Polarisation potentials for positron–molecule collisions: positron–H$_2$ scattering

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Abstract. Model polarisation potentials for use in calculating positron–molecule cross sections are often based on approximations in which terms that depend on the sign of the charge of the projectile are neglected. Thus, these potentials do not fully distinguish between electron and positron scattering. The validity of using such potentials for positron–H$_2$ collisions is investigated by performing scattering calculations using electron– and positron–H$_2$ model polarisation potentials. Results show that, because of differences in the way electrons and positrons distort the target charge cloud, sign-dependent terms in the adiabatic potential can significantly influence the total cross section. Low-energy cross sections are also shown to be rather sensitive to how non-adiabatic polarisation effects are taken into account. Using a cut-off fully adiabatic *positron*–H$_2$ polarisation potential, theoretical total cross sections in reasonably good agreement with recent measurements are obtained.

1. Introduction

Recent advances in experimental technology have stimulated increased activity in the measurement of cross sections for low-energy positron scattering from atoms and molecules. In particular, the development of sources for intense, reasonably mono-chromatic beams of low-energy positrons (cf Canter and Mills 1982) has made feasible accurate measurements at energies below 10.0 eV. A number of reviews have appeared recently of experimental (Griffith 1979, Stein and Kauppila 1982, Kauppila and Stein 1982) and theoretical (Humberston 1979, Massey 1982, Schrader and Svetic 1982, Ghosh *et al* 1983) research in this field.

With this activity has come renewed interest in scattering calculations for positron–molecule systems. Theoretical research on these systems is further motivated by the important role played in positron–molecule collisions by one of the most important interactions in low-energy charged-particle scattering: polarisation.

The high sensitivity of positron–molecule cross sections to polarisation effects derives from the nature of the positron–molecule interaction potential. The full interaction potential differs in several important respects from the more familiar *electron*–molecule interaction potential. The latter consists of static, exchange, and polarisation terms (see Morrison 1983 for a qualitative introduction). In contrast, the *positron*–molecule

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potential does not contain an exchange operator, since the positron is quantum mechanically distinguishable from the target electrons. This feature of the potential is partly responsible for the comparative simplicity of positron–molecule scattering calculations over their electron–molecule counterparts. (This simplification is somewhat offset at scattering energies above a few eV by the need to account for rearrangement channels that are not present in the electron scattering case, such as positronium formation and annihilation (Horbatsch *et al* 1983, Ray *et al* 1980, Khan and Ghosh 1983, Varracchio and Girardeau 1983).)

Another significant difference between positron– and electron–molecule interaction potentials is the character of the static contribution. This term arises from the Coulomb interactions between the scattering particle and the electrons and nuclei of the target. The electron–molecule static potential is attractive. However, because of the strong positron–nuclear repulsion, the positron–molecule static potential is strongly repulsive, dominating the interaction potential in the 'short-range region' very near and within the target charge cloud. This fact enhances the sensitivity of positron–molecule cross sections to the polarisation potential in the 'intermediate- and long-range' regions outside the charge cloud. (This sensitivity was first investigated by Lodge *et al* (1971).)

The importance of polarisation effects has been tacitly acknowledged in a wide variety of theoretical studies of positron–atom scattering, many of which use rather sophisticated methods for determining the positron–target polarisation potential (see the reviews by Schrader and Svectic 1979, Ghosh *et al* 1983, and references therein; for more recent work, see Sin Fai Lam 1982, Morgan 1982, Willis and McDowell 1982, Mukherjee and Sural 1982, Horbatsch *et al* 1983). By contrast, to date only a handful of positron–molecule studies have been published (see § 2.1.3).

The great preponderance of these studies have treated positron–H_2 scattering. In *all* prior theoretical calculations on this system, the polarisation potential used was taken without modification from the *electron*–H_2 literature. Implicit in this stratagem is the premise that positron–H_2 cross sections are insensitive to differences in the polarisation potential that arise from the sign of the charge of the projectile. Viewing the static positron–molecule interaction as an adiabatic perturbation due to a fixed charge, one can restate this premise in terms of perturbation theory (see § 2.1.2(i)): perturbation terms of higher than second order in the adiabatic polarisation potential are irrelevant to the determination of positron–molecule cross sections. (This assumption is a central tenet of the polarised orbital method; cf Drachman and Temkin (1972).)

