langle \psi | \delta(\vec{r}_1 - \vec{r}_p) (\partial/\partial r_{1p}) | \psi \rangle}{\langle \psi | \delta(\vec{r}_1 - \vec{r}_p) | \psi \rangle}. \quad (4.4)$$

It is seen in Table IV that the addition of linear terms to the expansion (2.6) serves to depress both the calculated annihilation rate and the magnitude of the cusp value, and that higher-order terms result in larger values for these quantities. Trends in the rate and cusp value are weak. In fact, the rate is fairly insensitive to the size of the basis set, at least for the open-shell functions 5, 6, and 7. This suggests the possibility that for positron-atom systems, reliable rates may be calculated with less labor than reliable binding energies. Further investigations are in progress.

B. Results for other Calculations

Binding energies and annihilation rates calculated from the wave functions of other workers are listed in Table V. The wave function of Neamtan *et al.*³¹ is identical to our open-shell function with no expansion, and Ore's function³⁰ is obtained from that of Neamtan *et al.* by setting the smallest exponential parameter equal to zero. The agreement between our results and those of Ore and Neamtan *et al.* is therefore not surprising. The size of the discrepancy between these results and those of Ludwig and Parr³⁴ and Goldanskii *et al.*^{32,33} is very large. The wave function of the latter authors is of the form (2.9) and hence has none of the important electron-positron correlation: The cusp value ν_{1p} [Eq. (4.4)] calculated with this

wave function is zero. That the calculated annihilation rate is an order of magnitude too small serves to emphasize the importance of electron-positron correlation in the calculation of annihilation rates. The enhancement factor is thus about 10, in rough agreement with calculations on scattering systems⁷² and solids.⁷³⁻⁷⁷

The annihilation rate calculated from the wave function of Ludwig and Parr⁷¹ may also be understood in terms of electron-positron correlation. It is well-known that the method used by these authors, namely, expansion in nuclear-centered configurations, is less efficient in representing accurately short-range correlation between light particles than the method used here, expansion in interparticle coordinates.⁷⁸⁻⁸¹ Indeed, this fact is reflected in the energies reported by Ludwig and Parr. Their best function is very complicated, being an expansion in nine configurations with a total of 30 independent variational parameters, and yet the binding energy obtained is about a tenth of that found by the present authors.

Accurately representing short-range correlation between light particles is accomplished by allowing one's trial wave function to represent accurately the Coulomb hole (in the case of repulsive particles) or "hill" (in the case of attractive particles) in interparticle space. The hill has a cusp at the top, and the hole has an inverted cusp at the bottom unless the particles are identical fermions with parallel spin. (In the latter case, which does not concern us here, the hole is called the "Pauli hole.") Of all points in two-particle space, only the peak of the hill is sampled by the delta function in Eqs. (4.1)-(4.4). Experience has repeatedly shown that accuracy in the wave function at this point can be achieved in small expansions only by including the interparticle coordinate directly. The situation is shown qualitatively in Fig. 1. Solid curves represent an accurate trial wave function, the dashed lines represent a partially correlated wave function such as that of Ludwig and Parr, and the dotted lines stand for the uncorrelated wave functions, such as the Hartree-Fock wave functions of Goldanskii *et al.* It is seen that insufficiently correlated trial functions underestimate the expectation values of a delta function between attractive particles and overestimate that quantity for repulsive particles. The trend of the calculated annihilation rates listed in Table V is consistent with this point of view.

TABLE IV. Calculated annihilation rate.

Wave function label ^a	P (nsec ⁻¹) ^b	Electron-positron cusp value ^c
1	2.009	-0.3054
2	1.900	-0.2897
3	2.200	-0.4312
4	2.265	-0.4521
5	2.023	-0.4163
6	2.019	-0.4069
7	2.095	-0.4070

^aSee Tables II and III.

^bEquation (4.3).

^cEquation (4.4)

TABLE V. Binding energies and annihilation rates from other calculations.

