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Polarisation effects in low-energy positron–molecule scattering

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Abstract

The UK molecular *R*-matrix method has been adapted to treat positron collisions from polyatomic targets. A simple empirical enhancement factor which corrects for the underestimation of electron–positron polarisation and correlation effects in the calculations performed with the static-plus-polarization model at low scattering energies is presented. Application of this model to positron scattering from carbon dioxide at energies below 8 eV is discussed. Introduction of the enhancement factor improves the integral cross sections significantly and introduces structures in the differential cross sections consistent with other studies. The prospects for a fully *ab initio* treatment of this problem are discussed.

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1. Introduction

Superficially it should be easier to treat low-energy collisions of positrons with molecules than electron collisions since one does not have to worry about exchange interactions. In practice this is not true: it transpires that it is much easier to allow for the anti-correlated motions found between a scattering electron and those of the target molecule than it is for the correlated motion of a scattering positron with these electrons. At long-range the effect of both the electron–electron and electron–positron correlation is to polarise the target wavefunction giving an attractive potential of the same magnitude as a function of distance. However, once the scattering particle begins to penetrate the target wavefunction the resulting multicentered interactions cannot truly be represented as a simple potential. Indeed detailed and very accurate calculations on positron collisions with one and two-electron atomic and molecular targets [1] have clearly demonstrated that the only completely satisfactory way dealing with this issue is by using wavefunctions which are explicitly a function of the positron–electron distance. Use of such wavefunctions for many electron problems is difficult but is an area of significant research activity [2].

To be able to make progress on actual positron–molecule collision problems of interest a number of less computationally demanding methods have been used including the distributed positron model [3], model potentials derived from density functional theory [4], single centre expansions [5], and close-coupling methods based on the Schwinger variational principle [6] and the *R*-matrix method [7]. All these methods have been applied to positron collisions with many electron targets at low-energies (here defined as being below the positronium formation threshold). We note that at high energies relatively simple procedures appear to give good results [8].

We have worked on the *R*-matrix treatment of low-energy positron collisions and have recently collaborated on the (re-)implementation of positron collisions within the UK molecular *R*-matrix codes [9]. This method gave

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good results for positron collisions with the polar water molecules [10], as it works well for cases where the interactions are dominated by the dipole interactions [11]. However it is known [7,12–14] that such calculations perform less well for collisions with non-polar target.

In this paper we consider positron collisions with the non-polar carbon dioxide molecule. CO_2 is a many electron system with which positron collisions have been studied both experimentally [15–20] and theoretically [8,21–23]. We show that for this system a standard but limited treatment using the *R*-matrix method significantly underestimates the elastic cross section for the system. However by introducing a single adjustable parameter, which scales the electron–positron interaction, we can bring the elastic cross as function of energy into excellent agreement with the experimental results. Furthermore the scaled interaction introduces more structure into the differential cross sections in line with other methods [21].

2. Computational models

2.1. R-matrix method with static-plus-polarisation model

In the static-plus-polarisation (SP) model the configuration space for the electrons is built up from the Hartree–Fock ground-state and all single electronic excited configurations. These single excitations include all excitations from occupied Hartree–Fock orbitals into all the virtual (i.e. unoccupied) target orbitals. In this model the positron is also allowed to occupy all target molecular orbitals (including those already doubly occupied by electrons) as well as a set of single centered diffuse Gaussian orbitals which are used to represent the continuum within the *R*-matrix sphere [24]. These configurations are only subject to the constraint of overall space–spin symmetry and an additional constraint which couples the electrons to the appropriate electronic spin symmetry.

We note in passing that use of an equivalent model for electron collisions would actually result in a phenomenon known as "over-correlation", where the energy levels of the scattering system are too low relative to those of the corresponding target calculation. The distinct nature of the positron, whose wavefunction does not have to be anti-symmetrised to the target electrons, means that there is little danger of over-correlation in these calculations. Indeed as the results shown below demonstrate, the SP model is actually under-correlated for positron collisions as it gives an insufficient treatment of the polarisation effects arising from electron–positron correlation effects.

