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Low-energy, elastic positron–molecule collisions using the *R*-matrix method: e^+–H_2 and e^+–N_2

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Abstract. The *R*-matrix method, which has proved successful in the study of electron-molecule collisions, is used to calculate, *ab initio*, eigenphases and elastic cross sections for the impact of positrons on diatomic molecules. Good agreement is obtained at several levels of approximation with previous calculations on the e^+-H_2 problem, provided sufficient orbitals are included in the calculation to allow for short-range charge polarisation effects. Calculations on e^+-N_2 reproduce the magnitude of the observed cross section between 0.1 and 0.5 Ryd, but are too low outside this range. This is explained at low energy by the neglect of long-range polarisation and at high energy by the absence of inelastic effects in the calculation.

1. Introduction

The *ab initio* calculation of electron (e^-)-molecule collision parameters has made significant advances in recent years, with several techniques available for the calculation of electron-diatomic collision cross sections. Among these is the *R*-matrix method of Burke *et al* (1977, 1983) which has been applied to collisions between e^- and N_2 (Burke *et al* 1983, Morgan 1986), CO and LiH (Salvini *et al* 1984), H_2^+ (Tennyson *et al* 1984, Tennyson and Noble 1985), F_2 (Morgan and Noble 1984), O_2 (Noble and Burke 1986), NO (Tennyson and Noble 1986) and H_2 (Baluja *et al* 1985). The last work was part of a study where comparable results were obtained using the linear algebraic approach (Schneider and Collins 1985) and the Schwinger multichannel method (Lima *et al* 1985). Reviews of these and other e^- scattering methods can be found in Buckley *et al* (1984) and Burke and Noble (1986).

In contrast to this, there has been very little *ab initio* work on positron (e^+)-molecule collisions, an exception being several studies of e^+-H_2 impact by Armour (Armour 1984, 1985, Armour and Baker 1985) using the Kohn variational method and elliptical coordinates. Experimentally, there have been a number of studies of e^+-molecule impact; see, for example, Hoffman *et al* (1982), Charlton *et al* (1983) and Charlton (1985a, b). There are now considerable data, some contradictory, covering both elastic and inelastic effects.

In view of this, it would appear timely to study e^+-molecule collisions *ab initio* using a technique that has proved successful for e^--molecule scattering. The absence of exchange interaction and the attractive nature of the e^+-e^- interaction introduces new features into the e^+ compared with the e^- scattering problem. These include enhanced polarisation effects because of the importance of e^+-e^- correlation, and the

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possibility above some energy threshold of positronium, the quasimolecule e^+e^-, formation:

$$AB + e^+ \rightarrow AB^+ + Ps. \qquad (1)$$

Conversely, resonance effects due to long-lived complex formation are as yet unknown in e^+ scattering. In this work, results are presented for the elastic collisions of e^+ with H_2 and N_2 calculated using the *R*-matrix method of Burke, Noble and co-workers.

2. Method

In the *R*-matrix method, the total positron-molecule scattering wavefunction can be written

$$\psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N, \boldsymbol{r}) = \Phi_0(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) F(\boldsymbol{r}) + \sum_{i=1}^{M} \phi_i(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \phi_i'(\boldsymbol{r}) b_i \qquad (2)$$

where $\boldsymbol{x}_i$ and $\boldsymbol{r}$ are the space-spin coordinates of the N electrons and the positron, respectively, Φ_0 is the target wavefunction calculated within the Hartree-Fock approximation, F is a wavefunction describing the scattered positron, and ϕ_i and ϕ_i' are short-range functions, which are used to represent correlation and charge polarisation effects. Although the functions in this equation depend on the molecular geometry, all results presented here will be for nuclei fixed at the equilibrium separation. There are, as yet, no vibrationally resolved experimental results for e^+ scattering.

The wavefunction F is expanded about the centre of gravity of the molecule in an *R*-matrix basis

$$F(\boldsymbol{r}) = \sum_{ij} r^{-1} u_{ij}(r) Y_{l_i m}(\hat{r}) a_j \qquad (3)$$

where Y_{lm} are spherical harmonics. The radial basis functions u_{ij} are obtained by solving numerically the zero-order coupled equations

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + V_0(r) + k_i^2\right) u_{ij}(r) = 0 \qquad (4)$$

subject to the boundary conditions

$$\left.\begin{aligned} &u_{ij}(0) = 0 \\ &\frac{a}{u_{ij}} \frac{du_{ij}}{dr}\bigg|_{r=a} = 0 \end{aligned}\right\} \text{ all } i \text{ and } j \qquad (5)$$

where the *R*-matrix boundary, denoted a, is chosen so that the target functions are effectively zero; it was fixed at $10a_0$ in the calculations presented here. These functions are then Schmidt orthogonalised to the short-range e^+ molecular orbitals, denoted ϕ_i' above.