	Reference	Binding energy (eV)	Annihilation rate (nsec ⁻¹)
Ore ^a	30	+ 0.0686	2.045 ^b
Neamtan <i>et al.</i>	31	+ 0.226	2.015 ^c
Goldanskii <i>et al.</i> ,	32 } Ivanova and Prokopev	- 2.24	0.22 ^d
Ludwig and Parr	34	+ 0.068	0.82 ^e
This work		+ 0.657	2.095

^aRefined values for the parameters in Ore's wave function are given by Darewych (Ref. 69).

^bCalculated by the present authors. Tkachenko (Ref. 70) reports 1 nsec⁻¹, a value which we are unable to reproduce.

^cCalculated by the present authors. Neamtan *et al.* report 1.978 nsec⁻¹, Darewych (Ref. 69) reports 2.024 nsec⁻¹

^dCalculated by the present authors from wave functions given graphically by Goldanskii *et al.* who report 12.5 nsec⁻¹. *Note added in proof:* Goldanskii now reports (private communication) 0.3 nsec⁻¹

^eLudwig and Parr report 6.6 nsec⁻¹ in their paper, but owing to an error in their calculation, this is incorrect. Recalculation (Ref. 71) yields the result listed above.

It is interesting that, up to the present work, all the annihilation rates in the literature appear to be wrong. In the case of Neamtan *et al.*³¹ the error is very small and apparently arises from a trivial arithmetic mistake. Tkachenko⁷⁰ and Goldanskii *et al.*³² use a formula for the annihilation rate which we do not understand. In addition some numerical errors were made in evaluating the terms of their formula.⁸² Some errors were made also in the calculation of Ludwig and Parr.⁷¹

5. DISCUSSION

The major source of error in the calculations reported here is the omission of the positron-nuclear coordinate r_p from the wave function. The omission makes the calculated wave function F cusp up at the positron-electron coalescence position independently of the distance of the coalesced pair from the nucleus. The effect of this omission is probably not great because it is felt only in three-particle (electron-positron-nucleus) space, but, on the other hand, it is probably not insignificant because F is large where r_1 or $r_2 \sim$ zero. Practical considerations (see Sec. 3.A and the Appendix) dictated that F be independent of either r_{12} or r_p and our preliminary calculations (Table I) showed the desirability of including r_{12} in ψ instead of r_p . The inclusion of both would probably have a small effect on the calculated properties for the ground state, but might lead to a bound excited ^{2,4}S state as well.

The effects of spin-spin interactions, finite nuclear mass, and relativistic effects are certain to be small.

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APPENDIX

The method of integral evaluation is rather inelegant and in some cases wasteful, and we describe the procedure here in the hope that a reader will suggest a better way.

The most difficult integral encountered in this work can be represented by diagram (A1) in Fig. 2, where the dashed lines indicate the presence in the integrand of nonzero integral powers of the coordinates r_{12} and r_p . The solid lines denote the presence of the indicated coordinate as the argument of an exponential times an integral power of the coordinate itself. The simplest integrals are those like diagram (A2) in Fig. 2, where we have suppressed the particle labels. The other two

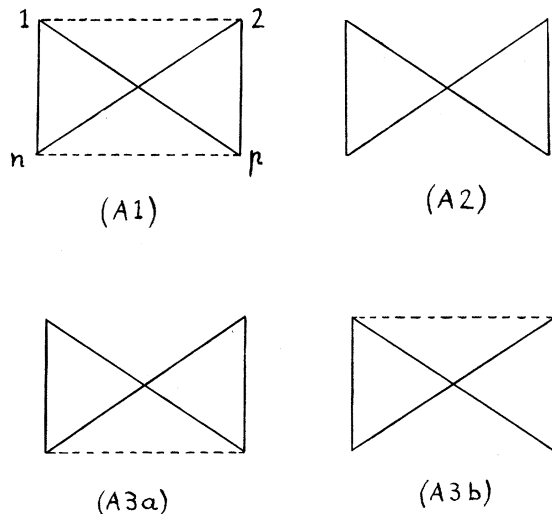


FIG. 2. Diagrams for the integrals discussed in the Appendix.

possibilities are shown in diagrams (A3a) and (A3b) in Fig. 2, which are not to be distinguished from each other since an integral of the first type can be converted to one of the second by placing origins of coordinate systems on other particles or, equivalently, by renaming integration variables.