This premise defines the primary questions for the present study: must one properly take account of the sign of the charge of the projectile in determining polarisation potentials for positron–molecule scattering calculations? Is it valid to use a very accurate *electron–molecule* polarisation potential in *positron–molecule* scattering calculations? A secondary question concerns *non-adiabatic* polarisation effects: how important are these effects when the polarisation potential is determined explicitly for the positron–molecule system, and how sensitive are low-energy positron–molecule cross sections to the way these effects are taken into account?

To initiate study of these questions, we consider here the positron–H_2 system. In § 2 we review briefly the nature of the polarisation interaction and how it has been treated in prior positron–molecule calculations. These remarks are followed by a description of the positron–H_2 and electron–H_2 polarisation potentials considered in the present study and of the scattering theories used to calculate cross sections. In § 3, we present and discuss our results, which include positron–H_2 cross sections calculated using an explicitly determined positron–H_2 polarisation potential. We also

discuss the possibility of a Ramsauer–Townsend minimum in this system. We conclude in § 4 by discussing the strengths and weaknesses of the present treatment of polarisation and the prognosis for future work on this problem. Unless otherwise noted, atomic units are used throughout†.

2. Theory

2.1. The polarisation interaction

The subject of polarisation in charged-particle scattering is complicated, and the relevant literature is vast. In order to provide a context for understanding the results of the present study and to elucidate key approximations, it is necessary to briefly sketch several widely used strategies for determining polarisation potentials. We shall limit ourselves to methods that have been used in positron–molecule studies.

Polarisation effects in the scattering of charged particles arise from correlations between the projectile and the target electrons (cf Lane 1980). In a rigorous quantum mechanical formulation of the collision, these effects manifest themselves as *virtual electronic excitations* of the target, i.e., through the influence of closed electronic channels (cf Castillejo *et al* 1960).

The physics of polarisation is perhaps most easily understood in terms of a semi-classical model: an incident projectile of charge q establishes a time-varying electric field that distorts the electron cloud of the target. The resulting 'polarised' charge distribution interacts, in turn, with the scattering particle, giving rise to an *induced* change in the electronic energy of the system. This change in energy is the polarisation potential, which we shall denote $V_{pol}^{\pm}$, the superscript indicating the sign of the charge of the projectile ($q = \pm 1$ au for a positron or an electron, respectively). Properly, this potential should depend on the position and velocity of the projectile. However, most polarisation potentials are based on the adiabatic approximation, in which the velocity dependence is neglected (§ 2.1.1). However, non-adiabatic effects are known to be important for low-energy scattering, and a variety of approximate strategies have been developed to incorporate them in model polarisation potentials (§ 2.1.3).

Characteristically, the polarisation potential $V_{pol}^{\pm}$, which is a function of the spatial coordinate of the projectile, r_q, is non-spherical and predominantly attractive. Its asymptotic behaviour (i.e., as $r_q \to \infty$) is quite simple‡, i.e.,

$$V_{pol}^{\pm}(r_q; R) \sim -\frac{\alpha_0}{2r_q^4} - \frac{\alpha_2}{2r_q^4} P_2(\cos \theta_q) \tag{1}$$

where α_0 and α_2 are the spherical and non-spherical polarisabilities, respectively, of the target. Significantly, the *asymptotic* form of $V_{pol}^{\pm}$ is independent of the sign of q. The positron–molecule interaction potential is simply the sum of V_{pol}^{+} and the (repulsive)

† In atomic units, $\hbar = m_e = a_0 = 1$. The charge of the projectile is $q = \pm 1$ for an electron or positron, respectively. The unit of energy is $\hbar^2/m_e a_0^2 = 1 E_h = 2$ Ryd $= 27.212$ eV. The unit of distance is the first Bohr radius, $a_0 = 1$ Bohr $= 0.529\,18 \times 10^{-10}$ m. Cross sections are measured in units of square bohr, $a_0^2 = 0.29 \times 10^{-20}$ m².

‡ Coordinates are referred to a molecular ('body-fixed') reference frame. The target molecule is described in the Born–Oppenheimer approximation. Parametric dependence of potentials and wavefunctions on certain coordinates is indicated by placing those coordinates after a semicolon in arguments, e.g., $V_{pol}^{\pm}(r_q; R)$.