The potential V_0 is in principle arbitrary. In practice V_0 was chosen as the isotropic part of the static target potential. The effect of this choice can be measured by the comparison, in table 1, of static approximation e^+-H_2 calculations using functions generated using V_0 appropriate for e^+ scattering, and $-V_0$, the potential appropriate for e^- scattering. The eigenphases in the two calculations are in good agreement. However, in more sophisticated calculation the 'electronic' basis functions gave rise to linear dependence problems and all other results presented here used functions generated with the isotropic potential appropriate to e^+-molecule interactions.

Table 1. Eigenphase sums for e^+-H_2 scattering with Σ_g symmetry calculated using the *R*-matrix and Kohn methods.

	Static approximation				Σ polarisation		$\Sigma+\Pi$ polarisation		
	Kohn[a]	*R*-matrix			Kohn[a]	*R*-matrix	Kohn[b]	*R*-matrix	
k^2 (Ryd)	's'	e^+ basis s+d	e^- basis s+d	Correlation s+d+g	's'	s+d+g	's'	s+d+g	s+d+g[c]
0.01	−0.0662	−0.0676	−0.0673	−0.0663	−0.0280	−0.0349	0.0900	−0.0192	0.0733
0.16	−0.2122	−0.2724	−0.2726	−0.2662	−0.1686	−0.1679	0.0258	−0.1146	0.0221
0.49	−0.3629	−0.4461	−0.4424	−0.4429	−0.3380	−0.3180	−0.1798	−0.2457	−0.1589
1.00	−0.5544	−0.5820	−0.5856	−0.5692	−0.4146	−0.4215	−0.2776	−0.3440	−0.2864

[a] Armour (1985).

[b] Armour (1985) as amended (Armour private communication).

[c] With extra π functions, see text.

Having chosen the functions Φ_0, ϕ_i, ϕ'_i and u_{ij} (in practice the short-range positronic orbitals were chosen to be the same as the electronic ones), the Hamiltonian matrix is constructed and diagonalised yielding the coefficients a_i and b_j. From these Buttle (1967) corrected R matrices can be constructed on the boundary (Burke *et al* 1977) and the resulting energy-dependent second-order differential equations solved (Noble and Nesbet 1984) to give eigenphases and cross sections. In the present calculations only the molecular Hartree-Fock quadrupole was included in the external region potential. The Hamiltonian matrix is constructed and diagonalised using a generalisation of Noble's (1982) e^- scattering adaptation of the ALCHEMY package (McClean 1971). Changes include the construction of two independent sets of molecular orbitals, electronic and positronic, each orthonormal, and options to neglect e^+-e^- exchange integrals and alter the sign of the appropriate Coulomb interactions. An existing option which allows the spin coupling of the N target electrons to be specified was also utilised. The resulting package can be used, in principle, for any e^+-diatomic scattering problem.

In this work two approximations are applied to e^+-molecule impact: the static approximation, in which no relaxation of the target is allowed, and the static plus polarisation (SP) model, in which one-electron excitation of the target (two particle-one hole states) are added to allow for short-range e^+-e^- correlation effects. The simplest version of the static approximation involves using only the numerical functions to carry the e^+ motion. As the partial-wave expansion of equation (3) is necessarily truncated (mostly at $l \leq 5$ in the current calculations), high l effects, important in the region of the nuclear singularities, can be accounted for by allowing the e^+ to occupy short-range orbitals of the appropriate symmetry, giving so-called correlation configurations.

3. Calculations on e^+-H_2

Calculations were performed on e^+-H_2 system using the target Slater-type orbital (STO) basis of Fraga and Ransil (1961). Initially π orbitals were obtained by following Baluja *et al*'s (1985) e^--H_2 scattering calculations and choosing a single $2p_\pi$ atomic orbital on each H with the same exponent as the $2p_\sigma$ function. Continuum orbitals were chosen by taking all the solutions of equation (4) with appropriate l and $k^2 \leq 10$ Ryd. These gave a good, probably better than necessary, representation of the low-energy region, $k^2 \leq 1$ Ryd, for which calculations were performed.

