

Positronium-hydrogen scattering using the stochastic variational method

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The stochastic variational method (SVM) is used in conjunction with stabilization ideas in order to compute low-energy phase shifts. The method is tested by applying it to a simple model problem, and to s -wave positron-hydrogen scattering. The SVM is then applied to the calculation of the s - and p -wave phase shifts for Ps-H scattering. The scattering lengths obtained were $4.34a_0$ for the electronic-spin-singlet state and $2.22a_0$ for the triplet state. The present scattering lengths are probably accurate to $\pm 3\%$ and are the most accurate that have so far been computed for the Ps-H systems.

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I. INTRODUCTION

One of the most difficult problems in atomic collision theory is the positronium-atom scattering problem since both the projectile and the target are composite objects with an internal structure. This means that the interaction matrix elements involve multicenter integrals that are very difficult to evaluate [1]. The sources of concern are the matrix elements describing the exchange interaction between the electrons in the target and the electron forming part of the positronium and matrix elements describing the van der Waals interaction between the positronium (Ps) projectile and the atomic target. These difficulties mean that considerable uncertainties exist even for the simplest of Ps-atom scattering systems, namely, the Ps-H system. Although Ps-H scattering has been the subject of numerous theoretical investigations [2–13], the results of these many investigations have given somewhat conflicting results and the scattering length is not known with any degree of precision.

In the present paper, the stochastic variational method (SVM) [14–18] is applied to the calculation of low-energy Ps-H scattering. The SVM uses explicitly correlated Gaussians (ECGs) as basis functions and has the advantage that it is relatively easy to evaluate all of the multicenter matrix elements. The method as applied uses stabilization ideas [2,19–22] to extract the phase shifts from the positive-energy pseudocontinuum that results from the SVM diagonalization of the Hamiltonian. Since the dimension of the final ECG basis was relatively large (of order 10^3) it is expected that the resulting scattering lengths should be close to the variational limit. An earlier version of the calculation has been presented in abbreviated form [23].

The original idea behind the stabilization method is that the positive-energy pseudostates of a bound-state calculation give a reasonable approximation to the exact scattering wave function [2,19,20]. Further research has shown that while the

convergence of the pseudostate to the continuum wave function is relatively slow, matrix elements formed by the pseudostate often have reasonable convergence properties [21]. In effect, while the point-wise properties of the wave function can be inaccurate, the convergence in the mean of the wave function over a suitable range can be quite good.

In the original application of the stabilization method to Ps-H scattering [2], the positive-energy pseudostate was projected onto the product of the Ps and H ground states as a function of R , the distance between Ps and H center of masses. The amplitude and phase shift of this projected wave function were found to be stable for R between $5a_0$ and $10a_0$. The phase shift determined from this region of the projection was taken to represent the asymptotic phase and used in the determination of the scattering length and effective range. The determination of the “stable region” does depend to a certain extent on a subjective judgement. Therefore, a modified version of the stabilization method has been developed that does not look for a stable region, but instead fits the wave function to a predetermined region of r space just outside the interaction volume.

The reliability of the stabilization method is first tested by applying it to a simple model problem. An application to a physical situation with complicated interparticle interactions, namely, positron-hydrogen scattering is then made as a further and more demanding test. Finally the method is applied to Ps-H scattering and phase shifts for the $L=0$ and $L=1$ partial waves are determined.

II. DESCRIPTION AND TESTS OF THE STABILIZATION METHOD

A. Test for the exponential potential

1. s -wave scattering

Consider the scattering problem for the Hamiltonian,

$$\hat{H} = -\frac{\nabla^2}{2} - V_0 \exp(-r). \quad (1)$$

The parameter V_0 of the exponential potential was chosen at $V_0=1.4$ and this potential has a bound state with the energy

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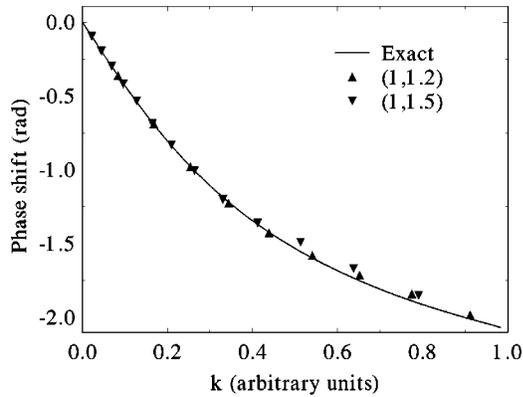


FIG. 1. The comparison between the exact s -wave phase shift (modulo π) and phase shifts extracted from the positive-energy pseudostates for the model problem given by Eq. (1). The up triangles represent a basis with $N=26$, $\alpha_1=1.0$, $T=1.5$ the down triangles represent a basis with $N=20$, $\alpha_1=1.0$, $T=1.2$, while the solid curve represents gives the exact phase shift.