static potential, namely,

$$V_{int}^+(r_q; R) = V_{st}^+(r_q; R) + V_{pol}^+(r_q; R). \tag{2}$$

2.1.1. The adiabatic polarisation potential. The starting point in the determination of model polarisation potentials is the adiabatic polarisation potential, $V_{AD}^{\pm}(r_q; R)$. In the adiabatic approximation, the molecular electrons respond to the field of a *fixed* projectile. The change in the total energy of the system due to resulting distortion is calculated from the *adiabatic Hamiltonian* of the system, $\mathscr{H}_{AD}^{\pm}$, which is just the sum of the target electronic Hamiltonian and the electrostatic projectile–target potential V. The adiabatic polarisation potential is equal to (Drachman and Temkin 1972)

$$V_{AD}^{\pm}(r_q; R) = \langle \psi_0^{(P)} | \mathscr{H}_{AD}^{\pm} | \psi_0^{(P)} \rangle - \langle \psi_0 | \mathscr{H}_{AD}^{\pm} | \psi_0 \rangle \tag{3}$$

where $\psi_0^{(P)}(r_m; R)$ and $\psi_0(r_m; R)$ are the polarised and undistorted ground-state electronic molecular wavefunctions, respectively. In equation (3), the matrix elements indicate integration over the molecular electronic coordinates, collectively denoted by r_m (cf Morrison and Hay 1979, Eades *et al* 1979, Truhlar *et al* 1979, Gibson and Morrison 1982, 1983).

The resulting adiabatic polarisation potential, which is an approximation to the optical potential (Drachman and Temkin 1972), is too strongly attractive in the region of space near the target owing to neglect of non-adiabatic effects (§ 2.1.3).

2.1.2. Approximations to the adiabatic polarisation potential. In most model potentials based on $V_{AD}^{\pm}$, additional assumptions (unrelated to non-adiabatic effects) have been implemented. These approximations fall into two classes: those based on a perturbation approximation to the polarised wavefunction $\psi_0^{(P)}$, and those in which the multipole expansion of the Coulomb potential V in $\mathscr{H}_{AD}^{\pm}$ is truncated.

(i) *Perturbation theory approximations.* In many applications, notably those within the *polarised orbital method*, the Coulomb potential for a target with N_e electrons at positions r_i and N_n nuclei at R_α,

$$V^{\pm}(r_m; r_q, R) = \mp \sum_{i=1}^{N_e} \frac{1}{|r_q - r_i|} \pm \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|r_q - R_\alpha|} \tag{4}$$

is treated as a perturbation, and the polarised target function $\psi_0^{(P)}$ is evaluated to *first order* in this potential. The resulting second-order adiabatic polarisation potential, $V_{AD}^{(2)}$, is *independent of the sign of q*. (This result can easily be seen from the expansion of $V_{AD}^{(2)}$ in intermediate unperturbed states (Drachman and Temkin 1972).)

Higher order perturbation terms, which are neglected in $V_{AD}^{(2)}$, do depend significantly on the sign of q, as is well known from research on positron- and electron–atom polarisation (cf figure 6.3.2 of Drachman and Temkin 1972). These terms are attractive (regardless of the sign of q); hence near the target $V_{AD}^{(2)}$ is *weaker* than $V_{AD}^{\pm}$. As the scattering coordinate r_q increases, $V_{AD}^{\pm}$ goes smoothly over to $V_{AD}^{(2)}$, the higher order perturbation terms dying off, and, eventually, $V_{AD}^{(2)}$ reduces to the asymptotic form (1). The essential approximation in studies based on the second-order adiabatic potential, however, is that these terms are negligible everywhere. The validity of this assumption for positron–H_2 scattering is investigated in § 3.

(ii) *Multipole suppression approximations.* A separate class of widely used approximations derives from the expansion of the projectile–target-electron Coulomb terms in

(4) in multipoles, e.g.,

$$\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_q|} = \sum_{\lambda=0}^{\infty} \frac{\zeta_<^{\lambda}}{\zeta_>^{\lambda+1}} P_{\lambda}(\cos \Theta_{iq}) \tag{5}$$

where Θ_{iq} is the angle between $\boldsymbol{r}_i$ and $\boldsymbol{r}_q$ and $\zeta_<$ ($\zeta_>$) is the minimum (maximum) of r_i and r_q. Of course, this expansion includes multipoles of all orders. The most troublesome of these is the monopole term ($\lambda = 0$), which causes $V_{\mathrm{AD}}^{\pm}$ to be far too strong near the origin. The monopole suppression approximation, in which this term is neglected, has been shown to improve agreement with experimental cross sections and is widely used in both electron and positron scattering calculations. It is considered to be 'good, but arbitrary' (Drachman and Temkin 1972) and could be thought of as a highly approximate way of including non-adiabatic effects (cf § 2.1.3).

