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# Positron collisions with molecular hydrogen: cross sections and annihilation parameters calculated using the $R$-matrix with pseudo-states method

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**Abstract.** The molecular R-matrix with pseudo-states (MRMPS) method is employed to study positron collisions with $H_2$. The calculations employ pseudo-continuum orbital sets containing up to h ($l = 5$) functions. Use of these high $l$ functions is found to give converged eigenphase sums. Below the positronium formation threshold, the calculated cross sections agree with other high accuracy theory and generally with the measurements. Calculation of the positron annihilation parameter $Z_{\text{eff}}$ with the MRMPS wave functions gives values significantly higher than other R-matrix wave functions but still do not completely converge with h functions. Extrapolation to higher $l$-values leads to a predicted value of $Z_{\text{eff}}$ for $H_2$ of about 10.4. The MRMPS method is both completely general and *ab initio*; it can therefore be applied to positron collisions with other molecular targets.

## 1. Introduction

Positron collisions with molecules introduce a number of features not present in the better studied electron-molecule collision problem. These include positron annihilation at all collision energies and positronium (Ps) formation above the Ps formation threshold, which is 8.63 eV for molecular hydrogen. These processes, and much else in low-energy positron-molecule collisions, are very sensitive to polarisation effects since the positron is attracted to the electrons in the target molecule and therefore shows very strong correlation effects. These effects, which are sometimes refered to as virtual Ps formation, are particularly difficult to model in an *ab initio* and general manner (Armour & Humberston 1991). Positron annihilation, as usually represented by parameter $Z_{\text{eff}}$, particularly tests the wave functions at points where the positron and one of the electrons coincide. The cusp condition at this point is very hard to reproduce correctly without using methods which explicitly include the positron – electron coordinate in the wave function (Armour et al. 2006).

$H_2$ is the simplest molecule and serves as a benchmark system. Low-energy collisions between positrons and $H_2$ have been well studied theoretically (Tennyson 1986, Danby & Tennyson 1990, Armour et al. 1990, Gibson 1992, Reid et al. 2004, Arretche et al. 2006, Mukherjee & Sarkar 2008, Zhang, Mitroy & Varga 2009) and experimentally (Hoffman et al. 1982, Charlton et al. 1983, Deuring et al. 1983, Zecca et al. 2009). The most successful theoretical calculations of positron – $H_2$ cross sections have used sophisticated procedures (Armour et al. 1990, Gibson 1992, Reid et al. 2004, Arretche et al. 2006, Mukherjee & Sarkar 2008, Zhang, Mitroy & Varga 2009) which are hard to generalise to many-electron molecular targets.

As demonstrated below, the calculation of accurate, fully *ab initio*, positron annihilation parameters places considerable demands on the wave functions used. For this reason most such studies of annihilation in molecules studies have focussed on $H_2$. Calculations of $Z_{\rm eff}$ for $H_2$ have been carried out using the Schwinger multichannel method (Varella et al. 2002), the body-fixed vibrational-close-coupling method (Gianturco & Mukherjee 2000), the complex Kohn variational method (Cooper et al. 2008, Cooper & Armour 2008) and the confined variational method (Zhang, Mitroy & Varga 2009). Franz & Gianturco (2006) corrected Gianturco and Mukherjee's calculation for lack of energy normalization of the wave function; they also give $Z_{\rm eff}$ values which included an enhancement factor to account for the local increase in positron density in the vicinity of the bound molecular electrons. The comparable experiments were performed by Heyland et al. (1982) and Laricchia et al. (1987).

In this work we explore the use of a general procedure, based on the so-called R-matrix with pseudo-states method (Gorfinkiel & Tennyson 2004, Gorfinkiel & Tennyson 2005), to the calculation of both low-energy position-molecule collision cross sections and the positron-molecule annihilation parameter $Z_{\rm eff}$. The molecular RMPS (MRMPS) method is in principle a completely general method. It has been used successfully to study a number of electron collision problems including those with $H_2$ and $H_3^+$ (Gorfinkiel & Tennyson 2004, Gorfinkiel & Tennyson 2005), $C_2^-$ (Halmová & Tennyson 2008, Halmová et al. 2008) and $Li_2$ (Tarana & Tennyson 2008). It has been shown to give an excellent representation of the polarisability for a selection of small molecules (Jones & Tennyson 2010), something which is not usually obtained with more standard close-coupling expansions. In this paper, the MRMPS method is used to treat positron collisions with $H_2$ molecule at energies up to the Ps formation threshold: both cross sections and annihilation are considered.

## 2. Method

### 2.1. Molecular R-matrix

The standard expression for a close-coupling expansion can be written:

$$\psi_k^{N+1} = \sum_{ij} a_{ijk}\Phi_i^N(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N)u_{ij}(\tilde{\mathbf{x}}) + \sum_i b_{ik}\chi_i^{N+1}(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N, \tilde{\mathbf{x}}) \ , \quad (1)$$

where $\Phi_i^N$ is the $N$-electron target wave function and $u_{ij}$ are continuum orbitals carrying the positron, whose coordinate is denoted by $\tilde{\mathbf{x}}$. The second sum in eq. (1) contains $L^2$ functions in which the positron occupies short-range target orbitals. In a calculation, such as ours, where a common set of orbitals are used for the positron and the electrons, the positron is of course free to enter orbitals already fully occupied by electrons.

In the R-matrix method the wave function, $\psi_k^{N+1}$ with discretised energy $E_k$, is only used to represent the wave function within a finite, inner region represented by a sphere of radius $a$, here taken as 10 $a_0$, centred on the target centre-of-mass. This wave function is independent of the scattering energy but is used to construct the energy-dependent R-matrix on the boundary (Burke & Berrington 1993). The R-matrix can then be propagated to yield scattering observables. We note that this procedure avoids explicitly evaluating the scattering wave function, a point we will return to below when considering annihilation calculations. In the UK polyatomic R-matrix codes (Morgan et al. 1998) all the wave functions are expressed in terms of Gaussian Type Orbitals (GTOs). It should be noted all calculations were performed using $D_{2h}$ symmetry, the highest allowed by this code. One of us has recently reviewed the molecular R-matrix method (Tennyson 2010) and the reader is referred to this for derivations and technical details of the method.