The presence of a product of negative exponentials between attractive particle pairs renders all these integrals formally the same as those encountered in diatomic molecule calculations except that now we have to integrate over the position of one of the "nuclei". For example, integrals of the type (A2) can be written as $\int d\vec{r}_p f(\vec{r}_p)$ where $f(\vec{r}_p)$ is the product of two two-center overlap integrals between Slater-type ns atomic orbitals situated on points which here are the nuclear and positronic positions. The overlap integrals are most conveniently obtained by generalizing formulas given by Roothaan.⁸³ The final integration is easy and the integral is obtained in closed form.

Type (A3a) integrals involve in addition a factor of r_p raised to some nonzero integral power in the integrand and similarly are obtained in closed form. In the case of the type (A3b) the Slater orbitals are considered as centered on the appropriate electron, and the final integration is over r_{12} , but other than this name change there is no distinction between (A3a) and (A3b).

Type (A1) integrals are not so simple in general. However, if the non-exponential part of the integrand is $r_p^i r_{12}^2$ where i is a positive integer, the integral may be performed analytically by using the expression

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \{ \cos\gamma \cos\delta + (\sin\gamma \sin\delta) \cos\omega \}, \quad (\text{A1})$$

where γ is the angle between \vec{r}_p and \vec{r}_1 , δ is the angle between \vec{r}_p and \vec{r}_2 , and ω is the angle between the planes intersecting in \vec{r}_p (see Fig. 3). By orienting the z axis along the "internuclear" axis \vec{r}_p , ω can be written as $\varphi_1 - \varphi_2$, where φ_1 and φ_2 are the familiar ellipsoidal coordinates, the azimuthal angles of electrons 1 and 2. Integration over ω then yields zero for the second term within brackets of Eq. (A1). For the first term we use the law of cosines to write the product $\cos\gamma \cos\delta$ in terms of the radial variables r_1, r_2, r_{1p}, r_{2p} , and r_p . A sum of nine terms results on the left-hand side of Eq. (A1) leading to nine integrals of the type (A3) unless $i=2$, in which case four integrals of type (A2) and five of type (A3) arise. The same treatment applies in case the integrand contains the factor $r_{12}^i r_p^2$ instead of $r_p^i r_{12}^2$.

Type (A1) integrals which contain in our treatment one of the factors $r_p^i r_{12}^{\pm 1}$ or $r_{12}^i r_p^{\pm 1}$ times a product of exponentials (i is a positive integer) were the most difficult encountered in this work. In the case $r_p^i r_{12}^{-1}$ the integration

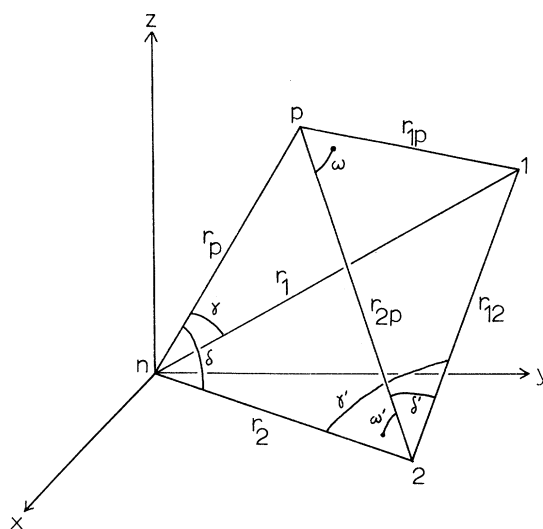


FIG. 3. The coordinate system. ω and ω' are interplanar angles. The other angles are between interparticle axes.

over the electrons is formally the same as evaluating a two-center interelectronic repulsion integral. Integration over the "internuclear" vector \vec{r}_p completes the evaluation. The repulsion integrals were evaluated by extracting an appropriate portion of the Harris-Taylor diatomic molecule program⁸⁴ and modifying it for our purposes. Each repulsion integral was evaluated for a number of values of r_p . Once these values are obtained, a final numerical integration over these values and the power of r_p is performed. In this work the change of variable $y = r_p/(1+r_p)$ was made and the range $0 \leq y \leq 1$ was divided into 13 unequal intervals and a three-point Gaussian rule applied on each interval.

