Positron Scattering and Annihilation from the Hydrogen Molecule at Zero Energy

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The confined variational method is used to generate a basis of correlated Gaussians to describe the interaction region wave function for positron scattering from the H_2 molecule. The scattering length was $\approx -2.7a_0$ while the zero energy $Z_{\rm eff}$ of 15.7 is compatible with experimental values. The variation of the scattering length and $Z_{\rm eff}$ with internuclear distance was surprisingly rapid due to virtual state formation at $R \approx 3.4a_0$.

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The lack of spherical symmetry makes the calculation of electron or positron scattering from molecules an especially intractable computational problem. The nonspherical potential couples different partial waves resulting in an enormous escalation in the size of the calculation when compared with atomic targets. One consequence of this is that it is difficult to identify a definitive calculation of low energy electron or positron scattering from the simplest of molecules, i.e., H_2, even under the simplifications of the fixed nucleus approximation.

A new approach to compute the wave function for electron or positron scattering from small molecules is developed. It utilizes existing computational technologies from few-body physics that had been used to describe the low energy scattering of simple and composite projectiles from atoms [1–3]. The method is applied to the calculation of positron scattering from the H_2 molecule. The cross section for positron annihilation at thermal energies was found to be compatible with experimental values [4–6]. This is a significant achievement since the annihilation cross section presents a stringent test to the accuracy of the scattering wave function [7] and its successful prediction solves a previously intractable problem. Our calculations also show the existence of an unexpected virtual state at a H_2 internuclear distance of $R \approx 3.4a_0$.

There have been a number of calculations of low energy e^+-H_2 scattering and annihilation [7–11]. At present, all previous calculations significantly underestimate the low energy annihilation cross section. The most sophisticated calculations are the Kohn variational calculations performed by Armour and colleagues at the University of Nottingham (UN) [9,11,12]. Their most recent calculations significantly underestimate the annihilation cross section at thermal energies.

We apply a variant of the confined variational method (CVM) [1,2] to describe low energy positron-H_2 scattering. In the CVM, an artificial confining potential is added to the scattering Hamiltonian thus converting the system into a bound system. This provides a framework that permits the wave function in the interaction region to be obtained with bound state techniques. Of crucial importance to this exercise is the use of the stochastic variational method (SVM) [13–15] to describe the interaction region wave function. The SVM and variants [16] constitute a powerful tool for studying few-body systems. The SVM uses a wave function that is a linear combination of explicitly correlated Gaussians (ECGs) which have easy to evaluate Hamiltonian matrix elements [14,17]. Therefore it is feasible to optimize the nonlinear parameters of the basis stochastically. Application to molecular systems is easy and ECGs have been recently used to describe the wave functions of a number of small molecules to high accuracy [18]. The close to zero energy scattering parameters were extracted from the interaction region by a stabilization technique [1] and a technique based on the energy [19].

The calculation of the interaction region wave function proceeded in a manner that was very similar to previous ECG based calculations on collision systems [1,3]. The Hamiltonian for e^+-H_2 scattering was

$$
\begin{aligned}
H = & -\sum_{i=0}^{2}\frac{\nabla_i^2}{2} + \sum_{i=0}^{2} W_{\rm CP}(r_i) - \frac{1}{|\mathbf{r}_0-\mathbf{r}_1|} - \frac{1}{|\mathbf{r}_0-\mathbf{r}_2|} \\
& + \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + \frac{1}{|\mathbf{r}_0-\mathbf{R}/2|} + \frac{1}{|\mathbf{r}_0+\mathbf{R}/2|} \\
& - \frac{1}{|\mathbf{r}_1-\mathbf{R}/2|} - \frac{1}{|\mathbf{r}_1+\mathbf{R}/2|} - \frac{1}{|\mathbf{r}_2-\mathbf{R}/2|} \\
& - \frac{1}{|\mathbf{r}_2+\mathbf{R}/2|} + \frac{1}{R}. \qquad (1)
\end{aligned}
$$

The positron coordinate is $\mathbf{r}_0$ while $\mathbf{r}_1$ and $\mathbf{r}_2$ are the electron coordinates. The vector $\mathbf{R}/2$ is the displacement of the two protons from the midpoint of the molecular axis. The confining potential $W_{\rm CP}(r)$ has the form

$$W_{\rm CP}(r) = G(r-R_0)^2\Theta(r-R_0), \qquad (2)$$

where $\Theta(r - R_0)$ is a Heaviside function and G is a small positive number.