The number of target states included in any close-coupling expansion is necessarily finite. This means that such expansions cannot include all target states and do not give a good representation of the target continuum. The RMPS method is designed to cure these problems by adding a supplementary set of functions to represent the bound and continuum states not included in the usual expansion. In an R-matrix method it is only necessary to represent these states in the inner region; under these circumstances the target continuum is discretised and, for a given energy range, it is only necessary to include a finite number of states.

In the MRMPS method, an extra set of pseudo-continuum orbitals (PCOs) is added centred at the origin. These PCOs are represented in terms of even-tempered GTOs (Wilson 1980), so that the exponents form a geometric series which is defined by

$$\alpha_i = \alpha_0 \beta^{(i-1)}, \qquad\qquad i = 1, ...., L, \tag{2}$$

and the choice of $(\alpha_0, \beta)$. This basis, which is in principle complete, is used to define a supplementary set of states for the close-coupling expansion. These extra states are known as pseudo-states since they do not represent physical states of the target.

### *2.2. Calculations of $Z_{eff}$*

The spin-averaged annihilation cross section at incident energies below the Ps formation threshold is usually given by

$$\sigma_{ann} = \pi r_0^2 \frac{c}{\nu} Z_{eff} \tag{3}$$

where $\nu$ is the velocity of the incident positron and $r_0$ is the classical (or Compton) radius of the electron and $c$ is the speed of light. The parameter $Z_{eff}$ gives the effective number of target electrons seen by the incoming positron. $Z_{eff}$ clearly depends on the energy of the incoming positron but is, by convention, often quoted for thermalized positrons at a room temperature of $T = 296$ K. Below we model this by considering a positron collision energy of 0.037 eV. Although our calculations use several partial waves, at this energy, s-wave scattering gives the dominant contribution to $Z_{eff}$; this can be seen by the good results obtained by studies which concentrated only on this lowest partial wave (Armour et al. 1990, Zhang, Mitroy & Varga 2009).

Given the energy-dependent scattering wave function, $\Psi_E(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N, \tilde{\mathbf{x}})$, $Z_{eff}$ can be calculated as the integrated probability that the positron and an electron will coincide:

$$Z_{eff} = \sum_{i=1}^{N} \int |\Psi_E(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N, \tilde{\mathbf{x}})|^2 \delta(\tilde{\mathbf{x}} - \mathbf{x}_i) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N d\tilde{\mathbf{x}} \,. \tag{4}$$

Within the R-matrix method the target electrons are confined to the inner region. In this region, the energy-dependent wave function is:

$$\Psi_E = \sum_k A_{Ek} \psi_k^{N+1} \,, \tag{5}$$

meaning that it is necessary to calculate the energy-dependent coefficient $A_{Ek}$. These take the form

$$A_{Ek} = \frac{1}{2a(E_k - E)} \sum_{ij} w_{ik}^T(a) R_{ij}^{-1} F_j(a) \tag{6}$$

where $w_{ik}(a)$ is the amplitude on the R-matrix boundary in the $i^{\text{th}}$ channel of the $k^{\text{th}}$ inner region wave function. $F_j(a)$ is the value the outer region wave function in channel $j$ on the boundary; $\mathbf{R}$ is the R-matrix. Although eq. (6) should remain well-behaved for all $E$, there are in practice numerical issues when $E \approx E_k$. It is possible to use the definition of the R-matrix to give an alternative expression for $A_{Ek}$

$$A_{Ek} = \frac{1}{2(E_k - E)} \sum_i w_{ik}^T(a) F_i'(a) \tag{7}$$

where $F_i'(a)$ is the derivative of the outer region wave function in channel $i$ at the boundary. In practice eq. (6) was found to give numerically more stable results.

To normalise the outer-region wave function, the density of the incident beam should be one positron per unit volume.

$$\underline{F} = (1 - i\underline{K})^{-1}(\underline{f} + \underline{K}\underline{g}). \tag{8}$$

where $\underline{K}$ is the $K$-matrix. $\underline{f}$ and $\underline{g}$ are the regular and irregular solutions of the set of coupled differential equations which are derived from the outer region Schrödinger equation (Burke & Berrington 1993). The normalisation term $(1 - i\underline{K})$ is obtained from transforming the asymptotic form involving the $S$-matrix to that written in terms of the $K$-matrix.

At long-range the outer region wave functions were obtained using an asymptotic expansion (Gailitis 1976) and were then numerically integrated inwards from $r = a'$, typically 30 to 50 $a_0$, to the R-matrix boundary at $r = a$. Runge-Kutta-Nystrom integration (Brankin et al. 1989) was used to integrate the outer region wave function to the boundary. Some care was required here and the best results were obtained using the "RKN12(10)17M" coefficients due to Baker et al. (1999).

In practice $Z_{eff}$ as a function of energy is evaluated in the inner region using

$$Z_{eff} = \sum_{k,k'} \frac{4\pi}{kk'} A^*_{Ek} Z_{kk'} A_{Ek'} \tag{9}$$

where the delta function matrices elements are donated by $Z_{kk'}$. These energy-independent matrix elements can be evaluated using a specialisation of the scattering Hamiltonian construction procedure of Tennyson (1996). To do this requires a set of integrals for the GTOs with a $\delta$-function. A new code, GAUSDELTA, was written for this based on the code GAUSTAIL (Morgan et al. 1997). Only two-electron integrals involving the positron are required. The energy dependent procedure for calculating $Z_{eff}$ has been implemented in a new outer-region module for the UK molecular R-matrix codes called ZEFF. We tested our programs on several simplified models, such as the Born approximation where the positron is represented by a plane wave and the resulting $Z_{\text{eff}} = N$ at all collision energies.

Finally all calculations below were performed at a fixed $H_2$ internuclear separation of 1.4 $a_0$ and neglected rotational motion. Treatment of rotational motion can be important for systems with long-range potentials (Zhang, Faure & Tennyson 2009) but has uniformly been neglected for studies of positron – $H_2$ collisions since the dominant interactions are all short-range. Similarly vibrational effects have also generally been ignored, although we note that the recent study Zhang, Mitroy & Varga (2009) suggests that $Z_{\text{eff}}$ increases markedly with internuclear separation and therefore that vibrational effects should not be completely ignored.

