Positron attachment to the $H_2(A\ ^3\Sigma_u)$ state

J. Mitroy* and J. Y. Zhang

Centre for Antimatter-Matter Studies and School of Engineering, Charles Darwin University, Darwin, Northern Territory 0909, Australia

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The stochastic variational method is used to compute the binding energy for positrons attached to the repulsive $H_2(A\ ^3\Sigma_u)$ state. Attachment occurs for internuclear separations between 1.616 a_0 and 1.818 a_0. At these distances the vertical ionization potential for the $H_2(A\ ^3\Sigma_u)$ state is close to the positronium binding energy of 0.250 a.u. The maximum attachment energy occurs at 1.67 a_0 and is 0.003532 a.u.

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I. INTRODUCTION

It is now accepted that positrons can form bound states with many atoms and molecules [1–3] and that positron binding to vibrationally excited states is the mechanism responsible for the large positron annihilation rates observed for many molecules in gas phase positron annihilation spectroscopy experiments [4]. While there have been many highly accurate calculations of positronic atom binding energies [1,2] the same is not true for positronic molecules. The only molecule for which precise estimates of the positron binding energy are known is the e^+LiH system [5–8]. There have been calculations of positron binding to a number of other molecules [9–14] but the accuracy obtained for these systems is relatively low.

There has been relatively little attention paid to the binding of positrons to atoms and molecules in excited states. The strongest evidence for the existence of such states is for the $^2P^o$ states of e^+Ca and e^+Sr (we exclude vibrationally excited states of molecules from this discussion) and the e^+He($^3S^e$) system [15,16]. Similarly, years of experimentation have revealed little evidence for the existence of resonant states in the positron scattering spectra of atoms and simple molecules [1,17].

This Brief Report examines the possibility of positron binding to an excited state of the hydrogen molecule. It is demonstrated by explicit *ab initio* calculation that a positron can attach itself to the $A\ ^3\Sigma_u$ potential curve of the hydrogen molecule. Attachment has been demonstrated to occur for internuclear separations between 1.616 a_0 and 1.818 a_0. The maximum binding energy of 0.0035 a.u. occurs when the vertical ionization potential of the parent atom is closest to the ionization potential of the positronium ground state. This relationship between the positron binding energy and the parent atom ionization potential is well known from previous work [1,18–20].

II. THE STOCHASTIC VARIATIONAL METHOD

The Hamiltonian for the e^+H_2 system with $N = 2$ electrons and one positron in the Born-Oppenheimer approximation can be written

$$H = -\sum_{i=1}^{N+1}\frac{\nabla_i^2}{2} - \sum_{i=1}^{N}\frac{1}{|\mathbf{r}_{N+1}-\mathbf{r}_i|} + \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + \frac{1}{|\mathbf{r}_{N+1}-\mathbf{R}/2|} + \frac{1}{|\mathbf{r}_{N+1}+\mathbf{R}/2|} - \sum_{i=1}^{N}\left(\frac{1}{|\mathbf{r}_i+\mathbf{R}/2|}+\frac{1}{|\mathbf{r}_i-\mathbf{R}/2|}\right)+\frac{1}{R}. \quad (1)$$

The vector $\mathbf{R}/2$ is the displacement of the two protons from the midpoint of the molecular axis.

The wave function, $|\Phi_0\rangle$, of the e^+H_2 ground state is written as a linear combination of explicitly correlated Gaussians (ECGs) with shifts, e.g.,

$$\Phi_k = \hat{P}\exp\left(-\frac{1}{2}\sum_{i=1}^{N+1}B_{k,i}|\mathbf{r}_i-\mathbf{s}_{k,i}|^2\right) \times \sum_{i<j}^{N+1}\exp\left(-\frac{1}{2}A_{k,ij}|\mathbf{r}_i-\mathbf{r}_j|^2\right). \quad (2)$$

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, $B_{k,i}$, and $\mathbf{s}_{k,i}$ are adjusted during the optimization process. The operator $\hat{P}$ is used to enforce Σ_u symmetry. This is done by generating each basis function as a combination of two ECGs. Once $\mathbf{s}_{k,i}$ is set, another ECG with $\mathbf{s}_{k,i} \rightarrow -\mathbf{s}_{k,i}$ is added. The pair of basis functions with the same exponential coefficients have linear coefficients with opposite signs in the case of Σ_u symmetry. Each ECG has a total of nine adjustable parameters. The two electrons are antisymmetrized and are in a spin-triplet state. The compound state with the bound positron can be found in a spin-doublet or spin-quartet state with Σ_u symmetry.