$E = -0.0521420446$. For $L=0$ the Schrödinger equation corresponding to Eq. (1) can be solved exactly [24] giving for the Jost function

$$F(k) = \exp[ik \ln(2V_0)] \Gamma(1-2ik) J_{-2ik}(2^{3/2}V_0). \quad (2)$$

Correspondingly the s -wave phase shift

$$\delta(k) = \frac{1}{2i} \ln \left[\frac{F^*(k)}{F(k)} \right]$$

can be written as an effective-range expansion,

$$k \cot \delta(k) = -\frac{1}{A} + \frac{1}{2} r_0 k^2 + O(k^4), \quad (3)$$

where the scattering length $A=4.409306$ and the effective range $r_0=1.7576088$.

The model Hamiltonian (1) was diagonalized in an even tempered basis of the Gaussians $\exp(-\alpha_i r^2)$ obeying,

$$\alpha_i = \frac{\alpha_1}{T^{i-1}}. \quad (4)$$

Two calculations were performed. In the first calculation, the Hamiltonian was diagonalized in a basis of 26 Gaussians with $\alpha_1=1.0$ and $T=1.5$. In the second calculation, the dimension of the basis was 20, $\alpha_1=1.0$, and $T=1.2$. A least-squares fit of the positive-energy eigenstates to $B \sin(kr + \delta_0)$ was performed over the interval $r \in [10, 25]$.

The phase shifts obtained as a result of the fit are presented in the Fig. 1 together with the exact phase shifts. Agreement between both calculations and the exact results is nearly perfect for $k < 0.4$. For the larger k values, both sets of phase shifts tend to slightly overestimate the exact phase shift, with the discrepancies for the $T=1.5$ calculation being slightly larger.

Another test of the fitting procedure is to extract the scattering length and effective range from the computed phase

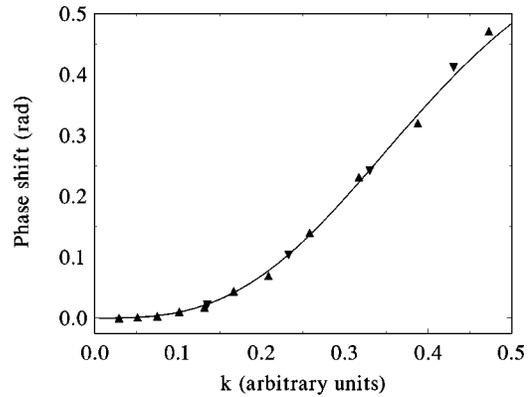


FIG. 2. The comparison between the exact p -wave phase shift and phase shifts extracted from the positive-energy pseudostates for the model problem given by Eq. (1). The up triangles represent a basis with $N=26$, $\alpha_1=3.84$, $T=1.4$, the down triangles represent a basis with $N=20$, $\alpha_1=2.85$, $T=1.30$, while the solid curve represents gives the exact phase shift.

shifts. Accordingly, a least-squares fit of the L^2 phase shifts to Eq. (3) was done for $k < 0.4$. The $T=1.2$ basis set had five points below $k < 0.4$ while the $T=1.5$ basis had ten points in this range. For $T=1.2$ the scattering length was $4.4090a_0$ and the effective range was 1.752. For $T=1.5$ the scattering length was 4.4086 and the effective range was 1.718. The scattering lengths of both calculations are within 0.05% of the exact result. The agreement with the exact value of the effective range is not so good, but is still of order 1%. Although it is not clear from Fig. 1 both sets of phase shifts tend to fluctuate about the effective-range fit with the fluctuations being slightly larger for the $T=1.5$ basis.

In general, there are two conflicting criteria that drive the choice of basis. The first is the desire to have a basis as large as possible. Given the effects of creeping linear dependence associated with a Gaussian basis, this would suggest using a larger value of T . However, the results of the numerical experiments have shown that a Gaussian basis with a smaller T generally gives phase shifts that have smaller fluctuations and are generally more accurate. The “denser” set of Gaussians seems to do a better job of approximating the wave function in the region used to match the wave function to its asymptotic form.