2.2. The f-factor to describe correlation effects

In order to model correlation effects which are not fully described in the SP model, we have experimented with scaling the electron–positron attraction integrals by an empirically adjusted enhancement factor, *f*. These integrals are the ones which are routinely referred to as two-electron integrals in standard quantum chemistry language. Here we wish to only increase the electron–positron attraction so do not alter the corresponding electron–electron integrals.

$$(pq|\overline{rs})_{\mathrm{enh}} = f(pq|\overline{rs}), \tag{1}$$

$$= f\int \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)\left(-\frac{1}{|r_{1\bar{1}}|}\right)\bar{\chi}_r(\mathbf{r}_{\bar{1}})\bar{\chi}_s(\mathbf{r}_{\bar{1}})\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_{\bar{1}}. \tag{2}$$

Here $\phi_p(\mathbf{r}_1)$ and $\phi_q(\mathbf{r}_1)$ are electron orbitals, $\bar{\chi}_r(\mathbf{r}_{\bar{1}})$ and $\bar{\chi}_s(\mathbf{r}_{\bar{1}})$ are positron orbitals, and $|r_{1\bar{1}}| = |\mathbf{r}_1 - \mathbf{r}_{\bar{1}}|$ is the electron–positron distance.

This form of scaling can be justified as follows. A Møller–Plesset type perturbative expansion of the electron–positron correlation energy gives the second-order contribution [25]

$$E^{(2)} = \sum_{ia\bar{i}\bar{a}} \frac{(ia|\overline{ia})^2}{\epsilon_i - \epsilon_a + \epsilon_{\bar{i}} - \epsilon_{\bar{a}}}.$$

Here ϵ_i and ϵ_a denote energies of occupied and virtual electronic orbitals, respectively. $\epsilon_{\bar{i}}$ and $\epsilon_{\bar{a}}$ are the same for positrons.

The first-order contribution is given by

$$E^{(1)} = \sum_{i\bar{i}} (ii|\overline{ii}).$$

Adding the first- and second-order contribution and rearranging the terms results in

$$E^{(1+2)} = \sum_{i\bar{i}} \left((ii|\overline{ii}) + \sum_{a\bar{a}} \frac{(ia|\overline{ia})^2}{\epsilon_i - \epsilon_a + \epsilon_{\bar{i}} - \epsilon_{\bar{a}}} \right)$$
$$= \sum_{i\bar{i}} \left((ii|\overline{ii}) + (ii|\overline{ii})^{(2)} \right).$$

Here we have introduced a second-order correction $(ii|\overline{ii})^{(2)}$ to the electron–positron attraction integral $(ii|\overline{ii})$. Since all denominators in the above expression are negative, this correction is always negative, and therefore has the same sign as the integral $(ii|\overline{ii})$ itself. For each electron–positron pair we can define the ratio

$$\gamma^{(2)}_{i\bar{i}} = \frac{(ii|\overline{ii})^{(2)}}{(ii|\overline{ii})}.$$

between second-order and first-order contribution to the interaction between both particles. By defining the pair-dependent enhancement factor

$$f_{i\bar{i}} = 1 + \gamma^{(2)}_{i\bar{i}}$$

we can express the electron–positron interaction energy as

$$E^{(1+2)} = \sum_{i\bar{i}} f_{i\bar{i}}(ii|\overline{ii}).$$

If we assume, that the ratio $\gamma^{(2)}_{i\bar{i}}$ between second- and first-order contribution is the same for each electron–positron pair, we can replace the pair-dependent enhancement factor by an averaged enhancement factor *f*

$$E^{(1+2)} \approx \sum_{i\bar{i}} f(ii|\bar{i}\bar{i}), \tag{3}$$

as used in this paper. However, one should note that this derivation has been made for the integral type $(ii|\bar{i}\bar{i})$ only. In our computations we have used integrals of the more general type $(ij|\bar{i}\bar{j})$, for which the second-order correction might be positive, resulting in enhancement factors smaller than one. Nevertheless we have used the same enhancement for all integral types.