Table 1 compares Σ_g symmetry results for e^+-H_2 scattering with those obtained by Armour for several models. To aid comparison the R-matrix calculations were performed using approximations which most nearly corresponded to those of Armour. Results are presented for the static approximation excluding and including short-range correlation configurations—terms of the form $\Phi_0\phi'_i$ in equation (2). These show that short-range, high l effects are comparatively unimportant. Within the SP model calculations were performed which included only Σ polarisation effects, in which the positron only occupied short-range σ orbitals, and $\Sigma+\Pi$ polarisation effects, in which both $\sigma+\pi$ orbitals were available for occupation. These polarisation configurations were generated by using all the virtual target molecular orbitals (MO) for electronic excitation and a complete set of target MO to carry the positron.

Table 1 shows general agreement between the Kohn and R-matrix calculations, except for the final $\Sigma+\Pi$ polarised results. This could be attributed to the smallness of our π orbital set and this calculation was therefore repeated using a set of ($2p_\pi$, $3p_\pi$, $3d_\pi$) STO on each H with exponents as optimised for the lowest $^2\Pi$ state of H_2^+ with $R = 1.4a_0$ by Cohen and Bardsley (1980). The more flexible π orbitals yielded sufficient polarisation to give positive eigenphases at low energy, again giving agreement with the Kohn results. This observation suggests that previous R-matrix e^- scattering calculations on H_2^+ (Tennyson *et al* 1984, Tennyson and Noble 1985) and H_2 (Baluja *et al* 1985), which used only a single $2p_\pi$ STO on each H, may have underestimated Π polarisation effects.

The agreement between the Kohn and R-matrix calculations is the more remarkable when one considers differences in the calculations. The Kohn calculation used a correlated H_2 target wavefunction which recovered about half the correlation energy (Armour 1984). Furthermore, the Kohn calculations, which used a partial-wave expansion in spheroidal coordinates, retained only the lowest, 's', partial wave. Finally, the polarisation effects included in the R-matrix calculation are entirely short-range (inside the R-matrix sphere of radius $10a_0$), which probably accounts for the slightly lower eigenphases in the polarised R-matrix calculations at the lowest energies, where long-range effects should be most significant. The best, $\Sigma+\Pi$ polarised, results with both methods give elastic cross sections in good agreement with each other, showing a Ramsauer minimum at 0.2 Ryd. However, except at the lowest energies, these cross sections are significantly lower than those observed experimentally—see figure 1 of Armour (1985).

4. Calculations on e^+–N_2

Calculations on e^+–N_2 scattering followed those performed on the e^-–N_2 problem by Burke *et al* (1983). However, in the light of criticism of these calculations (Schneider and Collins 1984), their double-zeta target basis set (Nesbet 1964) was augmented by a $3d_\delta$ polarisation function on each N, as suggested by Ermler and McLean (1980). Continuum functions were obtained for $k^2 \leq 9$ Ryd which gave about eight functions per channel and all the appropriate $l \leq 5$ were retained for a given symmetry.

Initially calculations were performed for the Σ_g symmetry using a number of models. As there had been little previous theoretical work on this problem, and most of that phenomenological (e.g. Darewych 1982), this approach was felt necessary in order to gain understanding. Figure 1 gives the result of five calculations. The largest cross section was obtained using the static approximation, including correlation configurations; the cross section decreases with increasing polarisation, details of which are given in table 2. The SP1 model comprises the polarisation configurations used by Burke *et al* for the e^-–N_2 calculations. This model is probably not appropriate for e^+ scattering because it does not allow for occupation of the 'occupied' N_2 orbitals by the e^+. This deficiency is corrected in the SP2 model, which results in a significant drop in the elastic cross section. The SP3 model allows for the polarisation of the inner target electrons, which is seen to be a relatively small effect. The SP4 model additionally allows for δ-orbital polarisation effects, which is again seen to give only a small lowering of the elastic cross section.