The adjustable parameters of the ECG basis are optimized by the trial and error process that is called the stochastic variational method (SVM) [3,21,22]. Random changes to the A_k, $B_{k,i}$, and $\mathbf{s}_{k,i}$ parameters are made and those changes that lead to a lower energy are retained. Such a process is possible since the ECG matrix elements of the Hamiltonian functions are algebraically compact and straightforward to compute. Coupled with the fact that the memory requirements of a typical calculation are relatively modest, this means that close to exact calculations for few-body systems containing as many as four to five particles are feasible with modest computational resources.

*jxm107@rsphysse.anu.edu.au

III. RESULTS OF CALCULATIONS

The condition for positron attachment to any system depends on the binding energy of the parent system. In the case of the H_2 system this is vertical ionization potential with respect to the $H_2^+(^2\Sigma_g)$ state. When the ionization potential is greater than 0.250 a.u. (the binding energy of the positronium ground state) the energy of the e^+H_2 system must be lower than the energy of the H_2 parent for the positron to be bound. When the ionization potential is less than 0.250 a.u. the energy of the e^+H_2 system must be lower than that of the $H_2^+(^2\Sigma_g)$ plus the positronium energy. These two conditions are expressed most succinctly with the identities

$$E(e^+H_2) - E(H_2) < 0 \quad I(H_2) > 0.25 \tag{3}$$

$$E(e^+H_2) - E(H_2^+) + 0.25 < 0 \quad I(H_2) < 0.25 \tag{4}$$

The H_2 ground state does not bind a positron although a virtual state exists for an internuclear separation of $R \approx 3.2\,a_0$ [23,24]. The H_2 state most likely to attach a positron is the repulsive $H_2(A\ ^3\Sigma_u)$ state. The conditions for positron binding are most favorable when the parent system ionization potential is close to 0.25 a.u. [1]. The $H_2(A\ ^3\Sigma_u)$ state has a vertical ionization potential to the $H_2^+(^2\Sigma_g)$ state that is very close to 0.25 a.u. at an internuclear separation close to 1.67 a_0.

Table I lists the energies of the $H_2^+(^2\Sigma_g)$ state, the $H_2(A\ ^3\Sigma_u)$ state, and the $e^+H_2(^{2,4}\Sigma_u)$ state at internuclear separations between 1.616 and 1.818 a_0. The H_2^+ energies were taken from SVM calculations with a basis of 40 ECGs. The energies should be correct to all quoted digits. The $H_2(^3\Sigma_u\ A)$ state energies came from SVM calculations with a basis of 120 ECGs. The energy uncertainties should be about 1×10^{-6} Hartree. The calculations of the e^+H_2 energies were made with basis sets consisting of 600 ECGs. These energies are expected to be converged to better than 5×10^{-5} a.u.

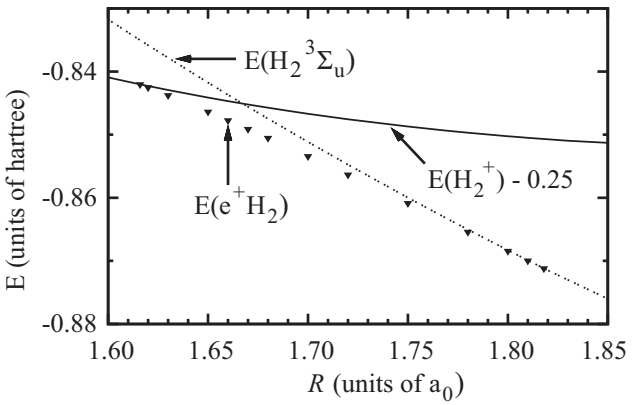

FIG. 1. The energies of the $H_2^+(^2\Sigma_g)$ state (minus 0.25 hartree), the $H_2(A\ ^3\Sigma_u)$ state and the $e^+H_2(^2\Sigma_u)$ state as a function of internuclear distance, R (a_0). The data for $e^+H_2(^2\Sigma_u)$ are shown as a set of discrete points.