## 3. Calculations

We tested a number of models for low-energy positron – $H_2$ collisions including, for completeness, models used in earlier R-matrix studies of this problem (Tennyson 1986, Danby & Tennyson 1990), which are known to give poor results for this problem. Starting from the simple models, we performed calculations using a static model, a static plus polarisation (SP) model and standard close-coupling (CC). The target calculation all used a 6-31 G** GTO basis set (Hariharan & Pople 1973). The static and SP models are based on a Hartree-Fock $H_2$ wave function while the CC calculation used a near-full configuration interaction (CI) representation of the target wave function which is therefore independent of the choice of molecular orbitals. This wave function is represented (in $D_{2h}$ symmetry) by the configurations:
$(1\text{-}3a_g, 1b_{2u}, 1b_{3u}, 1\text{-}2b_{1u}, 1b_{2g}, 1b_{3g})^2$
For continuum functions we used the GTO basis functions with $\ell \leq 4$ (up to g orbitals) of Faure et al. (2002).

**Table 1.** Polarisabilities of $H_2$ for an spd-PCO basis set with $\beta = 1.4$ for different $\alpha_0$. The results were obtained by summing over the 99 lowest RMPS states except for the case marked * which used a sum over only the 15 lowest states. The accurate values are from the *ab initio* calculation of Augspurger & Dykstra (1998)

| $\alpha_0$ | $\alpha_{\parallel}$ | $\alpha_{\perp}$ |
|---|---|---|
| 0.16 | 6.236 | 4.612 |
| 0.17 | 6.228 | 4.586 |
| 0.17* | 6.200 | 4,539 |
| 0.18 | 6.202 | 4.550 |
| 0.19 | 6.202 | 4.509 |
| Accurate value | 6.445 | 4.507 |

A number of MRMPS models were tested. For these we started from the Hartree-Fock molecular orbitals (MOs) for $H_2^+$. The PCOs exponents generated using $\beta = 1.4$ and $\alpha_0 = 0.17$ following tests with $\alpha_0 = 0.16$, 0.18, 0.19. The chosen set gave a good representation of the $H_2$ polarisability, see table 1, and stable eigenphases. This PCO basis actually corresponds to the one used to study electron – impact ionisation in $H_2$ (Gorfinkiel & Tennyson 2005).

All previous studies using the MRMPS method have used PCOs containing only s, p and d functions. Here we present calculations using PCOs basis functions with an extended set of angular functions: our largest PCO set has (10s, 10p 6d, 6f, 6g, 6h) orbitals. Below these sets are labelled s-PCOs, sp-PCOs, spd-PCOs, spdf-PCOs, spdfg-PCOs and spdfgh-PCOs, respectively. To avoid problems with linear dependence, a deletion threshold $\delta_{thrsh-tar}$ must be set at an appropriate value for symmetric orthogonalization of the PCOs to the MOs based on eigenvalues of the overlap matrix. Tests showed that $\delta_{thrsh-tar} = 2 \times 10^{-4}$ gives satisfactory results. A second deletion threshold, $\delta_{thrsh-scat} = 2 \times 10^{-7}$, was used to orthogonalise the continuum orbitals to the full target set. Note that GTOs with exponents greater than $\alpha_0$ are removed from the continuum basis at the start of the calculation, leaving a reduced continuum basis of (6s, 7p, 7d, 7f, 6g) functions. For the spdfg-PCOs and spdfgh-PCOs calculations $\delta_{thrsh-scat} = 2 \times 10^{-6}$ was used as this higher threshold gives smoother eigenphase sums and corresponding cross sections.

The extra target configurations used to generate the pseudo-states with the spd-PCOs basis are:

$1a_g^1(4\text{-}20a_g,\ 2\text{-}8b_{2u},\ 2\text{-}8b_{3u},\ 1\text{-}5b_{3u},\ 3\text{-}10b_{1u},\ 2\text{-}6b_{2g},\ 2\text{-}6b_{3g})^1$

For larger PCO basis sets, a greater number of PCOs and hence configurations are included in the calculations. For example, the spdfgh-PCOs calculation has the MRMPS configurations:

$1a_g^1(4\text{-}28a_g,\ 2\text{-}26b_{2u},\ 2\text{-}26b_{3u},\ 1\text{-}12b_{3u},\ 3\text{-}28b_{1u},\ 2\text{-}13b_{2g},\ 2\text{-}13b_{3g})^1$

For the MRMPS calculations, 8 target states are included for s- and sp-PCOs case, 15

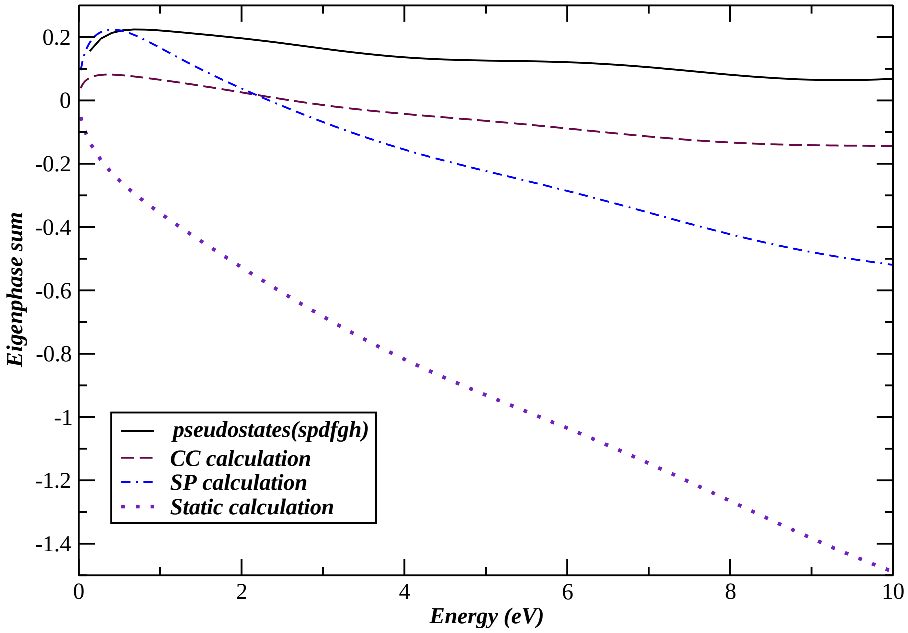

**Figure 1.** Eigenphase sums for $\Sigma_g^+$ symmetry for the static, static plus polarisation (SP), close-coupling and PCO-spdfgh RMPS models.

for spd-PCOs, 22 for spdf-PCOs and 31 for spdfg- and spdfgh-PCOs calculations.

