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2011 J. Phys. B: At. Mol. Opt. Phys. 44 035203

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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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Received 20 October 2010, in final form 22 November 2010

Published 19 January 2011

Online at stacks.iop.org/JPhysB/44/035203

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 theories and generally with the measurements. Calculation of the positron annihilation parameter Z_{eff} with the MRMPS wavefunctions gives values significantly higher than other R -matrix wavefunctions but still do not completely converge with h functions. Extrapolation to higher l -values leads to a predicted value of Z_{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.

(Some figures in this article are in colour only in the electronic version)

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 polarization 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 referred to as virtual Ps formation, are particularly difficult to model in an *ab initio* and general manner (Armour and Humberston 1991). Positron annihilation, usually represented by the parameter Z_{eff} , particularly tests the wavefunctions 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 wavefunction (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 and Tennyson 1990, Armour *et al* 1990, Gibson 1992, Reid *et al* 2004, Arretche *et al* 2006, Mukherjee and Sarkar 2008, Zhang *et al* 2009b) 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 and Sarkar 2008, Zhang *et al* 2009b) which are hard to generalize to many-electron molecular targets.

As demonstrated below, the calculation of accurate, fully *ab initio*, positron annihilation parameters places considerable

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demands on the wavefunctions used. For this reason most such studies of annihilation in molecule studies have focussed on H_2 . Calculations of Z_{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 and Mukherjee 2000), the complex Kohn variational method (Cooper *et al* 2008, Cooper and Armour 2008) and the confined variational method (Zhang *et al* 2009b). Franz and Gianturco (2006) corrected Gianturco and Mukherjee's calculation for lack of energy normalization of the wavefunction; they also give Z_{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 (RMPS) (Gorfinkiel and Tennyson 2004, 2005), for the calculation of both low-energy positron–molecule collision cross sections and the positron–molecule annihilation parameter Z_{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 and Tennyson 2004, 2005), C_2^- (Halmová and Tennyson 2008, Halmová *et al* 2008) and Li_2 (Tarana and Tennyson 2008). It has been shown to give an excellent representation of the polarizability for a selection of small molecules (Jones and 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 as

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

where Φ_i^N is the N -electron target wavefunction and u_{ij} are continuum orbitals carrying the positron, whose coordinate is denoted by $\tilde{\mathbf{x}}$. The second sum in equation (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 wavefunction ψ_k^{N+1} , with discretized energy E_k , is only used to represent the wavefunction within a finite, inner region represented by a sphere of radius a , here taken as $10a_0$, centred on the target centre-of-mass. This wavefunction is independent of

the scattering energy but is used to construct the energy-dependent R -matrix on the boundary (Burke and Berrington 1993). The R -matrix can then be propagated to yield scattering observables. We note that this procedure avoids explicitly evaluating the scattering wavefunction, a point we will return to below when considering annihilation calculations. In the UK polyatomic R -matrix codes (Morgan *et al* 1998) all the wavefunctions are expressed in terms of Gaussian-type orbitals (GTOs). It should be noted that 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 discretized 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

$$\alpha_i = \alpha_0 \beta^{(i-1)}, \quad i = 1, \dots, L, \quad (2)$$

and the choice of (α_0, β) . 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

$$\sigma_{\text{ann}} = \pi r_0^2 \frac{c}{v} Z_{\text{eff}} \quad (3)$$

where v is the velocity of the incident positron, 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 *et al* 2009b).

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

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

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

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

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

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

where $w_{ik}(a)$ is the amplitude on the R -matrix boundary in the i th channel of the k th inner region wavefunction. $F_j(a)$ is the value of the outer region wavefunction in channel j on the boundary; \mathbf{R} is the R -matrix. Although equation (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} :

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

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

To normalize the outer region wavefunction, the density of the incident beam should be one positron per unit volume:

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

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, respectively, which are derived from the outer region Schrödinger equation (Burke and Berrington 1993). The normalization term $(1 - i\underline{K})$ is obtained from transforming the asymptotic form involving the S -matrix into that written in terms of the K -matrix.