The first stage of the diagonalization of Eq. (1) was to use the SVM to generate an interaction region basis of energy optimized ECGs. The ECGs were a generalization of those used previously in purely atomic calculations [16]. Their functional form was

$$\phi_k = \hat{P}\exp\left(-\frac{1}{2}\sum_{i=0}^{2} b_{k,ij}|\mathbf{r}_i - \mathbf{S}_{k,i}|^2\right) \times \exp\left(-\frac{1}{2}\sum_{i=0}^{1}\sum_{j=i+1}^{2} a_{k,ij}|\mathbf{r}_i - \mathbf{r}_j|^2\right). \qquad (3)$$

The vector $\mathbf{S}_{k,i}$ displaces the center of the ECG for the ith particle to a point on the internuclear axis. This ensures the three-particle wave function is of Σ symmetry. The values of $a_{k,ij}$, $b_{k,ij}$, and $\mathbf{S}_{k,i}$ are adjusted during the optimization process. The operator $\hat{P}$ is used to enforce Σ_g symmetry. Each ECG has a total of nine stochastically adjustable parameters.

Table I lists the energy of the confined e^+-H_2 system for a succession of basis sets. These energies were generated with the confining potential parameters $G = 1.55 \times 10^{-4}$ and $R_0 = 18.0a_0$. The internuclear separation was set to $1.40a_0$ which is very close to the position of the minima in the H_2 potential curve.

Extracting scattering information requires embedding the interaction region wave function into a formalism for $e^{\pm}$-H_2 scattering. However, one of our major aims is to demonstrate that ECG technologies make it easy to get a good description of the e^+-H_2 collision dynamics. Accordingly, attention is focused on the very low energy region where the outgoing wave is essentially spherical.

There are two advantages to restricting the current calculation to very low energy. First, the most reliable experimental information comes from traditional positron annihilation experiments using thermal positrons that yield annihilation cross sections at very low energies [20]. Second, the collision can be treated as s-wave scattering and thus the molecular aspects of the asymptotic wave function can be neglected with minimal error.

Positron annihilation cross sections are reported as $Z_{\rm eff}$, which is interpreted as the number of electrons available for annihilation. The annihilation cross section and $Z_{\rm eff}$ are related by the identity

$$Z_{\rm eff}(k) = \frac{kc^3\sigma_{\rm ann}(k)}{\pi}, \qquad (4)$$

where c is the speed of light. In the first Born approximation, the number of electrons available for annihilation is equal to the number of electrons in the molecule.

The scattering length and near zero energy $Z_{\rm eff}$ were extracted from the wave function using a stabilization technique [1]. Initially, the energy optimized interaction region ECG basis is supplemented by a set of basis functions to describe the long-range part of the e^+-H_2 wave function. The functions were

$$\Psi_{i,\rm out} = \psi^{H_2}(\mathbf{r}_1, \mathbf{r}_2)\psi_i(\mathbf{r}_0) \qquad \psi_i(\mathbf{r}_0) = \hat{P}\exp\left(-\frac{1}{2}\alpha_i r_0^2\right). \qquad (5)$$

The target wave function $\psi^{H_2}(\mathbf{r}_1, \mathbf{r}_2)$ is represented by a linear combination of ECGs. A basis of dimension of 120 gave an energy of $-1.174\,475\,54$ a.u.. The H_2 energy at an internuclear separation of $1.40a_0$ is $-1.174\,475\,71$ a.u. [18]. Our wave function recovers 99.996% of the correlation energy of 0.040 84 hartree [21]. The $\psi_i(\mathbf{r}_0)$ are designed to describe the positron at asymptotic distances. The α_j were an even tempered set given by the identity $\alpha_j = \alpha_1/T^{j-1}$ with $\alpha_1 = 18.59$ and $T = 1.435$. A total of 36 long-range basis functions were added to the interaction region basis.