The present approach is not equivalent to scaling the positron or electron charge as such an approach would require a scaling of the positron–nuclear repulsion integrals or of the electron–nuclear attraction integrals in addition to the scaling done here. An increased positron–nuclear repulsion would enhance the repulsive interactions which would compensate the increased positron–electron attraction. Hence the net-effect on the cross section would be small. Furthermore, the interaction of the positron with the multipole moments of the target molecule in the outer region would require a similar scaling of the interaction. On the other hand, a scaling of the electron charge will increase the cross section, but will also change the properties of the target molecule. Furthermore this would induce a charge on the target, which have to be taken care of in the outer region. A related approach, the scaling of the nuclear charge, is used for the calculation of resonances in electron–molecule scattering [26,27]. However, we do not follow this route here for the same reasons mentioned for scaling the electron charge.

Clearly use of $f = 1$ results in the standard *ab initio* result used in previous *R*-matrix studies of positron–molecule collisions. As shown below the results are very sensitive to the choice of f and values of f only slightly bigger than unity yield surprisingly good results.

Finally, for large distances r_p between the positron and the scattering centre the second-order contribution to the electron–positron correlation energy goes over to the asymptotic polarisation potential which is given by (in a.u.) [28]

$$-\frac{\alpha_0}{2r_p^4} - P_2(\cos\theta)\frac{\alpha_2}{2r_p^4} \tag{4}$$

for a linear molecule. Here α_0 (α_2) is the spherical (anisotropic) polarisability of the target molecule, and $P_2(\cos\theta)$ is a Legendre polynomial, where θ is the angle between the vector linking the positron to the molecular centre-of-mass and that of the molecule. One should note that this long-range behaviour is quite different from the long-range behaviour, which would have been generated asymptotically by scaling the charge of one of the particles. A scaling of the positron charge would have introduced a scaling of the electrostatic interactions outside the box (here the leading term is the quadrupole moment), whereas a scaling of the charge of the target electrons would have introduced an attractive Coulomb-potential. The long-range polarisation is included automatically, if not completely, in calculations which use coupled states expansions [29,30] but not in the SP model. Below we also discuss the influence of including asymptotic polarisation potential outside the *R*-matrix box, something that was also tested in earlier *R*-matrix studies of positron–molecule collisions [12,13].

In all calculations the interaction due to the target quadrupole moment was allowed for in the outer region. In addition the spherical and non-spherical polarisability has been included in the outer region in some scattering runs. The effects on the integral cross section is discussed in Fig. 2, while the effects on the differential cross section is shown in Figs. 4 and 5, respectively.

3. Computational details

Calculations were performed with our recent positron implementation of the UK molecular *R*-matrix codes [10]. Unlike the earlier implementation [7], this version uses the polyatomic code [31] which is based on the use of Gaussian Type Orbitals (GTOs) to represent both the target and continuum wavefunctions.

In all studies presented here we used the double-zeta plus polarisation (DZP) GTO basis set of Dunning et al. shown in Table 1. The calculation has been performed in the D_{2h} symmetry group using a bondlength of $r_{CO} = 1.161$ Å. In the *R*-matrix calculations a box size of $10.0a_0$ has been used. The continuum GTO basis set was taken from Faure et al. [24]. Differential cross sections were calculated using the code POLYDCS [32].

For the calculation including the asymptotic polarisation potential we have used the values $\alpha_0 = 15.608a_0^3$ and $\alpha_2 = 14.910a_0^3$ which were calculated using density functional theory (DFT) with the Perdew–Burke–Ernzerhof

Table 1
Carbon dioxide target Gaussian basis set used in *R*-matrix calculations

Centre	Type	Exponent	Coefficient
C	s	4232.610, 634.882, 146.097, 42.4974, 14.1892, 1.9666	0.002029, 0.015535, 0.075411, 0.257121, 0.596555, 0.242517
C	s	5.1477	1.0
C	s	0.4962	1.0
C	s	0.1533	1.0
C	p	18.1557, 3.9864, 1.1429, 0.3594	0.018534, 0.115442, 0.386206, 0.640089
C	p	0.1146	1.0
C	d	0.75	1.0
O	s	7816.54, 1175.82, 273.188, 81.1696, 27.1836, 3.4136	0.002031, 0.015436, 0.073771, 0.247606, 0.611831, 0.241205
O	s	9.5322	1.0
O	s	0.9398	1.0
O	s	0.2846	1.0
O	p	35.1832, 7.904, 2.3051 0.7171	0.01958, 0.124189, 0.394727, 0.627375
O	p	0.2137	1.0
O	d	0.85	1.0