2. p -wave scattering

The model Hamiltonian was also diagonalized for the $L=1$ partial wave. The basis functions in this case were not simple Gaussians, rather they were Gaussians multiplied by r . Two calculations were once again done to illustrate the impact that different basis parameters have on the computed phase shifts. In the first case, the basis had $\alpha_1=2.85$, $T=1.3$, and dimension 20. In the second case, $\alpha_1=3.84$, $T=1.4$, and the dimension was 26. Once again a least-squares fit of the L^2 pseudostate was made to the asymptotic form for $L=1$, the regular and irregular spherical Bessel function of order 1. The results of these calculations are compared with the close to exact phase shifts obtained by numerical integration in Fig. 2.

Both L^2 calculations tend to follow the exact phase shifts as a function of k . However, the fluctuations of the L^2 phase shifts about the exact phase shift are larger than those for the s wave. When the exact phase shifts are fitted to the p -wave effective-range formula,

$$k^3 \cot \delta_1(k) = -\frac{1}{A_1} + \frac{1}{2} r_1 k^2 + O(k^4), \quad (5)$$

the parameters were $A_1=9.798$ and $r_1=0.1321$. A least-squares fit of the L^2 values of $k^3 \cot \delta_1(k)$ to Eq. (5) was done using all points with $k < 0.4$. The resulting effective-range parameters were $A_1=9.811$ and $r_1=0.2124$ for the basis of dimension 20 and $A_1=8.5309$ and $r_1=0.1374$ for the basis with dimension 26. The rather inaccurate value of A_1 for the basis with dimension 26 arose from the first few values of the phase shift that were rather small, typically being less than 0.01 rad. While the absolute error in the L^2 phase shifts was small, the relative errors were of order 20%. Discarding the first four L^2 phase shifts with the lowest momentum improved the accuracy and gave $A_1=9.478$ and $r_1=0.1988$ for the basis with 26 Gaussians.

The following general conclusions can be drawn. The overall quality of the L^2 phase shifts is not as good for the p wave as they were for the s wave. The relative errors in the computed phase shifts are larger for the low-momentum pseudostates. And once again, the basis with the smaller value of T does a better job at reproducing the exact phase shift.

B. Tests for positron-hydrogen scattering

Another and more exact test system for the current L^2 method is the positron-hydrogen system. This system is characterized by strong electron-positron correlations and, therefore, the successful prediction of the phase shifts requires a basis that gives a good representation of the wave function at small distances.

Configuration space was divided into an inner or interaction region and an outer or scattering region. In the inner region, the SVM is then used to construct a basis (dimension= K) of ECGs [15]. The spatial part of an ECG can be written as

$$G(\mathbf{x}, A^i) = \exp\left(-\frac{1}{2} \sum_{\mu, \nu=1}^{N-1} A^i_{\mu\nu} \mathbf{x}_\mu \cdot \mathbf{x}_\nu\right) = \exp\left(-\frac{1}{2} \mathbf{x}^T \cdot A^i \mathbf{x}\right), \quad (6)$$

where \mathbf{x} is the vector of Jacobi coordinates. One does an SVM calculation that aims to minimize the energy of the lowest-energy pseudostate. However, the exponents, α_i of the Gaussians connecting the electron and positron to the nucleus were restricted to be larger than a certain minimum size, say $\alpha_i > 0.01$. This constrained the electron and positron to be localized reasonably close to the nucleus and resulted in a SVM iteration procedure that effectively solves the Schrödinger equation in some sort of box. The inner basis is designed to give a good representation of the interactions between the electron and positron close to the nucleus.

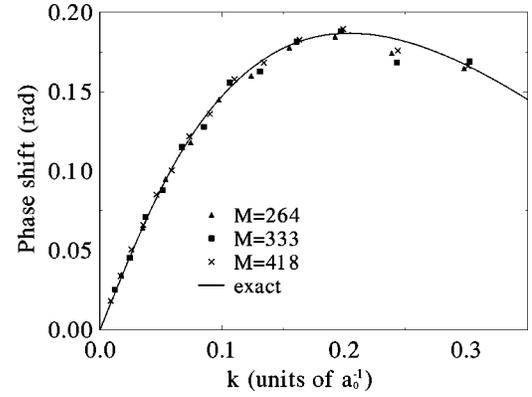


FIG. 3. The s -wave phase shifts (modulo π) for e^+ -H scattering as a function of k (in terms of a_0^{-1}). The discrete points represent the phase shifts from the $M=264$, 333, and 418 basis-set calculations. The solid line represents a continuous fit to phase shifts taken from a large-scale close-coupling calculation [27] that are about 0.5% below the close to exact phase shifts of Bhatia *et al.* [26].