In *electron* scattering calculations, the leading remaining term in (5), the dipole term ($\lambda = 1$), is often the only one that need be retained. This stratagem leads to the dipole approximation to $V_{\mathrm{AD}}^{\pm}$. The positron–electron Coulomb interaction is attractive, and neglect of multipoles of order higher than dipole slightly weakens the *electron*-target polarisation potential. However, extensive study of *positron–atom* collisions has shown that for these systems better agreement with experiment is obtained if all the multipoles with $\lambda \geq 1$ are retained (cf McEachran *et al* 1977 and the review by Ghosh *et al* 1983). Nevertheless, the dipole approximation has been used in some positron-molecule calculations (cf § 2.2).

2.1.3. Approximate inclusion of non-adiabatic effects. Short-range bound–free correlations are manifested in the so-called dynamic terms, which are neglected in the adiabatic approximation. These short-range terms are *repulsive* for positron (or electron) scattering, so they weaken the adiabatic potential near the target. The nature of the dynamic terms has been investigated for electron scattering from simple atoms(cf Kleinman *et al* 1969, Temkin 1957, Dalgarno *et al* 1968, Burke and Taylor 1966, Callaway *et al* 1969, Jean and Schrader 1978), but for positron–molecule systems their range and strength is at present unknown. Because the strongly repulsive potential dominates the positron–molecule interaction at short range, non-adiabatic effects may be less important for positron collisions than for electron collisions, but they cannot be neglected entirely (cf figure 6).

A great deal of attention has been given to strategies for approximating non-adiabatic effects in model potentials for scattering from molecules; since all of this work has focused on *electron* scattering, we shall not discuss it here (cf references in Gibson and Morrison 1983). Two methods have been implemented for positron-molecule scattering.

(i) *A parameter-dependent cut-off procedure.* The most widely used (and crudest) way to enforce the necessary weakening of the adiabatic polarisation potential is to simply remove it near the target via an *ad hoc* cut-off procedure. In almost all such treatments, the adiabatic potential (or its asymptotic form (1)) is simply multiplied by a cut-off function of the form (Burke and Chandra 1972)

$$C(r_q) = 1 - \exp[-(r_q/r_c)^6]. \tag{6}$$

The adjustable parameter in this function, the 'cut-off radius', r_c, can be chosen in a variety of ways, the most common being tuning to experimental data. In spite of its extreme simplicity and seemingly unphysical spherical symmetry, this form has proven

highly successful in electron–molecule scattering calculations (see examples in Lane 1980).

When a cut-off model potential is used in a positron–molecule scattering calculation, two choices are critical. First, r_c can either be taken without modification from the potential for the corresponding electron–molecule system *or* it can be newly determined for the positron–molecule system. Second, one can cut off either $V_{AD}^{\pm}$ or its asymptotic form (1).

(ii) *The non-penetrating approximation.* An appealing alternative to this method that is free of adjustable parameters is the non-penetrating approximation of Temkin (1957). This method has been widely and successfully used for electron–atom and electron–molecule scattering calculations. However, many authors have argued that it is not suitable for positron scattering (cf Drachman and Temkin 1972, McEachran *et al* 1977). Because of its importance, we shall look briefly at this approximation in the context of the semiclassical model of polarisation introduced in § 2.1.1.

Formally, the non-penetrating approximation is implemented by multiplying the projectile–target-electron Coulomb interaction in (4) by a step-function cut-off that removes it from $\mathcal{H}_{AD}^{\pm}$ whenever the projectile is inside the molecular charge cloud (cf Gibson and Morrison 1983, Onda and Temkin 1983). Conceptually, one can argue the reasonableness of this procedure for electron scattering. As the electron nears the target, it feels the strong nuclear attraction and acquires a local kinetic energy that is comparable with that of the molecular electrons. Under these circumstances, the assumption that the target electrons respond adiabatically to the field of the projectile ceases to be appropriate. By removing the *repulsive* bound–free electron–electron Coulomb terms from the potential whenever the projectile is within the charge cloud, one tries to mimic the complicated short-range bound–free correlations, which act to weaken the adiabatic polarisation potential.

The physical environment encountered by a positron is quite different. The positron–nucleus interaction is strongly repulsive, so the positron is accelerated far less in the near-target region than an electron with the same energy. (Indeed, at low scattering energies, this repulsion acts to *slow* the projectile and should enhance the validity of the adiabatic approximation.) When non-adiabatic effects do become important, it is not clear that neglecting the *attractive* positron–electron Coulomb terms in V is a reasonable way to mimic the neglected dynamic terms (cf McEachran and Stauffer 1983). (For this reason we have not explicitly implemented the non-penetrating approximation for the positron-H_2 system. However, we have considered a non-penetrating electron-H_2 polarisation potential—see § 2.3.)