At long range the outer region wavefunctions were obtained using an asymptotic expansion (Gailitis 1976) and were then numerically integrated inwards from $r = a'$, typically 30–50 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 wavefunction 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

$$Z_{\text{eff}} = \sum_{k,k'} \frac{4\pi}{kk'} A_{Ek}^* Z_{kk'} A_{Ek'} \quad (9)$$

where the delta function matrix elements are denoted by $Z_{kk'}$. These energy-independent matrix elements can be evaluated using a specialization of the scattering Hamiltonian

construction procedure of Tennyson (1996). To do this requires a set of integrals for the GTOs with a δ -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 *et al* 2009a) 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 *et al* 2009b) suggests that Z_{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 and 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 polarization (SP) model and standard close-coupling (CC). The target calculation all used a 6-31 G** GTO basis set (Hariharan and Pople 1973). The static and SP models are based on a Hartree–Fock H_2 wavefunction while the CC calculation used a near-full configuration interaction (CI) representation of the target wavefunction which is therefore independent of the choice of molecular orbitals (MOs). This wavefunction is represented (in D_{2h} symmetry) by the configurations

$$(1-3a_g, 1b_{2u}, 1b_{3u}, 1-2b_{1u}, 1b_{2g}, 1b_{3g})^2.$$

For continuum functions we used the GTO basis functions with $\ell \leq 4$ (up to g orbitals) of Faure *et al* (2002).

A number of MRMPs models were tested. For these we started from the Hartree–Fock MOs for H_2^+ . The PCO exponents were 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 polarizability, see table 1, and stable eigenphases. This PCO basis actually corresponds to the one used to study electron-impact ionization in H_2 (Gorfinkiel and Tennyson 2005).

All previous studies using the MRMPs method have used PCOs containing only s, p and d functions. Here we present calculations using PCO 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,

Table 1. Polarizabilities of H₂ for an spd-PCO basis set with $\beta = 1.4$ for different α_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 and Dykstra (1988).

α_0	α_{\parallel}	α_{\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 deletion threshold $\delta_{\text{thrsh-tar}}$ 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 $\delta_{\text{thrsh-tar}} = 2 \times 10^{-4}$ gives satisfactory results. A second deletion threshold, $\delta_{\text{thrsh-scat}} = 2 \times 10^{-7}$, was used to orthogonalize the continuum orbitals to the full target set. Note that GTOs with exponents greater than α_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-PCO and spdfgh-PCO calculations $\delta_{\text{thrsh-scat}} = 2 \times 10^{-6}$ 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 $1a_g^1(4-20a_g, 2-8b_{2u}, 2-8b_{3u}, 1-5b_{3u}, 3-10b_{1u}, 2-6b_{2g}, 2-6b_{3g})^1$.

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

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

For the MRMPS calculations, 8 target states are included for s- and sp-PCOs case, 15 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 Σ_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 polarization 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 Σ_g^+ symmetry for the different PCO models. Results for the Armour *et al* (1990) calculation, which makes explicit use of the positron–electron coordinate in the wavefunction, are given for comparison. As can be seen, the calculations with spdfg-PCOs and spdfgh-PCOs give very similar results, suggesting that our eigenphase calculated with the MRMPS method is converged at low energies. These results are in good agreement with the Armour

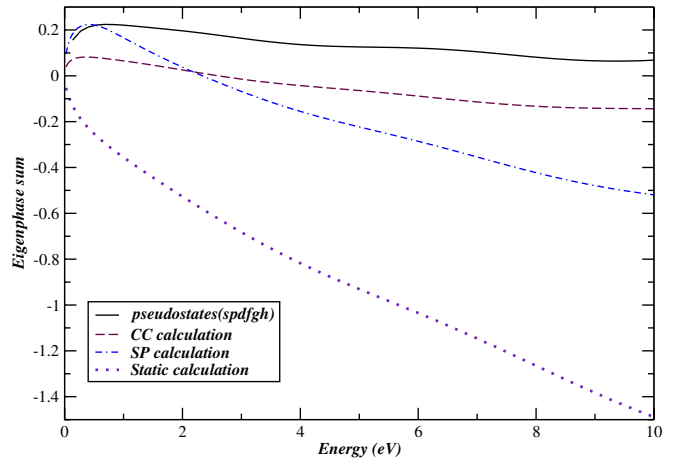


Figure 1. Eigenphase sums for Σ_g^+ symmetry for the static, static plus polarization (SP), close-coupling and PCO-spdfgh RMPS models.