Once the inner wave function has been obtained, a set of ECGs designed to represent the positive energy e^+ +H breakup was added to the basis. First an eight-Gaussian representation of the (infinite mass) H ground state was constructed (energy= -0.49999446 hartree). Then a series of ECGs were constructed by multiplying the H Gaussians to an evenly tempered set of Gaussians representing the positron motion. These basis functions are written as

$$\Psi_{out}^{ij} = \exp(-\alpha_i r_0^2) \phi_H^j(\mathbf{r}_1), \quad (7)$$

where \mathbf{r}_0 is positron coordinate and \mathbf{r}_1 is the electron coordinate. The $\phi_H^j(\mathbf{r}_1)$ are individual Gaussians from the superposition used to describe the H ground state.

The inner and outer basis functions were then checked for linear dependence and ECGs having large overlaps with existing basis functions were excluded giving a final basis of dimension M . The basis was diagonalized by standard techniques and the phase-shift information extracted by doing a least-squares fit of the projection,

$$P(r_0) = \int d^3 r_1 \Phi(\mathbf{r}_0, \mathbf{r}_1) \Psi_H(\mathbf{r}_1), \quad (8)$$

to $B \sin(kr_0 + \delta_0)$ over $R \in [10, 25] a_0$ [25].

Three calculations were performed. In the first, $K=120$, $\alpha_1=0.50$, $T=1.45$, $\alpha_{20}=4.3 \times 10^{-4}$, and $M=264$. In the second, $K=150$, $\alpha_1=1.52$, $T=1.45$, $\alpha_{25}=2.03 \times 10^{-4}$, and $M=333$. The final calculation had $K=200$, $\alpha_1=4.65$, $T=1.45$, $\alpha_{30}=9.72 \times 10^{-5}$, and $M=418$. The phase shifts of all three L^2 calculations are shown together in Fig. 3, and compared with phase shifts from a large basis close-coupling calculation [27]. The L^2 phase shifts are generally seen to lie close to the exact phase shifts. At the larger k values there is a tendency for the SVM phase shifts to fluctuate about the exact phase shifts.

The SVM phase shifts were fitted to the effective-range expansion [29,30]

$$\tan \delta(k) = -Ak - \frac{\alpha_d \pi k^2}{3} - \frac{4A \alpha_d k^3}{3} \ln k^2 + Bk^3 + Ck^4 \quad (9)$$

over the $k \in [0.0, 0.18] a_0^{-1}$ interval in order to derive the scattering lengths. The SVM scattering lengths for the $M = 264, 333,$ and 418 basis sets were $-2.092a_0,$ $-2.096a_0,$ and $-2.119a_0,$ respectively. All of these scattering lengths are within a percent of the accepted value of the scattering length, namely, -2.104 [28].

On the basis of the test calculations for the exponential potential and positron-hydrogen system it appears that the simple stabilization method is capable of predicting the scattering length at an accuracy level of about 1%.

III. RESULTS AND DISCUSSION FOR Ps-H

The procedure used to generate the inner wave function depended on whether the two electrons were in a spin-singlet or a spin-triplet configuration. The Ps-H system supports a bound state in its singlet configuration. Therefore the inner wave function was simply computed by doing a standard SVM calculation of the Ps-H bound state (no calculation had to be done as stored Ps-H basis sets existed from previous investigations [18,31]). The triplet Ps-H configuration does not have a bound state and an SVM calculation minimizing the energy of the lowest-energy pseudostate with the Gaussian exponents connecting the electron and positron to the nucleus constrained to be larger than 0.01 was used to define the inner basis.

The outer basis functions, designed to represent the positive-energy Ps-H breakup, was constructed from a (properly symmetrized) set of the functions written as

$$\Psi_{out}^{ijk} = \exp(-\alpha_i R^2) \phi_{Ps}^j(\mathbf{r}_0, \mathbf{r}_1) \phi_H^k(\mathbf{r}_2). \quad (10)$$

Here \mathbf{r}_0 is positron coordinate, R is the relative distance between the Ps and H centers of mass, and the \mathbf{r}_i ($i > 0$) are the electron coordinates. The $\phi_{Ps}^j(\mathbf{r}_0, \mathbf{r}_1)$ [the $\phi_H^k(\mathbf{r}_2)$ term has been described previously] are individual Gaussians from the superposition used to represent the Ps ground state (the energy of the eight-term superposition was -0.24999723 hartree). The exponents, i.e., α_i form an even tempered sequence.

Two different approaches can be used to extract the phase shifts from the positive-energy pseudostates. In the first, the overlap integral between the antisymmetrized product of the Ps and H ground states, $\delta((\mathbf{r}_0 + \mathbf{r}_1)/2 - \mathbf{R}) \Psi_H(\mathbf{r}_2) \Psi_{Ps}(\mathbf{r}_0, \mathbf{r}_1)$, with the positive-energy pseudostate $\Phi(\mathbf{r}_0, \mathbf{r}_i)$ was computed at a succession of values of R . Then a least-squares fit over the $R \in [10, 25] a_0$ interval to $B \sin(kR + \delta_0)$ was used to extract the phase shift [32].