The complexity of the literature on polarisation in electron and positron scattering derives in part from the use of one of these non-adiabatic approximations in conjunction with one or more of the approximations to $V_{AD}^{\pm}$ described in § 2.1.2. Doing so may result in fortuitous cancellation of various attractive and repulsive terms. (For example, both the perturbation-theory approximation and the dipole approximation weaken the adiabatic potential, as would the dynamic terms were they to be included.)

2.2. Polarisation potentials in positron–molecule studies

With the survey of § 2.1 as background, we can now identify the approximations underlying model polarisation potentials that have been used heretofore in positron–molecule scattering calculations. Doing so will enable us to state—in § 2.3—the central

concerns of the present research. As indicated above, treatments of polarisation in positron–molecule collisions are less sophisticated than in positron–atom or electron–molecule scattering. Within the context defined in § 2.1, they can be divided into two classes.

2.2.1. Asymptotic form with cut-off. In these models, the polarisation potential is based on the *asymptotic form* (1); this expression is cut off at short range, usually via the spherically symmetric cut-off function $C(r_q)$ of equation (6). In considering such methods, two points should be kept in mind. First, since the asymptotic form—and not the full adiabatic polarisation potential $V_{AD}^{\pm}$—is cut off, the cut-off procedure must account for several approximations, implicit in (1), that are invalid near the target:

neglect of higher order perturbation terms (§ 2.1.1(i));

neglect of multipoles other than the dipole (§ 2.1.1(ii));

neglect of dynamic terms (§ 2.1.2).

Although some of these neglected terms will cancel—to varying degrees in various regions of space—this is still a lot to ask of a spherically symmetric cut-off function!

The second point concerns the choice of the parameter r_c in $C(r_q)$. In a large number of positron–molecule studies the cut-off radius is taken without modification from scattering calculations on the corresponding electron–molecule system (Hara 1972, Darewych and Baille 1974, Bhattacharyya and Ghosh 1975, Sur and Ghosh 1982). In such calculations, *no* account is taken in the polarisation potential of the sign of q. Alternatively, the cut-off radius can be specified in some reasonable but *ad hoc* fashion; for example, Jain and Thompson (1983d) recently reported calculations of positron–CH₄ collisions in which r_c is chosen equal to the molecular bond length. Finally, r_c could be determined explicitly for the positron–molecule system by optimising the agreement of theoretical and experimental cross sections for some range of scattering energies.

Only two such studies of this nature have been reported. In recent work by Darewych (1982) on positron–N₂ scattering, r_c was systematically varied in an attempt to obtain agreement with recent experimental results (Hoffman *et al* 1982). Significantly, Darewych found that *no single value* of r_c would yield agreement over the energy range from zero to 10.0 eV. In order to obtain acceptable cross sections, it was necessary to resort to the extreme (and unsatisfactory) expedient of an *energy-dependent* cut-off radius. An identical finding was subsequently reported by Horbatsch and Darewych (1983) for positron–CO₂ scattering. These important studies strongly suggest that the sensitivity of positron–molecule cross sections to polarisation effects may be so great that this crude model, based on cutting off the asymptotic form of V_{AD}^{+} with a spherically symmetric function, is simply inadequate for these systems.

2.2.2. Adiabatic potential with the non-penetrating approximation. The great majority of polarisation potentials for positron scattering that are based on the adiabatic polarisation potential (§ 2.1.1) do not take full account of the effects of the sign of q—either because they implement the second-order perturbation theory approximation (§ 2.1.2(i)) or because they use an *electron*–molecule potential.

For example, the *ab initio* electron–H₂ polarisation potential of Lane and Henry (1968)—in which the non-penetrating approximation (§ 2.1.3(ii)) was implemented for the *full* adiabatic polarisation potential—has been used without alteration in positron–H₂ calculations by Lodge *et al* (1971), Baille *et al* (1974), Bhattacharyya and Ghosh (1975), Pande and Singh (1978) and Sur and Ghosh (1982). The analogous

electron–H$_2$ potential of Hara (1969)—which further implements the dipole approximation (§ 2.1.2(ii))—has been used by Darewych *et al* (1974). Since both of these electron–H$_2$ polarisation potentials include perturbation terms of higher than second order, which strongly depend on the sign of *q*, and are based on the non-penetrating approximation, they may be inappropriate for positron–H$_2$ scattering calculations (see the results in § 3 for the BTADE potential defined in § 2.3).