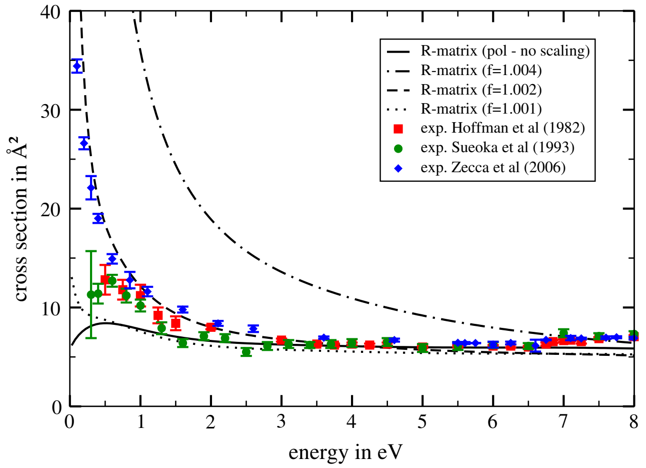

Fig. 1. Integral cross section for positron scattering off carbon dioxide. The experimental values are taken from Hoffman et al. [15], Sueoka and Hamada [16], and Zecca et al. [17].

(PBE) functional [33] and the TZVPP basis set [34] as implemented in the TURBOMOLE program-package [35]. These values agree well with previously calculated and measured values of the polarisability [36].

4. Results and discussion

Fig. 1 shows the integral cross section for positron scattering off carbon dioxide. The figure shows the unscaled and scaled *R*-matrix results together with experimental results from Hoffman et al. [15], from Sueoka and Hamada [16], and from Zecca et al. [17]. The best agreement between theory and experiment is reached with an enhancement factor $f = 1.002$, i.e. a scaling of only 0.2%.

When compared with experiments, the calculated integral cross section using no scaling is too low at small energies but agree reasonably well at higher energies. By using the enhancement factor, the failure to fully reproduce the effects of dynamic electron–positron interactions at low-energies is corrected, while the good agreement at higher energies is retained.

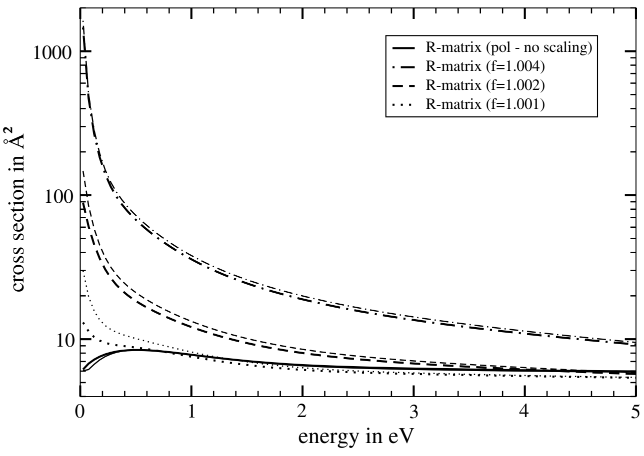

Fig. 2. Integral cross section for positron scattering off carbon dioxide for different *f*-factors with (thin lines) and without (thick lines) asymptotic polarisation potential in the outer region. Note that different scales are used than in Fig. 1.