In the second, the positron-nucleus correlation function defined by

$$C(x) = 4\pi x^2 \int d^3 r_i d^3 r_0 \delta(\mathbf{r}_0 - \mathbf{x}) |\Phi(\mathbf{r}_0, \mathbf{r}_i)|^2 \quad (11)$$

is computed for a succession of x values and fitted to $B \sin^2(kx + \delta_0)$ [32] over $x \in [10, 25] a_0$ (the electron-proton correlation function could also be used since it was usually within 0.1% of the positron-proton correlation function).

The two approaches of extracting the phase shifts generally gave phase shifts in good agreement. Formal considerations suggest that the projection approach is to be preferred, but it is also possible to use the simpler method based on the proton-positron correlation function without introducing a major error. For example, the singlet Ps-H scattering length computed by the two approaches differed by 1%. The SVM phase shifts for the s wave were computed with the projection method while the p -wave phase shifts were extracted from the correlation function.

A. The $L=0$ phase shifts

In order to make sense of the different calculations and relate them to each other in a sensible manner a brief review of the existing calculations is in order. The scattering lengths and effective ranges, for scattering in the electron-spin singlet and triplet states are listed in Table I.

In spite of recent activity, some of the best calculations were done more than 20 years ago. One of the most important calculations was the static-exchange calculation of Hara and Fraser [3] since it provides a reference point against which other calculations may be compared and can also be used to validate the more modern calculations. The variational calculation of Page [4] went beyond the static-exchange approximation as the trial wave function allows for distortions in the Ps projectile, however, this calculation did not allow for distortions in the hydrogen target. Drachman and Houston [2] used a stabilization approach to extract the phase shift from a trial wave function not much more sophisticated than that of Page. However, they also computed the binding energy of the Ps-H ground state using their trial wave function, and by comparing with an accurate Ps-H binding energy they were able to make an estimate of the singlet scattering length ($\sim 4.5a_0$) that would be expected from a close to converged calculation.

Campbell *et al.* have used the R -matrix method [5] to perform a series of calculations with a variety of channel spaces. The fact that their static-exchange scattering length agrees with the earlier determination of Hara and Fraser [3] suggests that they have correctly evaluated the difficult to compute Ps-H exchange matrix elements. The difficulties associated with matrix-element evaluation mean that they were not able to include target (i.e., H) excitations in their channel space, but within this restriction they use 22 Ps-type pseudostates to allow for distortion of the Ps projectile and in this respect their calculations are probably close to converged. However, the omission of hydrogen target excitations means that the calculation does not incorporate the van der Waals interaction between the Ps and H atoms. Therefore the 22-state R -matrix singlet scattering length of $5.20a_0$ is expected to be too large. This is confirmed by the fact that the 22-state R -matrix basis gives a Ps-H binding energy that is only about 60% of the accurate binding energy [31].

The momentum-space Lippmann-Schwinger equations for Ps-H scattering for various combinations of Ps and H chan-

TABLE I. Scattering length and effective range (in terms of a_0) for a number for Ps-H scattering calculations.

Method	Singlet		Triplet	
	A^s	r_0^s	A^t	r_0^t
Variational static exchange [3]	7.28		2.48	
Variational stabilization [2]	5.33	2.56	2.36	1.31
Variational stabilization (extrapolated) [2]	4.5	2.2		
Kohn variational [4]	5.84		2.32	
Kohn variational [10]	3.49 ± 0.20		2.46 ± 0.10	
T -matrix static exchange ^a [6]	~ 7.1		~ 2.5	
T -matrix 3 Ps states [8]	6.80	3.05	2.39	1.27
T -matrix Ps($1s, 2s, 2p$) + H($1s, 2s, 2p$) states ^b [8]	5.90	2.73	2.32	1.29
T -matrix 6 H pseudostates [9]	5.22	2.74	2.41	1.32
T -matrix static (model) exchange [11]	4.05	1.82	1.83	
T -matrix 3 Ps, 2 H states model exchange ^c [11]	3.72	1.67	1.68	
R -matrix static exchange [5]	7.25	3.07	2.49	1.36
R -matrix 9 Ps pseudostates [5]	5.51	2.63	2.45	1.33
R -matrix 22 Ps pseudostates [5]	5.20	2.52	2.45	1.32
Previous (superseded) SVM [23]	4.3		2.2	
Present SVM	4.34	2.39	2.22	1.29

^aThe static exchange scattering lengths of Ghosh were estimated from their phase shifts using Eq. (3).