The most recent applications of an adiabatic polarisation potential for positron–molecule scattering are those of Gillespie and Thompson (1975) for positron–N$_2$ scattering and of Jain (1983) and Jain and Thompson (1982, 1983a, b, c, d) for positron–CH$_4$ and positron–NH$_3$ collisions. In these calculations, a *second-order* polarisation potential was used, and the *non-penetrating* and *dipole approximations* were made. Recent experimental results for positron–N$_2$ scattering (Hoffman *et al* 1982) indicate that Gillespie and Thompson's results for this system are considerably too low, expecially at scattering energies below 2.0 eV. It is not clear whether this discrepancy arises from neglect of higher order perturbation terms, from monopole suppression, or from the use of the non-penetrating approximation.

2.3. Polarisation potential used in the present study

In order to explore various aspects of polarisation in positron–molecule systems, scattering calculations for positron–H$_2$ collisions have been performed using three polarisation potentials.

The first of these is the *ab initio electron*–H$_2$ potential of Gibson and Morrison (1983). This potential is similar to the widely used Lane and Henry (1968) and Hara (1969) electron–H$_2$ potentials in that it is based on a variationally determined adiabatic potential in which the dipole and non-penetrating approximations are made (perturbation terms of all order are included). Since the latter approximation makes this electron dipole potential 'better' than a purely-adiabatic model, we refer to it as the BTADE polarisation potential. This model has been extensively tested in calculations of cross sections for elastic scattering, rotational excitation, and vibrational excitation (Morrison *et al* 1983, Feldt *et al* 1983). In all cases, when combined with suitably defined static and exchange terms, it yields highly accurate cross sections. Thus we believe the BTADE potential to be a very good approximation to the true *electron*–H$_2$ polarisation potential. By using the BTADE potential in conjunction with the two models defined below we can investigate the validity of using a highly accurate *electron*–H$_2$ polarisation potential in positron–H$_2$ collision studies.

These other model potentials further enable us to study the importance of higher order perturbation terms and non-adiabatic effects in positron–molecule collisions. Both are based on the *adiabatic approximation* of § 2.1.1. In both cases, the full adiabatic potential $V_{AD}^{\pm}$ (*not* the asymptotic form (1)) is used, non-adiabatic effects being approximated by the spherical cut-off function of equation (6). (The choice of r_c for this function will be discussed in § 3.) The ADELEC model potential is based on the adiabatic potential V_{AD}^{-}, which is calculated with an electron as the distorting particle. In contrast, the ADPOS potential is based on V_{AD}^{+}, a positron being the projectile. Thus, the crucial difference between the ADELEC and ADPOS potentials arises from higher order perturbation terms, which explicitly depend on the sign of *q*.

In order to calculate full interaction potentials V_{int} these polarisation potentials were combined with the static potential (for the ground (X $^1\Sigma_g^+$) state), namely,

$$V_{st}^{+}(\boldsymbol{r}; R) = \langle \psi_0(\boldsymbol{r}_m; R) | V^{+}(\boldsymbol{r}_m, \boldsymbol{r}, R) | \psi_0(\boldsymbol{r}_m; R) \rangle \tag{7}$$

where the integration is to be performed over the molecular electronic coordinates r_m. Once a basis has been chosen to represent $\psi_0(r_m; R)$, this potential—and its projections on a basis of Legendre polynomials, which are required for scattering calculations—can be calculated using existing computer codes (Morrison 1980, Collins *et al* 1980). (Since the focus of this research is on *low-energy* collisions and on the polarisation interaction, no attempt was made to incorporate rearrangement channels† (e.g., for positronium formation).) A detailed description of the basis used for the neutral H_2 target and how it is augmented to allow for polarisation distortion and a comparison of the properties of the resulting near-Hartree–Fock wavefunction with experiment and more accurate structure calculations can be found in Gibson and Morrison (1983).

2.4. Scattering theory

Most of the cross sections to be presented in § 3 were calculated within the laboratory-frame close-coupling (LFCC) formalism (Arthurs and Dalgarno 1960) using the rigid-rotor approximation, in which the internuclear separation is fixed at its equilibrium value $1.4a_0$. In this formulation, the positron–molecule wavefunction is expanded in a basis of coupled angular functions. This basis is complete in the (laboratory frame) angular coordinates $\hat{R}$ and $\hat{r}$. The expansion leads to a set of coupled radial differential equations that can be solved for the scattering matrix. Cross sections for elastic scattering and rotational excitation can then be calculated from this matrix.