## 4. Cross sections

Figure 1 compares eigenphase sums for static, SP, CC and MRMPS models for the $\Sigma_g^+$ (actually $A_g$) symmetry. It can be seen that the eigenphases are strongly dependent on the model used. Only the static model, which neglects all attractive polarisation effects, gives negative eigenphases for all energies considered. Conversely, the eigenphases for the MRMPS calculations are positive at all energies considered. Eigenphases for the SP and CC models change sign at about 2.5 eV.

Figure 2 presents eigenphase sums with $\Sigma_g^+$ symmetry for the different PCOs models. Results for Armour et al. (1990)'s calculation, which makes explicit use of the positron – electron coordinate in the wave function, are given for comparison. As can be seen, the calculations with spdfg-PCOs and spdfgh-PCOs give very similar results, suggesting our eigenphase calculated with the MRMPS method are converged at low energies. These results are in good agreement with Armour et al. (1990)'s eigenphases at lower energies, and are higher at incident energies above 3 eV because only the lowest partial wave are included in Armour *et al*'s calculations. The $\Pi_u$, $\Sigma_u^+$ and $\Pi_g$ symmetry eigenphases show similar behaviour, see Fig. 3.

Figure 4 shows total cross sections given by various *R*-matrix models. As there are no open electronic excitation channels in the energy range we considered and rotational excitation is almost certainly negligibly small, these cross sections are largely elastic with a probably small contribution due to vibrational excitation. The measured cross sections

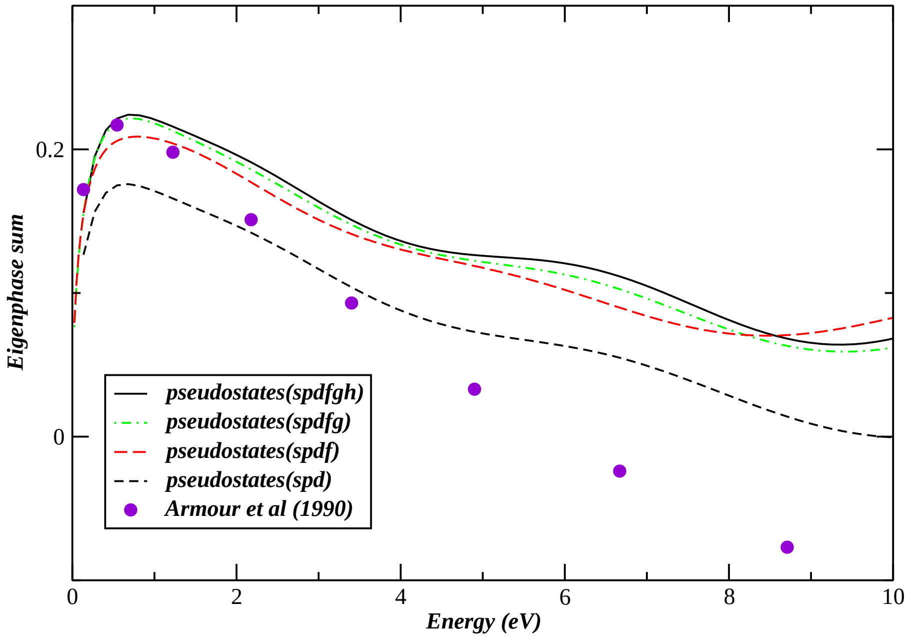

**Figure 2.** Eigenphase sums for $\Sigma_g^+$ symmetry for various PCOs models as a function of energy; results of Armour et al. (1990), column 7b in Table 2(a), are given for comparison.

probe the same processes. Obviously, the results of the static and SP calculations given Fig. 4 are poor as suggested by the eigenphases given above. The static model does not even give any increase in cross section at low energies. The CC calculation gives better results than the SP model, but still gives much smaller cross sections at low energies than calculations with the MRMPS method. The MRMPS cross sections increase as angular functions are added but, judging by both the eigenphase sums and the cross sections, are converged for calculations with the larger PCOs models studied.

Figure 5 compares our total cross sections calculated with the MRMPS method with various theoretical calculations. All studies give similar cross sections at energies below the Ps formation threshold. In particular, our results with the MRMPS method are in good agreement with Armour et al. (1990)'s integral cross sections, although there are minor differences between the corresponding eigenphase sums. At energies above 7 eV, Mukherjee & Sarkar (2008)'s cross sections increase rapidly due to the Ps formation, which is included in their study. For energies above 10 eV, the results of Mukherjee & Sarkar (2008) are in excellent agreement with experiment (Hoffman et al. 1982, Charlton et al. 1983, Deuring et al. 1983, Zecca et al. 2009).