When the factor is $r_p^i r_{12}$, r_{12} is rewritten as r_{12}^2/r_{12} . The numerator then expanded as in type (A1). Now, however, the $\cos\omega$ term does not integrate to zero but leads to a repulsion integral over Slater type $2p_\pi$ atomic orbitals. In all, 10 repulsion integrals result, and each one is evaluated as above.

Integrals involving the factors $r_{12}^i r_p^{\pm 1}$ are evaluated in the same way by renaming the integration variables. Further details are recorded elsewhere.⁸⁵

Clearly this method is extensible to more general forms of integrals, but experiments with some of these indicated computation time required is prohibitive. Other methods might be useful.⁸⁶⁻⁸⁸

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Exact Treatment of the Stark Effect in Atomic Hydrogen*

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A boundary-condition method is used to investigate the energy levels of atomic hydrogen in a uniform electric field. At low fields the misbehavior of trial eigensolutions in the nonclassical region enables one to obtain high-accuracy upper and lower bounds to the Stark shift. At higher fields the energy levels are treated as resonant states imbedded in a continuum. A modified WKB approach is used to obtain both the position and width of these resonances. Comparison is made with the usual perturbation-theory results.

I. INTRODUCTION

An adequate explanation of the Stark effect in atomic hydrogen was one of the first tests applied to the old¹ and new^{2,3} quantum theories. The application of perturbation theory was successful in confirming both the linear and quadratic Stark effects.^{2,4} Recently these results have been extended to higher order.⁵ Several authors have also treated the Stark effect using the WKB technique.^{6,7} As yet, however, no exact solution of the appropriate Schrödinger equation has been undertaken. This is perhaps due to the well-known fact that at large distances from the proton the potential energy becomes infinitely negative.^{3,8,9} Thus the electric field, however weak, eventually strips off the atomic electron. The problem then becomes more complicated than a simple determination of bound-state energy levels.

In this paper we use a modification of the boundary-condition method, recently used by Rosenthal and Wilson,^{10,11} to investigate the energy levels of atomic hydrogen in a uniform electric field. We obtain series solutions to the appropriate Schrödinger equation for various trial eigenvalues. At low fields the nature of the misbehavior of these solutions in the nonclassical regions changes as the sequence of trial eigenvalues crosses the true eigenvalue. This enables us to obtain high-accuracy

upper and lower bounds to the Stark Shift. The uncertainty in the energy caused by the unbounded character of the state is less than the difference between these bounds.

At higher fields it becomes necessary to consider explicitly the unbound character of the initially bound states, which now appear as resonant (metastable) states imbedded in a continuum. We use the boundary-condition method together with a modification of the WKB technique to obtain the phase shift of the asymptotic (unbound) eigenfunction. In exact analogy with elementary scattering theory, analysis of the energy dependence of this phase shift yields both the position and width of the metastable levels.

II. GENERAL REMARKS

The Schrödinger equation for atomic hydrogen in a uniform electric field of strength F directed along the z axis is separable in parabolic coordinates, ξ, η, ϕ , yielding the three ordinary differential equations^{9,12}

$$\left(\frac{d^2}{d\phi^2} + m^2\right)\Phi(\phi) = 0, \quad (1)$$

$$\left[\frac{d}{d\xi} \left(\xi \frac{d}{d\xi}\right) - \frac{F\xi^2}{4} + \frac{E\xi}{2} - \frac{m^2}{4\xi} + Z_1\right]M(\xi) = 0, \quad (2)$$