In the LFCC formulation, channels are labelled by the quantum numbers $(l, j; J)$, where we use l for the quantum number for the orbital angular momentum of the projectile, j for the rotational angular momentum of the nuclei, and J for the total angular momentum. Since the latter observable is a constant of the motion, channels with different values of J are uncoupled.

Convergence of the reported cross sections to better than 1% was achieved by using five rotational states in the expansion basis and including values of J through five in the cross sections. For each value of J, all allowed partial waves (l) were included, as were all allowed potential expansion coefficients‡. Integration of the coupled scattering equations (by an integral equations algorithm which has been discussed elsewhere (Morrison 1979)), was fully converged by $r_q = 60.0a_0$.

In order to investigate the possibility of a Ramsauer–Townsend minimum in the total positron–H_2 cross sections (see § 3.3), we also performed *body-frame fixed-nuclei* (BFFN) scattering calculations (cf Burke and Chandra 1972, Lane 1980, and references therein). In this theory, the rotational Hamiltonian is completely neglected except in the asymptotic region, where it is reintroduced by performing a rotational-frame transformation (Chang and Fano 1972) on the scattering matrix. The Schrödinger equation is written in a body-fixed reference frame, the polar axis of which is chosen to lie along the internuclear axis $\hat{R}$. The system wavefunction is expanded in a basis of spherical harmonics, and the resulting coupled radial differential equations are solved numerically.

† The thresholds for dissociation, positronium formation and electronic excitation to the B $^1\Sigma_u^+$ state are 4.476, 8.63 and 11.36 eV, respectively. Dissociation does not become energetically favourable, however, until about 8.8 eV.

‡ Most other positron–H_2 calculations in the literature include only s and p waves (cf Lodge *et al* 1971, Darewych *et al* 1974). We have tested this approximation and found it to be a reasonable one. The percentage error in the total cross section at 0.1, 1.0 and 8.0 eV due to neglect of partial waves of order greater than $l = 2$ is 0.5, 1.6 and 3.0, respectively.

Channels in the BFFN theory are labelled by $(l; \Lambda)$, where Λ is the absolute value of the projection of the orbital angular momentum of the projectile along the internuclear axis (in atomic units). In the fixed-nuclei approximation, the coupled scattering equations separate into independent sets according to the value of Λ and the parity η of the system wavefunction. Therefore, the total integrated cross section (the sum of the elastic scattering and all rotational excitation cross sections) can be written as a sum of partial cross sections, namely,

$$\sigma_{\text{tot}} = \sum_{\Lambda, \eta} \sigma_{\Lambda, \eta}. \tag{8}$$

Each pair of labels Λ, η defines a *system symmetry*, e.g., Σ_g ($\Lambda = 0$, $\eta = \text{gerade}$).

In BFFN *electron*–H_2 calculations, only a few symmetries are required to converge the sum in equation (8). For example, accurate total e–H_2 cross sections at scattering energies below about 10.0 eV can be obtained retaining the Σ_g, Σ_u and Π_u contributions to this summation. In contrast, more symmetries are required to converge positron–H_2 cross sections at the same energies. In particular, contributions to σ_{tot} of more than 10 per cent are made by the Π_g and Δ_g terms. In our BFFN positron–H_2 calculations, three partial waves (l) were required to converge each partial cross section $\sigma_{\Lambda, \eta}$.