^bThe basis consists of the H($1s$)Ps($1s$), H($1s$)Ps($2s$), H($1s$)Ps($2p$), H($2s$)Ps($1s$), H($2s$)Ps($2s$), H($2s$)Ps($2p$), H($2p$)Ps($1s$), H($2p$)Ps($2s$), and H($2p$)Ps($2p$) states.

^cThe basis consists of the H($1s$)Ps($1s$), H($1s$)Ps($2s$), H($1s$)Ps($2p$), H($2s$)Ps($1s$), and H($2p$)Ps($1s$) states.

nels were also solved by Ghosh and co-workers [6–9]. Their static-exchange estimates of the scattering lengths are certainly compatible with the variational [3] and R -matrix [5] values. Ghosh and co-workers have used relatively small channel spaces and their scattering lengths are far from convergence.

The recent calculations by Adhikari and Biswas [11] are somewhat difficult to categorize. They write the close coupling equations for Ps-H scattering as a momentum space Lippmann-Schwinger equation. The manner in which the Ps-H exchange interaction is treated has resulted in their static-exchange scattering lengths being much smaller than those quoted by other groups. They replaced the Ps-H exchange interaction by a model potential rather than attempting to calculate the exact matrix element explicitly. However, they do not fix the adjustable parameter in their model interaction by normalizing to previous static-exchange phase shifts, instead they fix the parameter to the most precise estimate of a singlet s -wave resonance [34] (since the parameter is fixed to a singlet resonance position there is no guarantee that the model potential will be reliable in the triplet channel). This procedure is problematic since it is done in the context of a relatively small coupled channels calculation [the H($1s$)Ps($1s$), H($1s$)Ps($2s$), H($1s$)Ps($2p$), H($2s$)Ps($1s$), and H($2p$)Ps($1s$) states] that cannot be expected to correctly predict the scattering length, resonance energy, and Ps-H binding energy. In effect, Adhikari and Biswas are also using the model potential to compensate for a limited channel space that only allows for the lowest Ps(nl) and H(nl) excitations. Thus, the resulting calculation of the

singlet scattering length is more akin to a fit to external data rather than an *ab initio* prediction. It is clear that the model potential of Adhikari and Biswas would significantly overestimate the Ps-H binding energy if a larger channel space was used.

A recent Kohn variational calculation of the Ps-H scattering length by Adhikari and Mandal is also problematic [10]. Although it is stated that the singlet scattering length of $(3.49 \pm 0.20)a_0$ is converged, the manifest fluctuations in their different calculations suggest that this result be treated with caution. As part of their calculation scheme, they expand certain difficult to compute matrix elements in a partial wave sum that may be prematurely truncated. Furthermore, the triplet scattering length of Adhikari and Mandal of $(2.46 \pm 0.10)a_0$ can also be discounted since their minimum scattering length is actually larger than some previous estimates. It is noted that Adhikari and Mandal also use a similar partial wave expansion to evaluate the the Ps-H elastic scattering cross section in the Born-Oppenheimer approximation [13]. Their cross sections are at variance [13] with the Born-Oppenheimer calculation of Ray and Ghosh [6]. However, the static Born-Oppenheimer (BO) matrix elements of Ray and Ghosh would seem to be reliable [33]; the BO matrix elements are an essential ingredient of their static-exchange calculations and as mentioned earlier, the Ray-Ghosh static-exchange phase shifts agree with variational [3] and R -matrix calculations [5]. The available evidence suggests that there may be systematic errors in the Adhikari and Mandal calculation associated with their evaluation and/or truncation of the partial wave sum.

The present SVM calculation used an inner basis for the spin-singlet channel that was based on an existing Ps-H basis with dimension $K=450$ that gave an energy of -0.789190 hartree. The outer wave function consisted of ten groups of Ps($1s$)-H($1s$) product ECGs with $\alpha_1=0.1$ and $T=1.3$. Some experimentation with different values of α_1 and T had been done and the smaller value of T gave the smoothest set of phase shifts. Linear-dependence problems prevented the use of a T value smaller than 1.3. The final dimension for the singlet case was $M=1083$. The inner basis for the triplet configuration had a dimension of $K=350$. A total of ten groups of Ps-H outer basis functions were used for the triplet case and the final basis size was $M=968$.