TABLE I. The convergence of the various properties of the e^+-H_2 system for the Σ_g symmetry at $R = 1.4a_0$ as a function of the number of ECGs N. The first number in the N column is the dimension of the inner region basis while the second entry is the dimension of the outer region basis. The energy of lowest energy state in the confining potential is given by the E_N column. The wave number k (in a_0^{-1}) is that of the lowest energy pseudostate when the entire basis was diagonalized without the confining potential. The scattering length $A_{\rm scat}$ (in a_0) and $Z_{\rm eff}$ were derived from the wave function projections parallel ($\|$) and perpendicular ($\perp$) to the internuclear axis, and from the system energy using the soft-box radius (SB).

N	E_N	k	$A_{\rm scat,\|}$	$A_{\rm scat,\perp}$	$A_{\rm scat,SB}$	$Z_{\rm eff,\|}$	$Z_{\rm eff,\perp}$	$Z_{\rm eff,SB}$
600 + 36	−1.169 447 60	0.006 355 81	−2.52	−2.62	−2.59	14.38	14.48	14.41
800 + 36	−1.169 457 80	0.006 355 59	−2.53	−2.63	−2.61	14.66	14.75	14.68
1000 + 36	−1.169 461 86	0.006 355 51	−2.53	−2.63	−2.61	14.74	14.83	14.76
Kohn: method of models, $R = 1.40a_0$, [9]				−2.2			10.3	
Kohn: $R = 1.40a_0$, [11]							≈9.8	
Kohn: method of models $R \approx 1.448a_0$, [12]							≈13.5	
Experiment, $k \approx 0.045a_0^{-1}$, $R \approx 1.448a_0$ [4]							14.7(2)	
Experiment, $k \approx 0.045a_0^{-1}$, $R \approx 1.448a_0$ [5]							14.61(14)	
Experiment, $k \approx 0.045a_0^{-1}$, $R \approx 1.448a_0$ [6]							16.02(08)	

The Hamiltonian was then diagonalized (with the confining potential omitted) with this augmented basis yielding a set of positive energy pseudostates. The phase shifts were derived by a least squares fit to the overlap of the target and projectile wave functions with the pseudostates [1]. The overlap function $C(\mathbf{r}_0)$ is defined as

$$C(\mathbf{r}_0) = \int d^3r_1 d^3r_2 \psi^{\mathrm{H}_2}(\mathbf{r}_1, \mathbf{r}_2)\Psi(\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}_2). \qquad (6)$$

The overlap function depends on the distance from the internuclear midpoint and the angle θ_0 from the internuclear axis. Least squares fits to $r_0C(r_0)$ over the finite interval, $r_0 \in [R_1, R_2]$, at fixed values of θ_0 were made to the asymptotic form $B\sin(kr_0 + \delta_0)$. The radial limits for the fit were chosen as $R_1 = 18a_0$ and $R_2 = 30a_0$. This procedure is reminiscent of an earlier method to determine molecular phase shifts using discrete functions [22]. The lowest energy pseudostate was at $k \approx 0.006a_0^{-1}$. The scattering length was extracted from the phase shift using $A_{\mathrm{scat}} \approx -\tan(\delta)/k$ while Z_{eff} is determined from the normalization constant. Table I gives the scattering length and Z_{eff} for the lowest energy pseudostate extracted for projections parallel and perpendicular to the internuclear axis.