Figure 1 depicts the energy of $e^+H_2(A\ ^3\Sigma_u)$ state with respect to its dissociation threshold as a function on internuclear distance. The positron binding energy with respect to the lowest energy dissociation channel is largest at 1.67 a_0 with a value of 0.003532 a.u. The parent molecule ionization potential decreases for $R < 1.67\,a_0$ leading to a decrease in the positron binding energy. Eventually at separation distances less than of 1.616 a_0 (the ionization potential here is 0.242994 a.u.) the systems becomes unstable. Similarly, when the internuclear distances increase for $R > 1.67\,a_0$, the H_2 ionization energy increases and the system has not been demonstrated to be stable for $R > 1.818\,a_0$.

A linear interpolation was done to determine the location the precise internuclear separation where the $H_2(A\ ^3\Sigma_u)$ state has vertical ionization energy of 0.25 a.u. This is found to be 1.6673 a_0 and the $H_2(A\ ^3\Sigma_u)$ energy is

TABLE I. Energies for the $H_2^+(^2\Sigma_g)$ state, the $H_2(A\ ^3\Sigma_u)$ state and the $e^+H_2(^{2,4}\Sigma_u)$ state. The attachment energy with respect to the lowest energy dissociation channel is given by ε. All values are given in a.u.

			$e^+H_2(^{2,4}\Sigma_u)$	
R	$E[H_2^+(^2\Sigma_g)]$	$H_2\ ^3\Sigma_u$	$E(e^+H_2)$	ε
1.610	−0.591629	−0.833811		
1.616	−0.592031	−0.835029	−0.842035	0.000004
1.620	−0.592292	−0.835837	−0.842520	0.000328
1.630	−0.592925	−0.837813	−0.843772	0.000847
1.650	−0.594123	−0.841762	−0.846382	0.002259
1.660	−0.594686	−0.843690	−0.847745	0.003183
1.670	−0.595220	−0.845590	−0.849122	0.003532
1.680	−0.595736	−0.847471	−0.850537	0.003066
1.700	−0.596694	−0.851158	−0.853417	0.002259
1.720	−0.597566	−0.854757	−0.856345	0.001588
1.750	−0.598716	−0.859991	−0.860856	0.000865
1.780	−0.599693	−0.865041	−0.865415	0.000374
1.800	−0.600253	−0.868307	−0.868437	0.000130
1.810	−0.600508	−0.869913	−0.869962	0.000049
1.818	−0.600700	−0.871183	−0.871192	0.000009
1.820	−0.600747	−0.871499		

estimated as -0.845075 a.u. The interpolated $e^+H_2(^2\Sigma_u)$ energy is -0.848749 giving a positron attachment energy of 0.003674 a.u.

IV. OUTLOOK

The implications of the present result for positron scattering from the H_2 ground state are minor since the positron cannot excite molecular hydrogen from a singlet into a triplet state. However, there are ramifications for orthopositronium scattering from H_2. With the present result it is now known that both electrons and positrons can be bound to the $H_2(A\ ^3\Sigma_u)$ state at certain internuclear separations. Electron attachment to this state occurs for $R \geqslant 3.0a_0$ [25] while positron attachment has now been demonstrated for $R \in [1.616, 1.818]\ a_0$. Under these circumstances it is possible that there exists a Feshbach resonance consisting of Ps attached to the $H_2(A\ ^3\Sigma_u)$ state. This resonance will most likely occur at internuclear separations that significantly exceed the mean internuclear separation of the H_2 ground state (i.e., 1.45 a_0).

Another implication concerns the possibility of positron attachment to excited states of molecules other than H_2. The strategy used to guide the search for positron attachment was based on first identifying excited states with vertical ionization potentials close to 0.25 a.u. since such conditions are known to promote positron attachment [1,19]. The significance of this point has not received much attention in existing works that investigate positron binding to molecules [9–14]. Such a strategy could be usefully applied to other molecules to guide a search aimed at identifying electronically excited states capable of attaching a positron into a Feshbach resonance. Such states are ubiquitous in electron scattering experiments. The experimental identification of such a state in a positron scattering experiment has been described as one of the holy grails of positron physics [17].

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