Figure 6 compares our total cross sections with spdfgh-PCOs with several experimental measurements (Hoffman et al. 1982, Charlton et al. 1983, Deuring et al. 1983, Zecca et al. 2009) for positron collisions with $H_2$. Our MRMPS results are in very good agreement with measurement of Hoffman et al. (1982) at energies below the Ps formation threshold. Zecca et al. (2009) is the only available measurement that gave total cross sections below 1 eV; in this region these measurements lie below

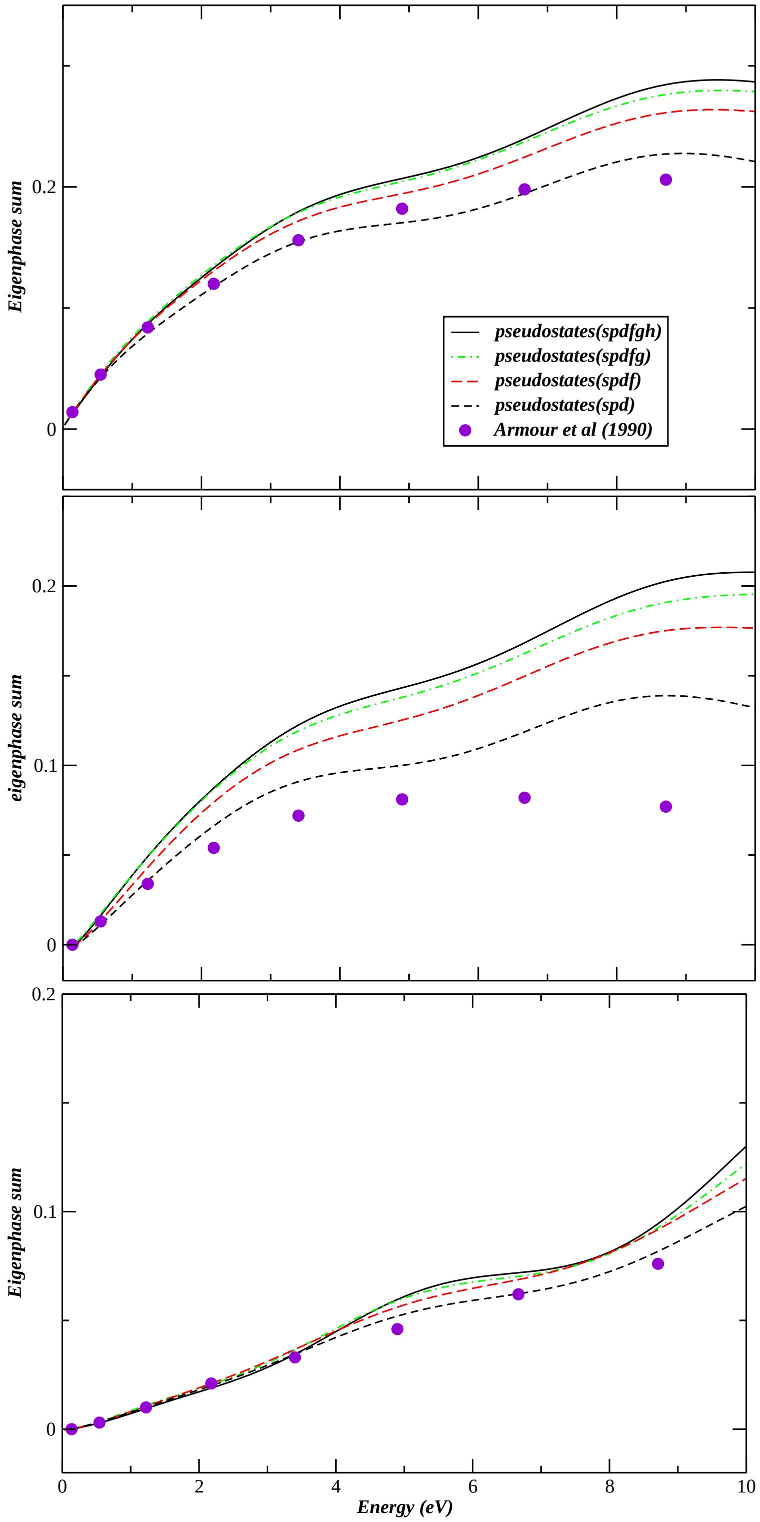

**Figure 3.** Eigenphase sums for $\Pi_u$ (upper), $\Sigma_u^+$ (middle) and $\Pi_g$ (lower) symmetries. Results from Armour et al. (1990), Table 5(a), are given for comparison.