Figure 3 shows the phase shifts for Ps-H scattering in the singlet configuration. The scattering length and the effective range were determined by doing a least-squares fit to Eq. (3) using the first six values of the phase shift. The values were

$$A^s = 4.34a_0 \quad \text{and} \quad r_0^s = 2.39a_0. \quad (12)$$

The estimated uncertainty in A^s is probably about $\pm 0.1a_0$ or better and the estimated uncertainty in r_0^s was $\pm 0.1a_0$. The overall uncertainty in the scattering length is probably not much larger than the uncertainty due to the fit (this point is discussed later).

The fit to the triplet configuration data using the first five phase shifts gave

$$A^t = 2.22a_0 \quad \text{and} \quad r_0^t = 1.29a_0. \quad (13)$$

The uncertainty in the scattering length was about $\pm 0.05a_0$ while the uncertainty in the effective range was probably about $\pm 0.5a_0$. The determination of the effective range in this case was problematic since it was relatively small and, therefore, did not have much of an effect on the phase shifts for the energies considered.

As expected, the present calculations of the scattering length, based on larger variational expansions than used previously, give slightly smaller scattering lengths than earlier *reliable* calculations (we do not regard the calculations by Adhikari and co-workers [11,10] as being reliable and they are discounted from the present discussion). The scattering length for the triplet channel is only about 5–10% smaller than the earlier calculations, consistent with the observation that the convergence of the triplet scattering length is relatively fast [2,5]. Prior to the present calculation, the lowest explicitly calculated singlet scattering length was that arising from the 22-state R -matrix calculation that gave a value of $5.20a_0$. That the present L^2 calculation gives a scattering length about 20% smaller is to be expected since the present ECG basis gives a close to exact representation of the Ps-H ground state. One of the most interesting comparisons is with the earlier variational-stabilization calculation of Drachman and Houston [2]. The scattering length and effective range they obtained when they performed an extrapolation on their limited basis calculation, namely, $4.5a_0$ and $2.2a_0$ respectively, are amazingly close to the present SVM phase shifts.

The conclusion to be drawn from the entire set of scattering lengths presented in Table I is that a consistent pattern,

relating scattering length to the sophistication of the calculation is beginning to emerge. The present scattering length is compatible with the calculations of the Ghosh and co-workers [6–8] and Campbell *et al.* when the additional variational flexibility of the present calculation is taken into consideration. The present calculation is rather unorthodox and this naturally raises the question as to what extent the SVM scattering lengths can be believed. Our original calculations of the Ps-H phase shifts performed in Ref. [23] aimed for an accuracy level of 5%. Subsequent calculations performed since then have revealed that these phase shifts are very stable to variations in the inner and outer basis. (Deficiencies in the outer basis also tend to reveal themselves with fluctuations in the phase shifts and the fluctuations that do occur are hardly noticeable in Fig. 3). The present phase shifts are hardly different from those reported in Ref. [23]. The major factor leading to the more precise estimate of the scattering length in Table. I, that supersedes our earlier value in Ref. [23], was the use of a better effective range expansion ([23] only used included the scattering length as an adjustable parameter). On the basis of the available evidence, there is no reason to disbelieve the conclusion that the present SVM scattering lengths have an overall accuracy of about 3%.

B. The $L=1$ phase shifts

The phase shifts for the p wave have not received the same degree of attention as the s wave. However, tables and plots of phase shifts have been reported by Ghosh and co-workers [6–8].

The present SVM calculation utilized the generalized vector representation developed to study bound states with non-zero angular momentum [15]. In this representation the angular momentum of the individual fragments, and the relative angular momentum between them is specified. The inner basis used in the present calculations was constructed from all allowable fragments with Ps, H, and relative angular momentum restricted to be less than 2. The total dimension of the basis was $K=500$ for the spin-singlet case and $K=500$ for the spin-triplet case. The outer basis was constructed from 12 groups of ECGs with $\alpha_1=0.3$ and $T=1.30$. The final dimensions of the basis for the singlet and triplet cases were $M=1332$. We estimate that the phase shifts are converged to within 5% with respect to further enlargement of the basis.

The p -wave phase shifts for both the singlet and triplet channels are shown in Fig. 4. As expected, the present SVM phase shifts are more positive than those of the three state H($1s$)Ps($1s$)+H($1s$)Ps($2s$)+H($1s$)Ps($2p$) model calculation of Sinha *et al.* [7]. The present SVM phase shifts are almost twice as large as the three-state phase shifts. However, the difference in phase shifts for the two triplet-model calculations is hardly noticeable. The more rapid convergence of the triplet-channel phase shifts is something that was noted for the s wave (Fig. 5).