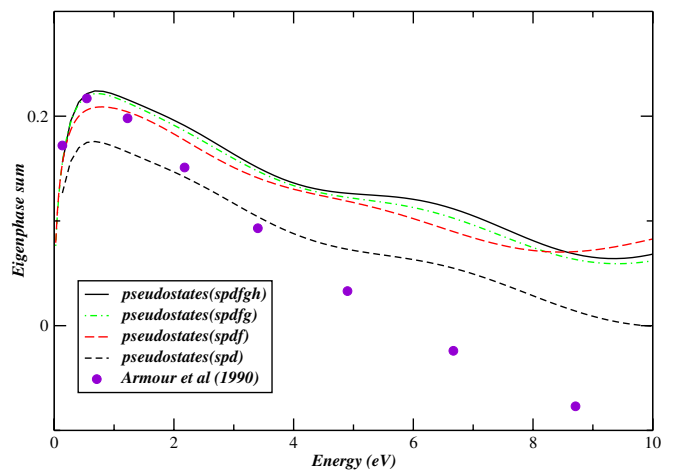


Figure 2. Eigenphase sums for Σ_g^+ symmetry for various PCO models as a function of energy; results of Armour *et al* (1990), column 7b in table 2(a), are given for comparison.

et al (1990) eigenphases at lower energies, and are higher at incident energies above 3 eV because only the lowest partial wave is included in Armour *et al*'s calculations. The Π_u , Σ_u^+ and Π_g symmetry eigenphases show similar behaviour, see figure 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 probe the same processes. Obviously, the results of the static and SP calculations given in figure 4 are poor as suggested by the eigenphases given above. The static model does not even give any increase in the 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,