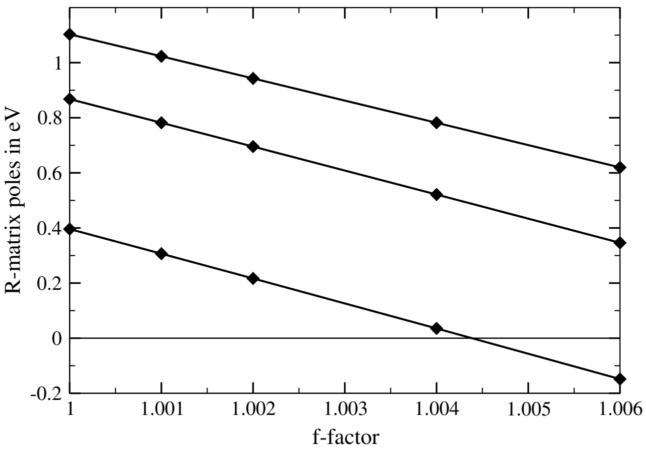

Fig. 3. Lowest *R*-matrix poles as a function of the enhancement factor *f*.

Fig. 2 shows the integral cross section calculated with the various *f*-factors with and without asymptotic polarisation potential in the outer region (using thin and thick lines, respectively). The unscaled cross section is nearly unaffected by switching on the asymptotic potential. For $f = 1.001$ the cross section near to zero positron-energy (0.025 eV) is doubled by switching on the asymptotic potential. This reduces to an increase of 15 per cent at 0.525 eV and to less than 8 per cent at 1.025 eV. For $f = 1.002$ the cross section increases at 0.025 eV by about 6%. At 0.525 eV and 1.025 eV the increases are 14% and 9.4%, respectively. For $f = 1.004$ the increases at the same energies are 11%, 7% and 6%, respectively. From these numbers we conclude that the influence of the asymptotic polarisation potential in the outer region decreases rapidly with increasing energy and with larger *f*-factors.

Fig. 3 shows the three lowest *R*-matrix poles as a function of the f-factor. The poles are shifted linearly towards lower energies with increasing *f*-factor. This becomes clear from a closer look at the definition of the *R*-matrix poles

$$\omega_{\mathrm{K}} = E_{\mathrm{K}}^{\mathrm{Ne1p}} - E^{\mathrm{Ne}},$$

where E^{Ne} is the ground-state energy of the target molecule and $E_{\mathrm{K}}^{\mathrm{Ne1p}}$ is the energy of the system including the target molecule and the positron inside the *R*-matrix box. $E_{\mathrm{K}}^{\mathrm{Ne1p}}$ depends approximately linearly on the *f*-factor, since we are scaling the electron–positron interaction linearly. In general the shift in energy is different for different poles, as can be seen in Fig. 3. By shifting *R*-matrix poles towards lower energies the integral cross section is increased. For *f*-factors slightly larger than 1.004 the first pole becomes negative, indicating the formation of a bound state for these *f*-factors.

Figs. 4 and 5 compare our calculations with the measured differential cross sections (DCS) of Przybyla et al. [19] whose measurements are not absolute so that we have

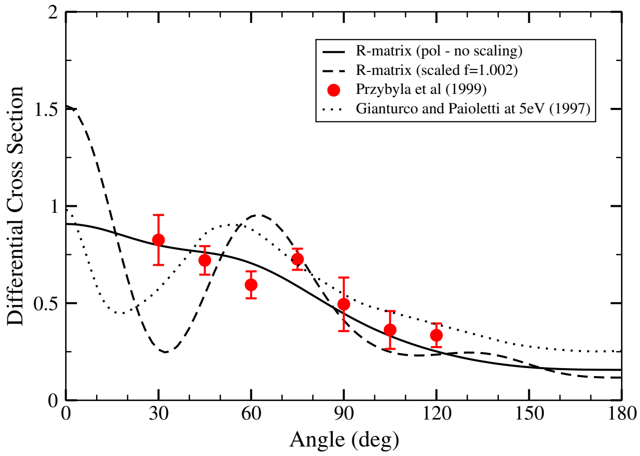

Fig. 4. Differential cross section, in Å^2/sr, at 4.75 eV for positron scattering off carbon dioxide performed with $f = 1$ and an enhancement factor of $f = 1.002$. The experimental values are taken from Przybyla et al. [19]. Note that the experimental data is given in arbitrary units.