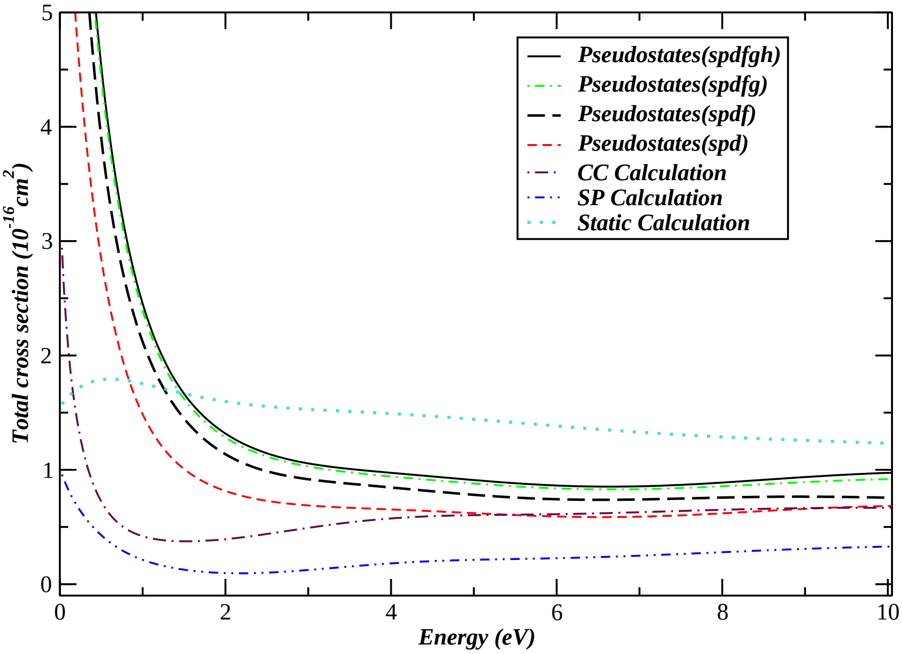

**Figure 4.** Total cross sections for various models without and with MRMPS method.

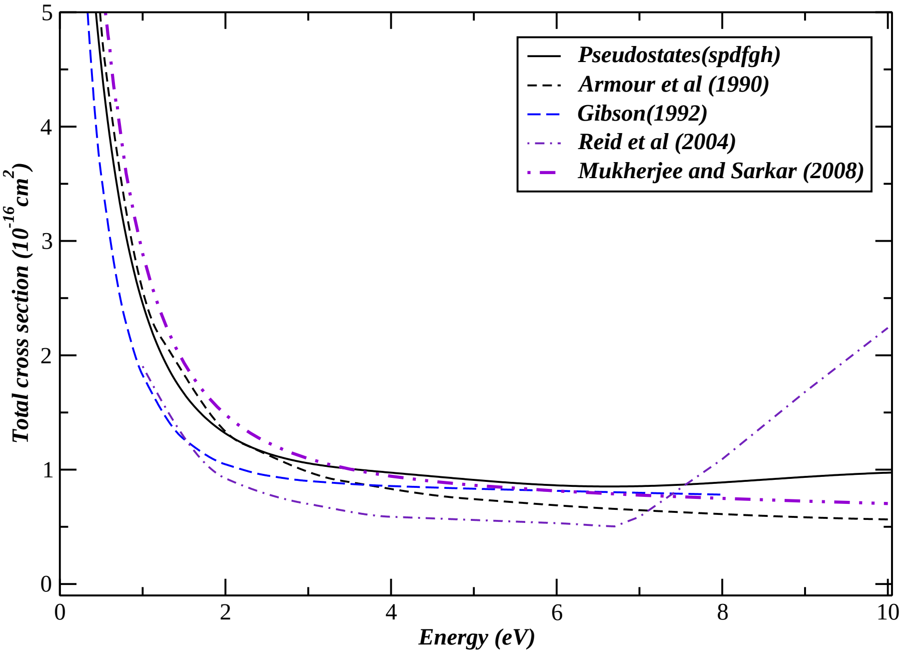

**Figure 5.** Total cross sections for positron-$H_2$ collisions calculated with various methods: MRMPS results of this study, compared to Armour et al. (1990), Gibson (1992), Reid et al. (2004) and Mukherjee & Sarkar (2008).

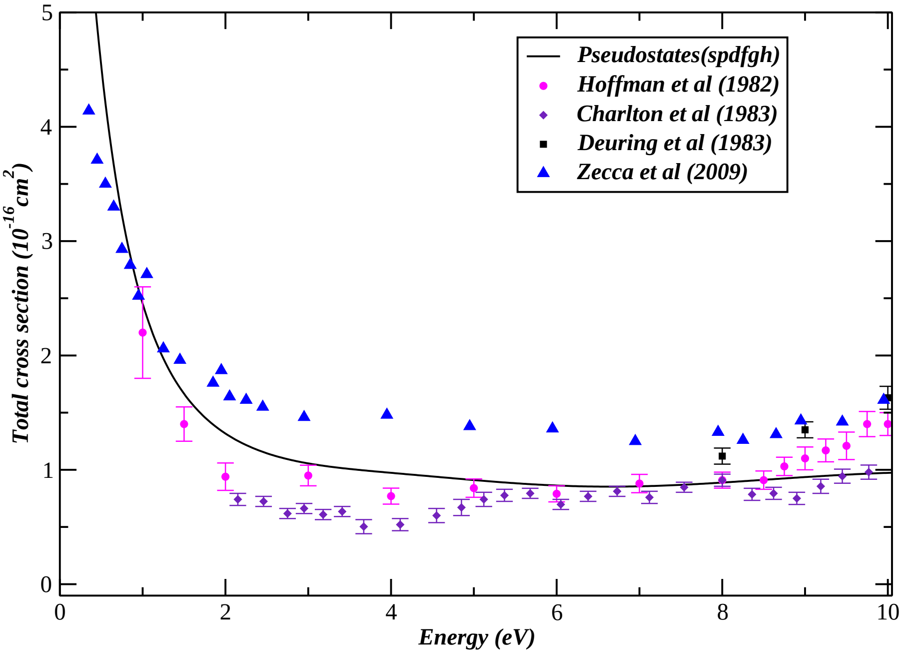

**Figure 6.** Total cross sections for positron-$H_2$ collisions: our MRMPS calculations compared to measurements of Hoffman et al. (1982),Charlton et al. (1983), Deuring et al. (1983) and Zecca et al. (2009).

all the reliable theoretical estimates including ours. However, at energies above 1 eV, Zecca et al. (2009)'s result lies higher than our calculation. Charlton et al. (1983) lies below our results at energies from 2 eV to 6 eV, and then agree with them above 6 eV.

## 5. Annihilation

Energy-dependent values for $Z_{\mathrm{eff}}$ were calculated for all the models tested above. These results are shown in Figure 7. As can be expected, the static model gives very poor results, even giving values of $Z_{\mathrm{eff}}$ smaller than the number of target electrons. The SP model gives a $Z_{\mathrm{eff}}$ value of 2.57 at 0.037 eV and results about double those of the static model. All calculations with the MRMPS method give significantly higher values compared to these two models. Furthermore, all the MRMPS models behave similarly as a function of incident energy: near zero energy, as $k \to 0$, $Z_{\mathrm{eff}}$ increases to its maximum value. Our largest calculation, that with spdfgh-PCOs, gives $Z_{eff} = 8.26$ at an incident positron energy of 0.037 eV.

Our results can be compared to the $Z_{eff}$=6.67 at an incident positron energy of 0.1 eV calculated by Varella et al. (2002) using the Schwinger multichannel method. The calculation using an enhancement factor to model the density of positron yields $Z_{eff}$=11.55 at 0.001eV (Franz & Gianturco 2006). $Z_{eff}$=7.14 was calculated using the Kohn variational method (Cooper & Armour 2008) at 0.14 eV. A reliable non-empirical calculation, which used very accurate variational wave functions at low scattering energy,