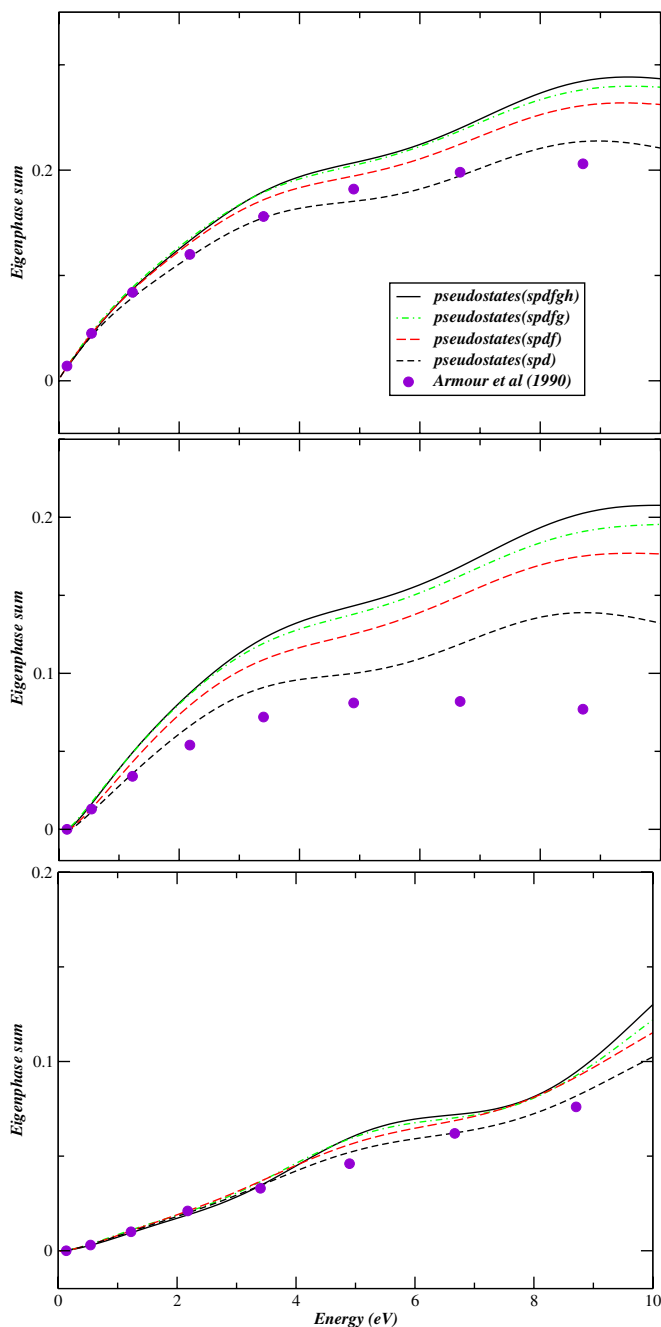


Figure 3. Eigenphase sums for Π_u (upper), Σ_u^+ (middle) and Π_g (lower) symmetries. Results from Armour *et al* (1990), table 5(a), are given for comparison.

judging by both the eigenphase sums and the cross sections, are converged for calculations with the larger PCO 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*'s (1990) integral cross sections, although there are minor differences between the corresponding eigenphase sums. At energies above 7 eV, the Mukherjee and Sarkar (2008) cross

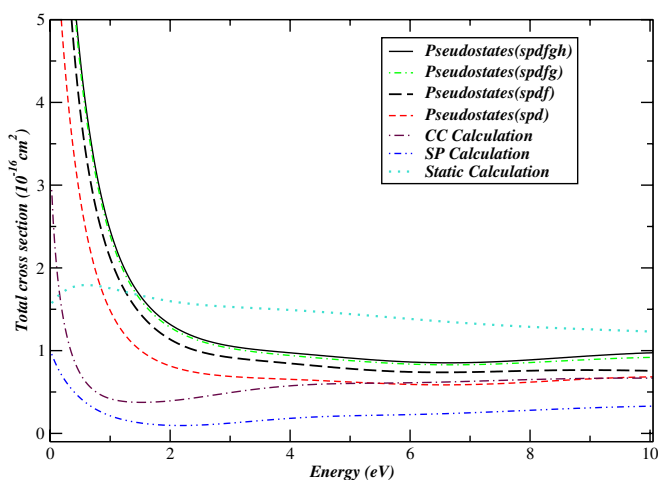


Figure 4. Total cross sections for various models without and with the MRMPS method.

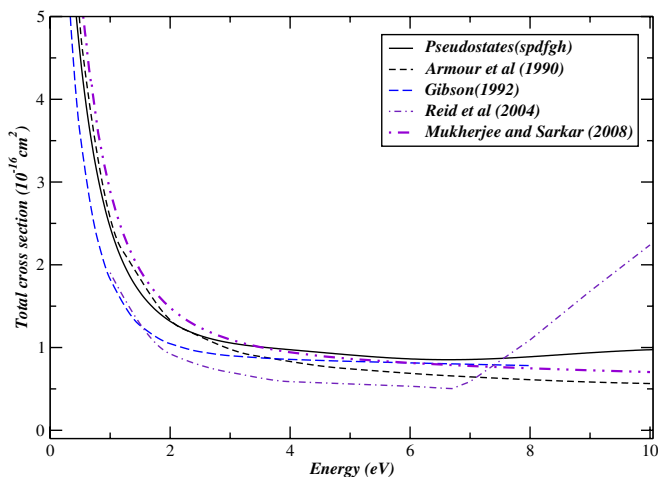


Figure 5. Total cross sections for positron–H₂ collisions calculated with various methods: MRMPS results of this study, compared to Armour *et al* (1990), Gibson (1992), Reid *et al* (2004) and Mukherjee and Sarkar (2008).

sections increase rapidly due to the Ps formation, which is included in their study. For energies above 10 eV, the results of Mukherjee and 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 H₂. Our MRMPS results are in very good agreement with the 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 all the reliable theoretical estimates including ours. However, at energies above 1 eV, Zecca *et al*'s (2009) result lies higher than our calculation. Charlton *et al*'s (1983) lies below our results at energies from 2 to 6 eV, and then agree with them above 6 eV.