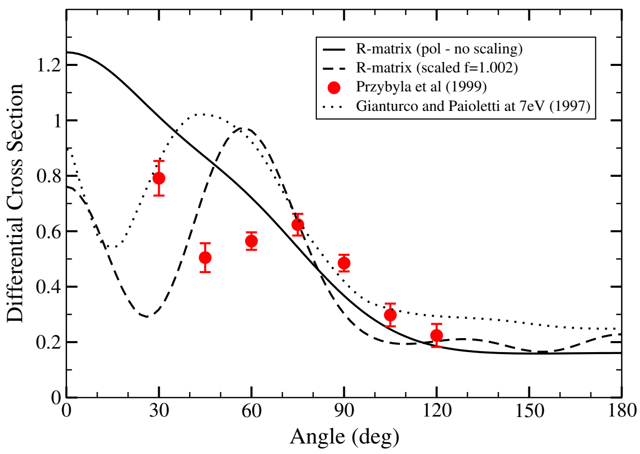

Fig. 5. Differential cross section, in Å^2/sr, at 6.75 eV for positron scattering off carbon dioxide performed with $f = 1$ and an enhancement factor of $f = 1.002$. The experimental values are taken from Przybyla et al. [19]. Note that the experimental data is given in arbitrary units.

scaled their results to give approximate agreement with theory. We have plotted the calculations using no scaling ($f = 1$) and using the optimized enhancement factor ($f = 1.002$) with and without inclusion of the asymptotic polarisation potential. The DCS at 4.75 eV and 6.75 eV are given in Figs. 4 and 5, respectively. Furthermore we have included the DCS calculated by Gianturco and Paioletta [21] at 5.0 eV and 7.0 eV in Figs. 4 and 5, respectively.

The calculations using no-scaling show maxima in the forward direction and nearly no oscillatory structure. The scaling introduces oscillations in the DCS and brings them into better agreement with results obtained in the calculations of Gianturco and Paioletta. Compared with Gianturco and Paioletta, we find the forward peak has larger magnitude and the second peak at somewhat higher angles. By including the asymptotic polarisation potential in the outer region, the forward peak is increased by roughly 20%, while nearly no change in the DCS is observable for angles larger than 30°. At angles above 90° our DCS show small oscillations, which might be artefacts of the calculation. However, given that Gianturco and Paioletta have used a fairly different approach, a model potential derived from density functional theory, the overall agreement is surprisingly good.

The comparison of the calculated DCS with experimental data is more difficult, as the measured DCS of Przybyla et al. [19] are the only available points. Some oscillatory behaviour can be seen in their data. However the overall agreement between all the calculated DCS and the experimental DCS remains unsatisfactory. It remains unclear if this problem is due to the calculations or the experiments themselves.

It is interesting to note, that the *f*-factor not only changes the position of the *R*-matrix poles, but also changes the amplitudes of the wavefunction at the boundary of the *R*-matrix box towards values that produce differential cross sections with more structure.

5. Conclusions

We present a simple prescription for correcting for omitted low-energy positron–electron polarisation effects in positron–molecule collision. In this method the two particle integrals between each electron and the positron are scaled by a factor. It is shown that use of a very modest scaling, only 0.2% in the value of the integral, gives a dramatic improvement in the quality of the calculation.

The results presented here for CO_2 are not unique. We have performed similar calculations for acetylene, another system for which the standard *R*-matrix treatment struggles to reproduce the correct low-energy behaviour [14]. Similarly good agreement is obtained in this case.

Of course resorting to scaling integrals, or the use of similar arbitrary parameters, destroys much of the value of a fully *ab initio* approach. It is our opinion that a full and correct treatment of low-energy positron collisions can only be obtained by explicitly including the positron–electron coordinate in the wavefunction ansatz. That this is true has already been amply demonstrated in detailed and rigorous calculations on one and two-electron atoms and molecules [1]. We are striving to be able to do this for the much more demanding case of positron collisions with many electron polyatomic systems.

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