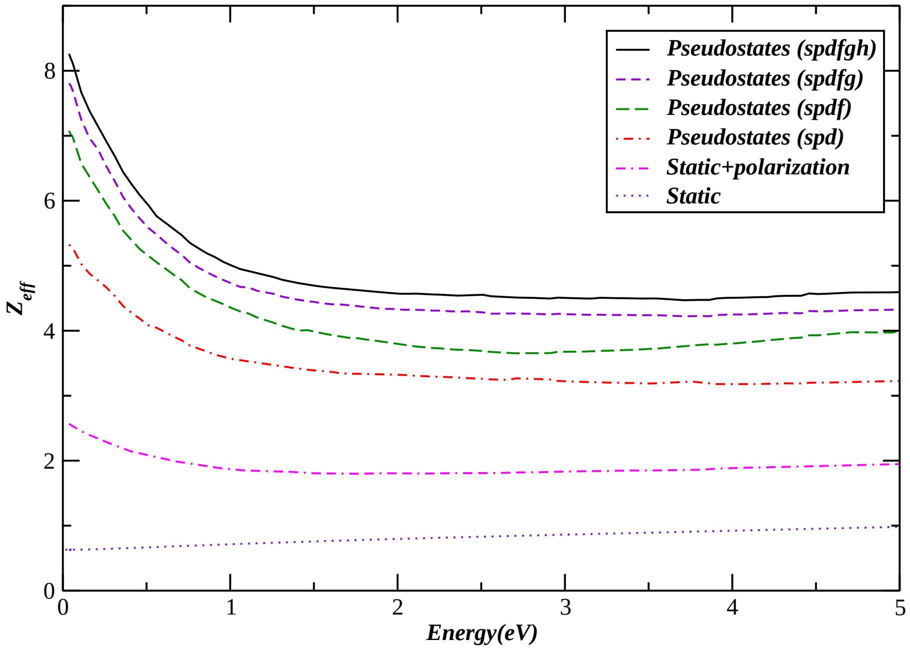

**Figure 7.** $Z_{\text{eff}}$ for $H_2$ molecule in terms of energies for different models for all the symmetries.

calculated by Armour et al. (1990) gives the value of $Z_{eff}$=10.2. Subsequent work using the same method demonstrated the sensitivity to the target wave function (Cooper et al. 2008). The highest *ab initio* $Z_{\text{eff}}$ result so far was obtained by Zhang, Mitroy & Varga (2009), who found $Z_{eff}$=15.7 at zero energy. The accepted experimental value for $Z_{\text{eff}}$ at room temperature is 14.61±0.14 as measured by Laricchia et al. (1987).

The results presented in Fig. 7 demonstrate the extreme sensitivity of $Z_{\text{eff}}$ values to the inclusion of polarisation in the calculation. The MRMPS calculations represent very significant improvement on more traditional models and result in a large increase in the predicted value for $Z_{\text{eff}}$. However, unlike the cross sections and eigenphase sums presented in the previous section, the MRMPS calculations do not appear to be converged even when h ($\ell = 5$) functions are included in the basis; our best value is only just over half the measured one.

The accurate calculation of $Z_{\text{eff}}$ relies on a good representation of the positron – electron correlation; it is well known, for example from studies on the helium atom (Kutzelnigg & Morgan 1992), that electron – electron (anti-)correlation effects only converge slowly with partial wave expansion. It should therefore be no surprise that this is also found for the positron – electron problem. In the next section we explore the idea of extrapolating our calculations to try and converge their dependence on $\ell$.

## 6. Extrapolation to high $\ell$

Gribakin & Ludlow (2002a) applied many-body theory to the calculation of positron binding energies and annihilation rates. They found that the partial-wave expansions for these parameters converged as $1/(l+\frac{1}{2})^4$ and $1/(l+\frac{1}{2})^2$, respectively. In particular, they derived an asymptotic expression for $Z_{eff}$,

$$Z^l_{eff} \sim Z^{l-1}_{eff} + \frac{C_{Z_{eff}}}{(l+\frac{1}{2})^2} \tag{10}$$

where $C_{Z_{eff}}$ is a constant. However, their numerical experiments showed that this behaviour was only found at very high $l$. Gribakin & Ludlow (2002b) found a fit for eq. (10) based on the calculation with $l$=9 and $l$=10,

$$Z_{eff} = Z^l_{eff} + \sum_{L=l+1}^{\infty} \frac{C_{Z_{eff}}}{(L+\frac{1}{2})^2} \tag{11}$$

$$\approx Z^l_{eff} + \frac{C_{Z_{eff}}}{l+\frac{1}{2}} \tag{12}$$

Using this approximation, the value of $Z_{\rm eff}$ gives an error of about 10%. In a similar fashion, the scattering length can be given as:

$$A_{scat} \sim A^l_{scat} + \frac{C_{A_{scat}}}{(l+\frac{1}{2})^3}. \tag{13}$$

Mitroy & Bromley (2006) suggested that a better approximation for eq. (11) is given by

$$\sum_{L=l+1}^{\infty} \frac{C_{Z_{eff}/A_{scat}}}{(L+\frac{1}{2})^n} \approx \frac{C_{Z_{eff}/A_{scat}}}{(n-1)(l+1)^{n-1}} \tag{14}$$

which gives an error about 0.1%.

To see if we can improve our results for $Z_{\rm eff}$ of the $H_2$ molecule we have tested these extrapolation methods. In doing this we note that for us $\ell$ represents the highest angular function used in our PCO basis which is similar to, but not the same as, the definition of $\ell$ adopted by the authors quoted above.

Figure 8 shows our $Z_{\rm eff}$ as function of the highest $\ell$ used in the MRMPS basis plotted against $(\ell+\frac{1}{2})^{-1}$ and $(\ell+1)^{-1}$. For this test calculations are performed for $\ell = 0, \ldots, 5$ ie increment of the pseudo-orbitals from s-PCOs to spdfgh-PCOs. In both cases the results with $\ell > 1$ lie on a reasonable straight line. After fitting our results, $Z_{eff}$ extrapolates to 10.30 and 10.53, respectively, as $\ell \rightarrow \infty$.

Given the sensitivity of our $Z_{\rm eff}$ results to extrapolation on $\ell$ it is interesting to test the low-energy cross sections. For this we calculated the scattering length at 0.1 eV, a value which was found to give stable results. Figure 9 shows the scattering length for MRMPS calculations as a function of $(\ell+\frac{1}{2})^{-3}$ (Gribakin & Ludlow 2002b) and $(\ell+1)^{-3}$ (Mitroy & Bromley 2006). Unlike the extrapolations for $Z_{\rm eff}$, our results do not vary linearly with $\ell$ when we use Gribakin & Ludlow (2002b)'s formula, or indeed the inverse when consider $A_s^{-1}$. However the small gap between $\ell = 5$ and $\ell = \infty$ does not make this a serious issue. Our calculated scattering lengths decrease monotonically with increasing $\ell$. Our scattering length for $\ell = 5$ of $-1.97$ a$_0$ can be extrapolated to $-2.06$ a$_0$ as $\ell \rightarrow \infty$. This can be compared to the calculations of Zhang, Mitroy & Varga (2009) which give a scattering length of $-2.59$ a$_0$.