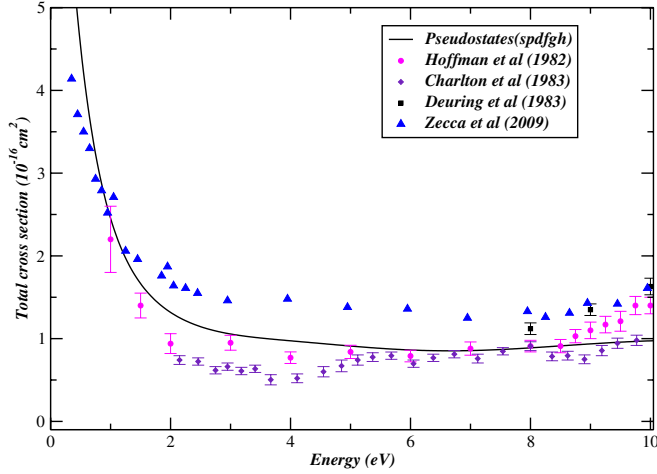


Figure 6. Total cross sections for positron–H₂ collisions: our MRMPS calculations compared to measurements of Hoffman *et al* (1982), Charlton *et al* (1983), Deuring *et al* (1983) and Zecca *et al* (2009).

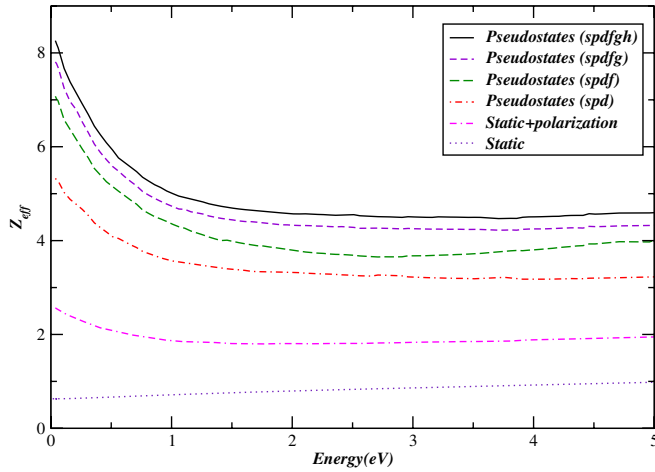


Figure 7. Z_{eff} for the H₂ molecule as a function of energy for different models summed over all the symmetries.

5. Annihilation

Energy-dependent values for Z_{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_{eff} smaller than the number of target electrons. The SP model gives a Z_{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 $k \rightarrow 0$, Z_{eff} increases to its maximum value. Our largest calculation, that with spdfgh-PCOs, gives $Z_{\text{eff}} = 8.26$ at an incident positron energy of 0.037 eV.

Our results can be compared to $Z_{\text{eff}} = 6.67$ 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 $Z_{\text{eff}} = 11.55$ at 0.001 eV (Franz and Gianturco 2006).

$Z_{\text{eff}} = 7.14$ was calculated using the Kohn variational method (Cooper and Armour 2008) at 0.14 eV. A reliable non-empirical calculation, which used very accurate variational wavefunctions at low scattering energy, calculated by Armour *et al* (1990) gives the value of $Z_{\text{eff}} = 10.2$. Subsequent work using the same method demonstrated the sensitivity to the target wavefunction (Cooper *et al* 2008). The highest *ab initio* Z_{eff} result so far was obtained by Zhang *et al* (2009b), who found $Z_{\text{eff}} = 15.7$ at zero energy. The accepted experimental value for Z_{eff} at room temperature is 14.61 ± 0.14 as measured by Laricchia *et al* (1987).

The results presented in figure 7 demonstrate the extreme sensitivity of Z_{eff} values to the inclusion of polarization 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_{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_{eff} relies on a good representation of the positron–electron correlation; it is well known, for example from studies on the helium atom (Kutzelnigg and 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 ℓ .

6. Extrapolation to high ℓ

Gribakin and 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} :

$$Z_{\text{eff}}^l \sim Z_{\text{eff}}^{l-1} + \frac{C_{Z_{\text{eff}}}}{(l+\frac{1}{2})^2} \quad (10)$$

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

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

$$\approx Z_{\text{eff}}^l + \frac{C_{Z_{\text{eff}}}}{l+\frac{1}{2}}. \quad (12)$$

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

$$A_{\text{scat}} \sim A_{\text{scat}}^l + \frac{C_{A_{\text{scat}}}}{(l+\frac{1}{2})^3}. \quad (13)$$