A least-squares fit of Eq. (5) was made to the present SVM phase shifts. The effective range parameters for the singlet channel were

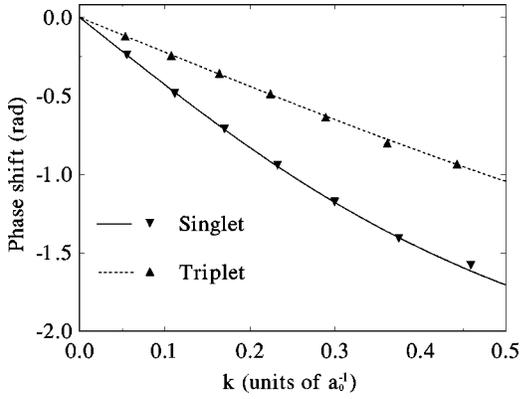


FIG. 4. The s -wave phase shifts (modulo π) for Ps-H scattering as a function of k (in terms of a_0^{-1}). Phase shifts are shown for the singlet and triplet electron-spin configurations. The lines represent effective range fits to the phase shifts using Eq. (3).

$$A_1^s = -20.7a_0^3 \quad \text{and} \quad r_1^s = 0.0416a_0^{-1}. \quad (14)$$

For the triplet channel they were

$$A_1^t = 6.80a_0^3 \quad \text{and} \quad r_1^t = -4.07a_0^{-1}. \quad (15)$$

The solid lines in Fig. 4 were computed from these effective range parameters. The parameters A_1^s and A_1^t are extracted with an accuracy of about 5–10%. The uncertainties in r_1^s and r_1^t are of the order of size of the quantity itself since the impact this term has on the phase shifts is roughly the same size as the fluctuations in the phase shift. The phase shift represented by the continuous lines in Fig. 4 probably have an overall accuracy of about 5–10% when the limitations of the basis and the inaccuracies inherent to the L^2 method are taken into consideration.

One of the problems with the present L^2 approach to Ps-H scattering is that the phase shifts are computed at energies

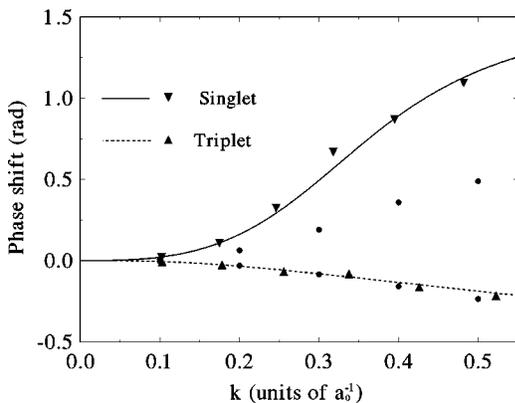


FIG. 5. The p -wave phase shifts for Ps-H scattering as a function of k (in terms of a_0^{-1}). Phase shifts are shown for the triplet electron-spin configuration. The lines represent effective range fits to the phase shifts using Eq. (5). Phase shifts from a three Ps-state close-coupling expansion [7] are shown for comparison as filled circles (●).

that cannot be determined in advance. This means that the L^2 phase shifts cannot be combined directly to compute the integral cross sections. In order to compute cross sections from the present paper it is necessary to use the s - and p -wave effective-range parameters to first compute the phase shifts at common energy points and then use these phase shifts to compute the cross section.

IV. SUMMARY

The stochastic variational method has been adapted to the calculation of the $L=0$ and $L=1$ phase shifts for Ps-H scattering in both the singlet and triplet electron-spin configurations. The philosophy behind the present L^2 method has been one of utter simplicity. Rather than add further sophistication and additional complications to the method, the aim has been to keep the calculations as simple as possible. The test cases that have been examined suggests that this primitive L^2 approach is able to generate phase shifts that are accurate at the 1% level. One of the most significant features of the present set of calculations is the speed with which they were performed. For example, the net CPU time for a single diagonalization of the Ps-H basis was about 1 h on a five year of workstation. The subsidiary calculations required to project the wave function onto its asymptotic form and to then extract the phase shift take hardly any time at all. The ability to compute scattering lengths for Ps-atom scattering relatively quickly obviously represents a major advance in the treatment of Ps-atom collisions.

There is certainly room for improvement in applying the SVM to scattering problems. One obvious possibility would be using linear combinations of ECGs rather than individual ECGs in the basis set designed to represent the asymptotic solution. The chief numerical limitations in applying the method were due to linear dependence issues. This problem could be eliminated, by replacing Eq. (7) by the products of Ps and H wave functions, i.e., to replace 8×8 ECGs by a single basis function written as a linear combination of 64 ECGs.

The main limitation of the present method is that it is limited to the elastic scattering region, i.e., it cannot be applied to energy regions with more than one open scattering channel. However, within this restriction it can be usefully applied to scattering problems that are very difficult to handle with conventional scattering techniques.

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