Even with the inclusion of all these short-range polarisation effects, all models gave negative eigenphases at low energy. The leading term in the asymptotic potential should be an attractive polarisation term, but the long-range potential of our calculations included only the higher-order quadrupole repulsion. This only appeared to

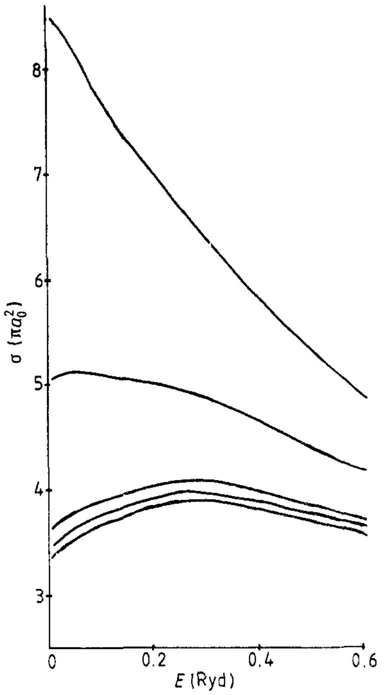

Figure 1. Elastic cross sections for e^+-N_2 scattering with Σ_g symmetry. The approximations used, in order of decreasing cross section, are static, SP1, SP2, SP3 and SP4. See table 2 and the text for details.

Table 2. Molecular orbitals available for building short-range polarisation (2p-1h) configurations for the e^+-N_2 calculation. The number of configurations corresponds to M in equation (2) for the case of Σ_g symmetry; this includes five correlation configurations generated by placing the e^+ in the $1\sigma_g$-$5\sigma_g$ orbitals.

Model	Available orbitals			Number of configurations
	e^- occupied	e^- virtual	e^+ virtual	
Static	—	—	—	5
SP1	$3\sigma_g$, $2\sigma_u$, $1\pi_u$	$4\sigma_g$, $5\sigma_g$, $3\sigma_u$, $4\sigma_u$, $2\pi_u$, $3\pi_u$, $1\pi_g$-$3\pi_g$	$4\sigma_g$, $5\sigma_g$, $3\sigma_u$, $4\sigma_u$, $2\pi_u$, $3\pi_u$, $1\pi_g$-$3\pi_g$	86
SP2	$3\sigma_g$, $2\sigma_u$, $1\pi_u$	$4\sigma_g$, $5\sigma_g$, $3\sigma_u$, $4\sigma_u$, $2\pi_u$, $3\pi_u$, $1\pi_g$-$3\pi_g$	$1\sigma_g$-$5\sigma_g$, $1\sigma_u$-$4\sigma_u$, $1\pi_u$-$3\pi_u$, $1\pi_g$-$3\pi_g$	105
SP3	$1\sigma_g$-$3\sigma_g$, $1\sigma_u$, $2\sigma_u$, $1\pi_u$	$4\sigma_g$, $5\sigma_g$, $3\sigma_u$, $4\sigma_u$, $2\pi_u$, $3\pi_u$, $1\pi_g$-$3\pi_g$	$1\sigma_g$-$5\sigma_g$, $1\sigma_u$-$4\sigma_u$, $1\pi_u$-$3\pi_u$, $1\pi_g$-$3\pi_g$	204
SP4	$1\sigma_g$-$3\sigma_g$, $1\sigma_u$, $2\sigma_u$, $1\pi_u$	$4\sigma_g$, $5\sigma_g$, $3\sigma_u$, $4\sigma_u$, $2\pi_u$, $3\pi_u$, $1\pi_g$-$3\pi_g$, $1\delta_g$, $1\delta_u$	$1\sigma_g$-$5\sigma_g$, $1\sigma_u$-$4\sigma_u$, $1\pi_u$-$3\pi_u$, $1\pi_g$-$3\pi_g$, $1\delta_g$, $1\delta_u$	225

affect the e^+-H_2 calculations slightly, but appears significant, at least at the lowest energies, in the e^+-N_2 case.

Table 3 compares e^+-N_2 eigenphases for the lowest symmetries, i.e. those arising from s- and p-wave scattering for energies below the positronium formation threshold. Results are for both the static and SP4 models; it is apparent that polarisation effects greatly reduce the magnitude of the eigenphases for both Σ_u and Π_u calculations. This means that both these symmetries give only a small contribution to the total elastic cross section. One would expect the contribution from higher (d-wave) symmetries to be even smaller at the low energies considered here.