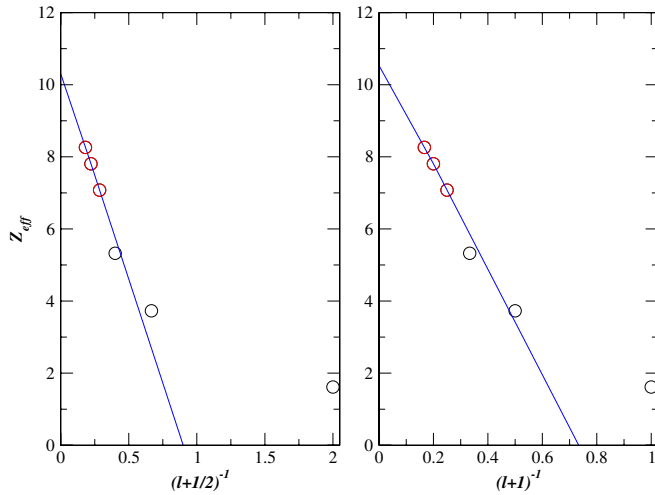


Figure 8. Z_{eff} for positron– H_2 collisions calculated at 0.037 eV as a function of maximum ℓ used in a 28-state MRMPS expansion. The straight line is a fit through the three highest l points.

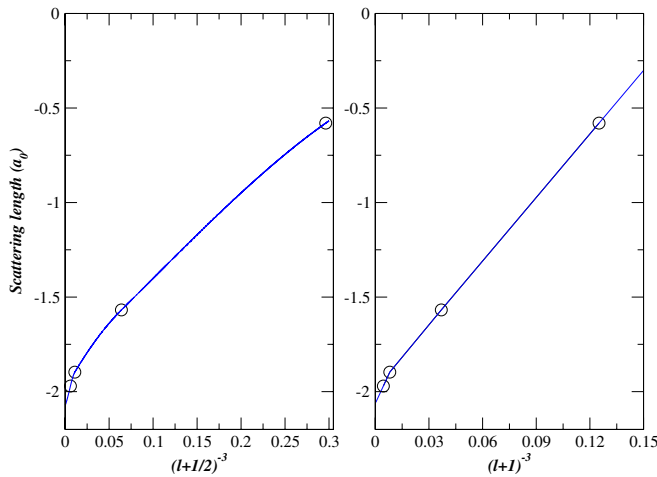


Figure 9. Scattering length for positron– H_2 collisions calculated at 0.1 eV as a function of maximum ℓ used in the MRMPS expansion.

Mitroy and Bromley (2006) suggested that a better approximation for equation (11) is given by

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

which gives an error about 0.1%.

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

Figure 8 shows our Z_{eff} as a function of the highest ℓ used in the MRMPS basis plotted against $(\ell + \frac{1}{2})^{-1}$ and $(\ell + 1)^{-1}$. For this test calculations are performed for $\ell = 0, \dots, 5$, i.e. increment of the pseudo-orbitals from s-PCOs to spdfgh-PCOs. In both cases the results with $\ell > 1$ lie on a reasonably 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_{eff} results to extrapolation on ℓ , 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 and Ludlow 2002b) and $(\ell + 1)^{-3}$ (Mitroy and Bromley 2006). Unlike the extrapolations for Z_{eff} , our results do not vary linearly with ℓ when we use the Gribakin and Ludlow (2002b) formula, or indeed the inverse when we 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 ℓ . Our scattering length for $\ell = 5$ of $-1.97a_0$ can be extrapolated to $-2.06 a_0$ as $\ell \rightarrow \infty$. This can be compared to the calculations of Zhang *et al* (2009b) which give a scattering length of $-2.59a_0$.

7. Conclusion

Total cross sections for positron collision with the 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 polarization 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 wavefunctions also gives a very significant improvement in the calculated positron annihilation parameter Z_{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 and Ludlow 2002b, Mitroy and Bromley 2006) improve this value significantly, but still result in values below that observed. It is clear that our MRMPS wavefunctions are good in the 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.

Acknowledgments

The authors thank Edward Armour, Alex Harvey and Gleb Gribakin for very helpful discussions. This work was performed with the support of UK Collaborative Computational Project 2 and EPSRC grant EP/C548027.

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