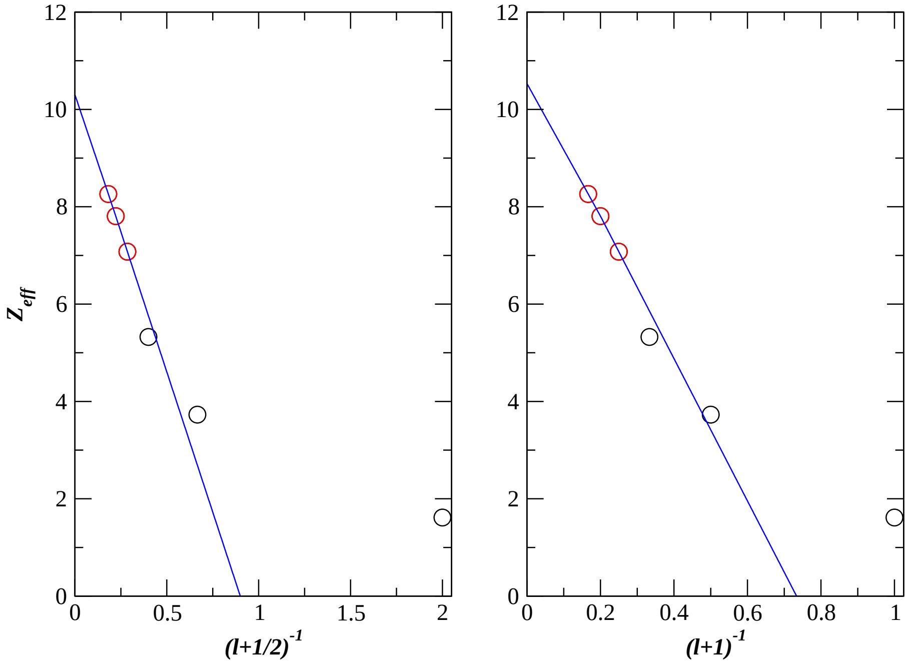

**Figure 8.** $Z_{\rm eff}$ for positron - $H_2$ collisions calculated at 0.037 eV as a function maximum $\ell$ used in a 28-state MRMPS expansion. The straight line is a fit through the three highest $l$ points.

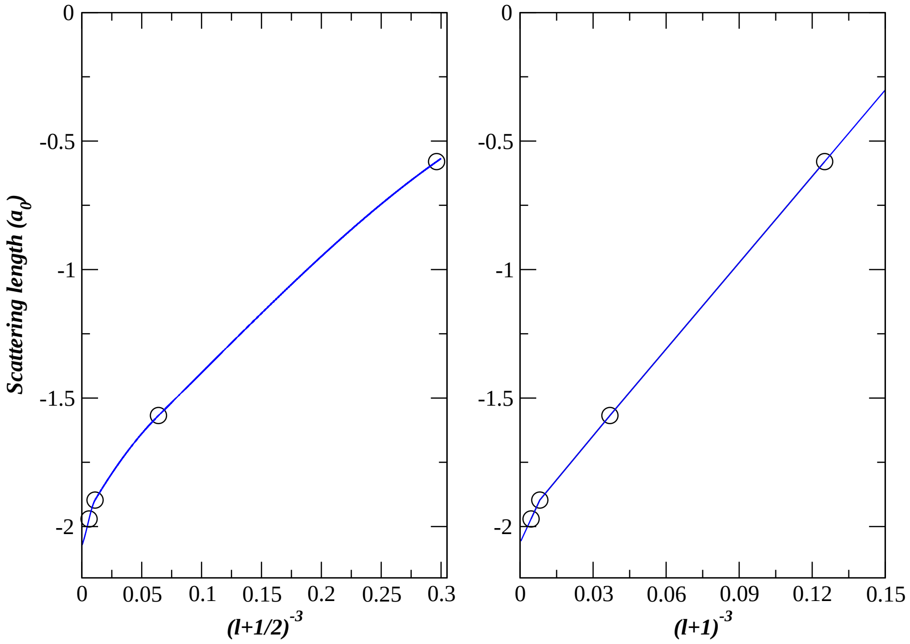

**Figure 9.** Scattering length for positron - $H_2$ collisions calculated at 0.1 eV as as a function maximum $\ell$ used in the MRMPS expansion.

## 7. Conclusion

Total cross sections for positron collision with $H_2$ molecule have been calculated using the molecular R-matrix with pseudo-states (MRMPS) method at energies below the positronium formation threshold. We find excellent agreement between our results and other reliable determinations from both theory and experiment. The MRMPS method would appear to provide a good enough representation of polarisation potential to obtain converged results for such collisions provided reasonably high (at least g) angular functions are included in the basis used to represent the pseudo-states.

Use of the same MRMPS wave functions also give a very significant improvement in the calculated positron annihilation parameter $Z_{\mathrm{eff}}$. However even the biggest of our calculations (going up to h functions) appear to be not entirely converged and gives results significantly lower than the accepted experimental value. The use of extrapolation formulae (Gribakin & Ludlow 2002b, Mitroy & Bromley 2006) improve this value significantly, but still result in values below that observed. It is clear that our MRMPS wave functions are good in electron – positron cusp region but need to be further improved.

Unlike a number of the procedures used for studies of positron – $H_2$ collisions, our MRMPS method is both fully *ab initio* and general. It can therefore, in principle, be used for studies of positron collisions with any molecule. However, it should be noted that the MRMPS method is much more computationally demanding than standard R-matrix calculations; the study of larger targets requires the use of both special procedures (Tennyson 2004) and significant computer power. We have performed a number of test MRMPS calculations for positron collisions with acetylene (Zhang 2010) with encouraging results. Full results of this study will be the subject of a future paper.

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