An alternate estimate of the scattering length was made from the energy. The evenly tempered asymptotic positron basis was diagonalized for a zero potential. This basis can be regarded as defining a soft-sided box [19]. The effective radius of this box can be estimated from the lowest energy $V = 0$ state, and the radius allows the scattering length and Z_{eff} to be determined [19]. These are designated in Table I as $A_{\mathrm{scat,SB}}$ and $Z_{\mathrm{eff,SB}}$. The methods used to estimate the scattering length do not take long-range polarization and quadrupole interactions into account past $r_0 \approx 24a_0$. Subsidiary calculations suggest an underestimation of $|A_{\mathrm{scat}}|$ by about 5%.

The scattering length in Table I becomes increasingly negative as the dimension of the basis increased. This is expected on physical grounds. Comparison between $A_{\mathrm{scat},\parallel}$, $A_{\mathrm{scat},\perp}$, and $A_{\mathrm{scat,SB}}$ and the $Z_{\mathrm{eff},\parallel,\perp,\mathrm{SB}}$ values reveals the extent to which the low energy scattering parameters are largely unaffected by the aspherical potential. The overall variations between the values of Z_{eff} and A_{scat} are about 1%. The calculations at this energy are equivalent to the H_2 molecule being its lowest rovibrational level. It must be kept in mind that our calculation is for a fixed axially symmetric target, while a non-Born-Oppenheimer calculation would treat the H_2 system as a spherically symmetric system.

The UN group had previously used the method of models within the Kohn variational method to determine the low energy Z_{eff}. The value listed in Table I is taken from the calculations labeled "ii" in Table 4 of [9]. This gave a Z_{eff} of 10.3. A Kohn variational calculation which explicitly included the H_2 wave function was very recently reported by the UN group [11]. The result given in Table I used a H_2 wave function which gave 99.7% of the correlation energy and were taken from the $\Psi_t^{(2,B)}$ curves in Figs. 7 and 8 of [11]. Some UN method of models calculations presented while this Letter was under review gave $Z_{\mathrm{eff}} = 13.5$ [12]. The same article also gave a $Z_{\mathrm{eff}} \approx 10$ with an explicit H_2 wave function and the UN group did not make a clear statement about which result should be preferred [12].

Calculations have also been performed at a series of internuclear separations between $1.0a_0$ and $4.4a_0$. The scattering length as a function of internuclear separation is shown in Fig. 1 while the zero-energy Z_{eff} is depicted in Fig. 2. Z_{eff} for the vibrational ground state was estimated by assuming the linear form $Z_{\mathrm{eff}}(R) \approx Z_0 + Z_1R$. The Z_{eff} for the vibrational ground state is then computed by evaluating Z_{eff} at the mean internuclear distance $\langle R\rangle$. Computing Z_{eff} at $\langle R\rangle = 1.448a_0$ [23] gives $\langle Z_{\mathrm{eff}}\rangle_{\mathrm{vib}} = 15.72$. The scattering length for the vibrational ground state was estimated at $-2.74a_0$.

Experimental Z_{eff} values of 14.7(2) [4], 16.02(8) [6], and 14.61(14) [5] have been measured. The differences appear to be related to variations in Z_{eff} with gas density for reasons that are not known [6]. The present calculation is compatible with experiment when consideration is given to the uncertainties in the experimental analysis. The traditional gas phase positron annihilation experiments simply inject high energy positrons into the gas and rely on the assumptions that the positrons are thermalized and no other processes are occurring when the lifetime spectrum is measured.