Figure 2 compares the experimentally observed total e^+-N_2 cross sections with the present elastic results obtained by summing the Σ_g, Σ_u and Π_u contributions within the SP4 model. Although the magnitude of the calculated cross section is approximately correct, the shape of the curve is not at both ends of the energy range considered. At

Table 3. Eigenphase sums for e^+-N_2 scattering.

k^2	Σ_g		Σ_u		Π_u	
(Ryd)	Static	SP4	Static	SP4	Static	SP4
0.01	−0.154	−0.099	−0.024	−0.022	0.005	0.006
0.04	−0.305	−0.200	−0.026	−0.011	−0.012	−0.004
0.09	−0.442	−0.297	−0.029	0.009	−0.044	−0.023
0.16	−0.571	−0.395	−0.061	0.006	−0.077	−0.033
0.25	−0.700	−0.502	−0.120	−0.024	−0.111	−0.014
0.36	−0.830	−0.613	−0.193	−0.075	−0.153	−0.058
0.49	−0.959	−0.728	−0.276	−0.143	−0.200	−0.081
0.64	−1.092	−0.853	−0.370	−0.228	−0.251	−0.115

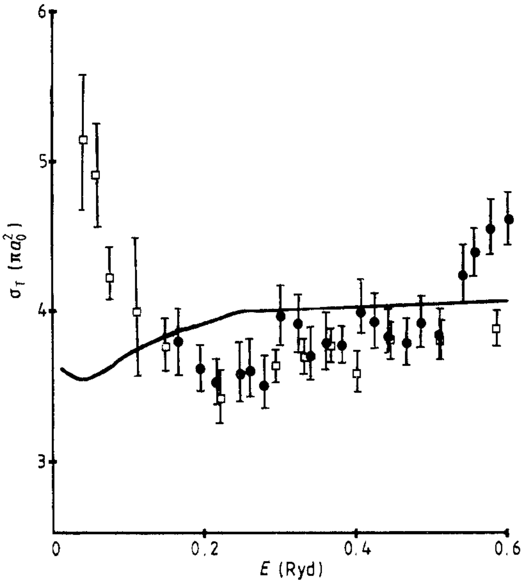

Figure 2. Comparison of the calculated e^+-N_2 elastic cross section (——) with the observed total cross sections of Hoffman *et al* (1982) (□) and Charlton *et al* (1983) (●).

low energy, this can be explained by our neglect of long-range polarisation, particularly in the Σ_g symmetry which is dominant at these energies. At high energy, the rise in the observed cross sections can be attributed to inelastic effects not considered in the current calculations. Which inelastic effect is involved remains unexplained. The rise is observed at different scattering energies by Hoffman *et al* (1982) and Charlton *et al* (1983), and is near both the positronium formation threshold and the lowest N_2 electronic excitation threshold. Neither experimental upturn corresponds exactly with either threshold. A theoretical consideration of this problem must await a more sophisticated calculation.

5. Conclusions

Calculations have been presented for elastic e^+ collisions with both H_2 and N_2 at low energy. The e^+-H_2 calculations were found to be in surprisingly good agreement with those of Armour (1985) when account is taken of the differences between the calculations. In particular, for this system the neglect of long-range polarisation caused only small changes at the lowest energies. In contrast, for e^+-N_2 it was not possible to obtain agreement with the observed cross sections at the lowest energies without this effect. The inclusion of long-range polarisation by the use of polarised pseudostates is under investigation for the e^--molecule problem (Noble 1986) and it is hoped to use this approach for the e^+ problem in future.

At higher energies, inelastic effects such as electronic excitation and positronium formation give significant contributions to the total cross section in both systems. Molecular R-matrix calculations which explicitly considered electronic excitation have already been performed by Tennyson *et al* (1984), Tennyson and Noble (1985), Baluja *et al* (1985) and Noble and Burke (1986). There should be no difficulty in transferring their methodology to the e^+-molecule case. Inclusion of the positronium formation channel is a more challenging task. This has only been achieved for the simplest atomic systems (Humberston 1986), but remains to be done, *ab initio*, for molecular targets. This problem will be the subject of future work.

Finally, one can compare these e^+ scattering results with the equivalent e^- scattering ones. For both molecules, the e^- scattering cross sections are larger by a factor of about 4 in the low-energy region (Charlton 1985b); this is due, at least in part, to the presence of low-lying resonances in both the e^--H_2 (in $^2\Sigma_u$ symmetry) and e^--N_2 (in both $^2\Sigma_u$ and $^2\Pi_g$ symmetries) systems. A comparison of the non-resonant $^2\Sigma_g$ e^--N_2 scattering (Burke *et al* 1983) with the corresponding e^+ problem shows that, while the low-energy elastic cross sections are of similar magnitude in the static (exchange) approximation, polarisation effects lead to a much greater reduction of the e^+ collision cross section.

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