The zero-energy vibrational Z_{eff} still needs to be converted to thermal energies. A rough estimate of the size of the correction can be made by using an approximate form for the energy dependence of Z_{eff} [24], e.g.,

$$Z_{\mathrm{eff}}(k) = \frac{Z_{\mathrm{eff}}(0)}{1 + (A_{\mathrm{scat}}k)^2}. \qquad (7)$$

Application of this result with a scattering length of

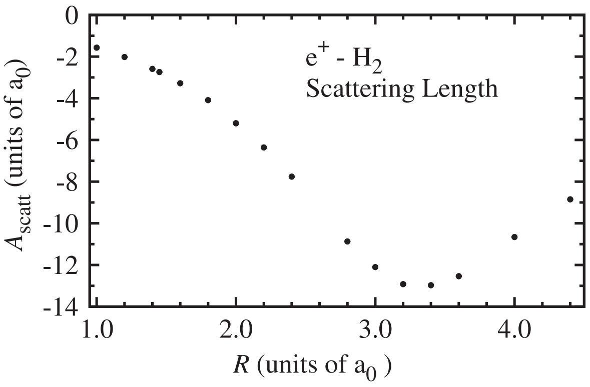

FIG. 1. The scattering length (in a_0) as a function of internuclear distance R for positron scattering from H_2.

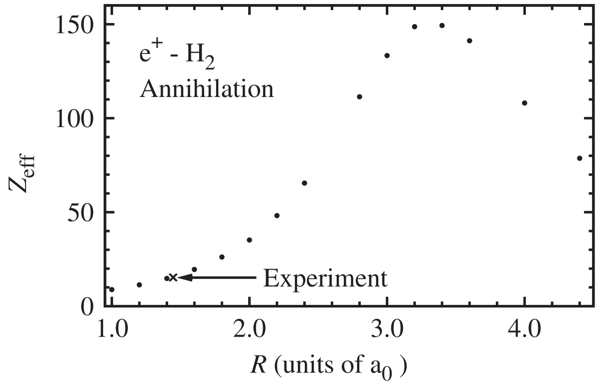

FIG. 2. The close to zero energy Z_{eff} as a function of internuclear distance R. The cross indicates the location of the $R = 1.448a_0$ experimental values listed in Table I.

$-2.7a_0$ suggests a 1.5% reduction in the annihilation parameter at thermal energies to a value of 15.5.

The scattering length implies a zero energy cross section of $\sigma(0) \approx 30\pi a_0^2$. A recent experiment by Zecca *et al.* [25] had a cross section of $8.3\pi a_0^2$ at $k \approx 0.086a_0^{-1}$. The experimental cross section is absolutely incompatible with the present scattering length and that of the UN group [9]. Improving the quality of the CVM wave function would only lead to the magnitude of the scattering length increasing, thus leading to larger discrepancies with the Zecca *et al.* cross section [25].

The scattering length shows a tendency to increase in magnitude as the internuclear separation is increased and a virtual state is formed around $R \approx 3.4a_0$. The maximum scattering length is $-13.0a_0$ at $R = 3.4a_0$. The peaking of Z_{eff} around $3.4a_0$ is expected since it is known that a large scattering length leads to a large threshold Z_{eff} [24]. The large scattering length was a surprise. However, it is known that the critical value for an electric quadrupole to bind a charged particle is $2.4ea_0^2$ [26]. The quadrupole moment of H_2 increases from $0.91ea_0^2$ at $R = 1.4a_0$ before reaching a maximum value of $2.03ea_0^2$ at $R = 3.0a_0$ [27]. We speculate that the large increase in scattering length can be understood in terms of the larger quadrupole moment. The recent method of models calculation by the UN group exhibited a qualitatively similar variation of Z_{eff} versus R for $R \leq 2a_0$ [12].

While the present calculation was performed under the fixed nucleus approximation, it represents the first description with an unrestricted treatment of the positron-electron interactions in the e^+-H_2 collision system. The strong increase in Z_{eff} and A_{scat} with increasing internuclear distance due to virtual state formation at $R \approx 3.4a_0$ was totally unexpected. One of the most significant methodological aspects was the ease with which the inner region wave function was generated. Using the present e^+-H_2 wave function within a more formal scattering framework, such as the Kohn variational method, would require substantial development work, but this would involve the application of known procedures and would be straightforward.

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