3. Results and discussion

The various approximations made in the BTADE, ADELEC and ADPOS potentials give rise to differences in these potentials, particularly near the target. These potentials will be discussed in § 3.1. The important question of the significance of these differences to positron–H_2 cross sections will be addressed in § 3.2 and the possibility of a Ramsauer–Townsend minimum will be explored in § 3.3.
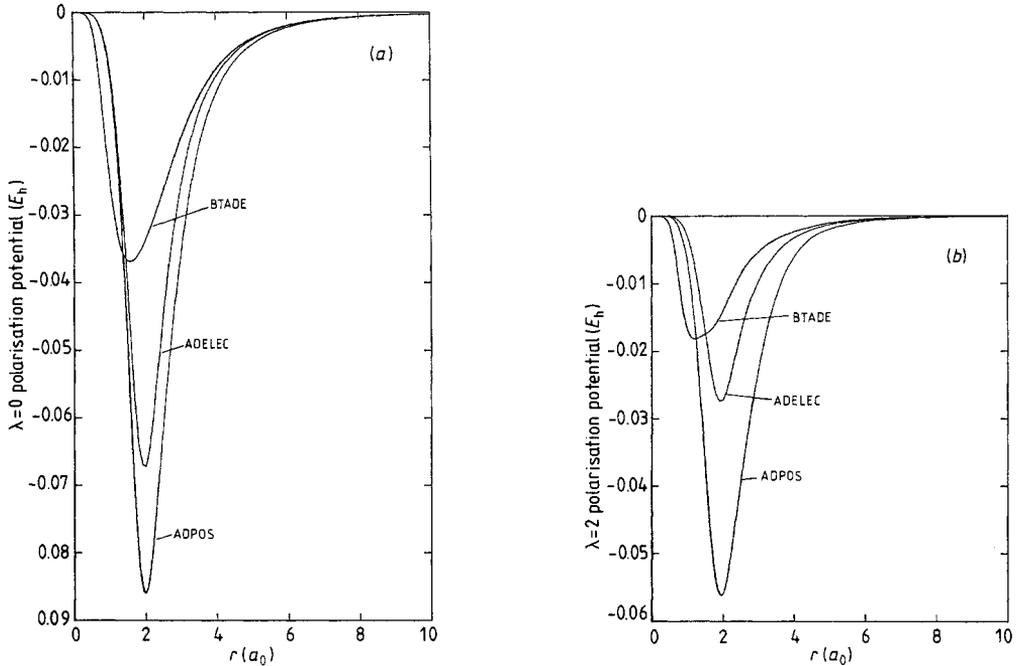
3.1. Potentials

The three polarisation potentials of § 2.3 can conveniently be compared by examining the radial coefficients in a Legendre expansion,

$$V_{\text{pol}}^+(r_q; R) = \sum_{\lambda = 0}^{\infty} v_{\lambda}^{\text{pol}}(r_q; R) P_{\lambda}(\cos \theta_q). \tag{9}$$

In figures 1(a) and (b), the $\lambda = 0$ and $\lambda = 2$ components of the three polarisation potentials under consideration are shown.

Clearly, these three polarisation potentials are quite different. The dipole non-penetrating, electron–H_2 BTADE potential is noticeably weaker than either the cut-off adiabatic electron–H_2 or positron–H_2 potentials. Also evident in figure 1 are substantial differences between the ADELEC and ADPOS potentials. In this figure these potentials are cut off using the same value of r_c, so the differences between them derive entirely from higher order perturbation terms in the adiabatic polarisation potential, terms that depend on the sign of q. Changing the charge from $q = -1$ (electron) to $q = +1$ (positron) causes a substantial strengthening of the adiabatic polarisation potential in the near-target region.

The differences shown in figure 1 give rise to two questions. First, to what extent (if any) do these differences affect cross sections for this system? And second, can the differences that result from higher order perturbation terms be understood in terms

Figure 1. (*a*) Spherical ($\lambda = 0$) and (*b*) non-spherical ($\lambda = 2$) radial expansion coefficients (see equation (9)) of the three polarisation potentials discussed in § 2.3: the adiabatic electron–H₂ potential (ADELEC), the adiabatic positron–H₂ potential (ADPOS) and the non-adiabatic electron–H₂ potential (BTADE). The ADELEC and ADPOS potentials were cut off using equation (6) with $r_c = 1.5a_0$.

of the distortion of the target charge cloud? The first of these questions will be taken up in § 3.2.

Turning to the second question, we can conveniently display the effects of polarisation by expanding polarised and unpolarised single-particle probability densities of the target in Legendre polynomials (Morrison 1980). For example, for the neutral target, with density $\rho(r_q; R)$, the radial coefficient in such an expression is

$$a_\lambda(r_q; R) = \frac{2\lambda + 1}{2} \int_0^\pi \rho(r_q; R) P_\lambda(\cos \theta_q) \, \mathrm{d}(\cos \theta_q). \tag{10}$$

In figure 2, the $\lambda = 0$ and $\lambda = 2$ projections of the neutral, electron polarised and positron polarised H₂ single-particle densities are compared. (For the (adiabatic) polarised densities in this figure, the (fixed) scattering particle is located along the z axis at $z_q = 2.5a_0$.)

Clearly, the distortion induced by a positron is quite different from that due to an electron, especially for $\lambda > 0$. The ADELEC and ADPOS potentials of figure 1, which are the energy changes resulting from these distortions, are consequently quite different in the vicinity of the target charge cloud.

The differences seen in figure 2 can be understood in terms of the semi-classical picture given in § 2.2. If the scattering particle is near the target, the molecular electronic charge distribution distorts in such a way that, on average, it either moves away from the projectile (for an electron) or towards the projectile (for a positron).
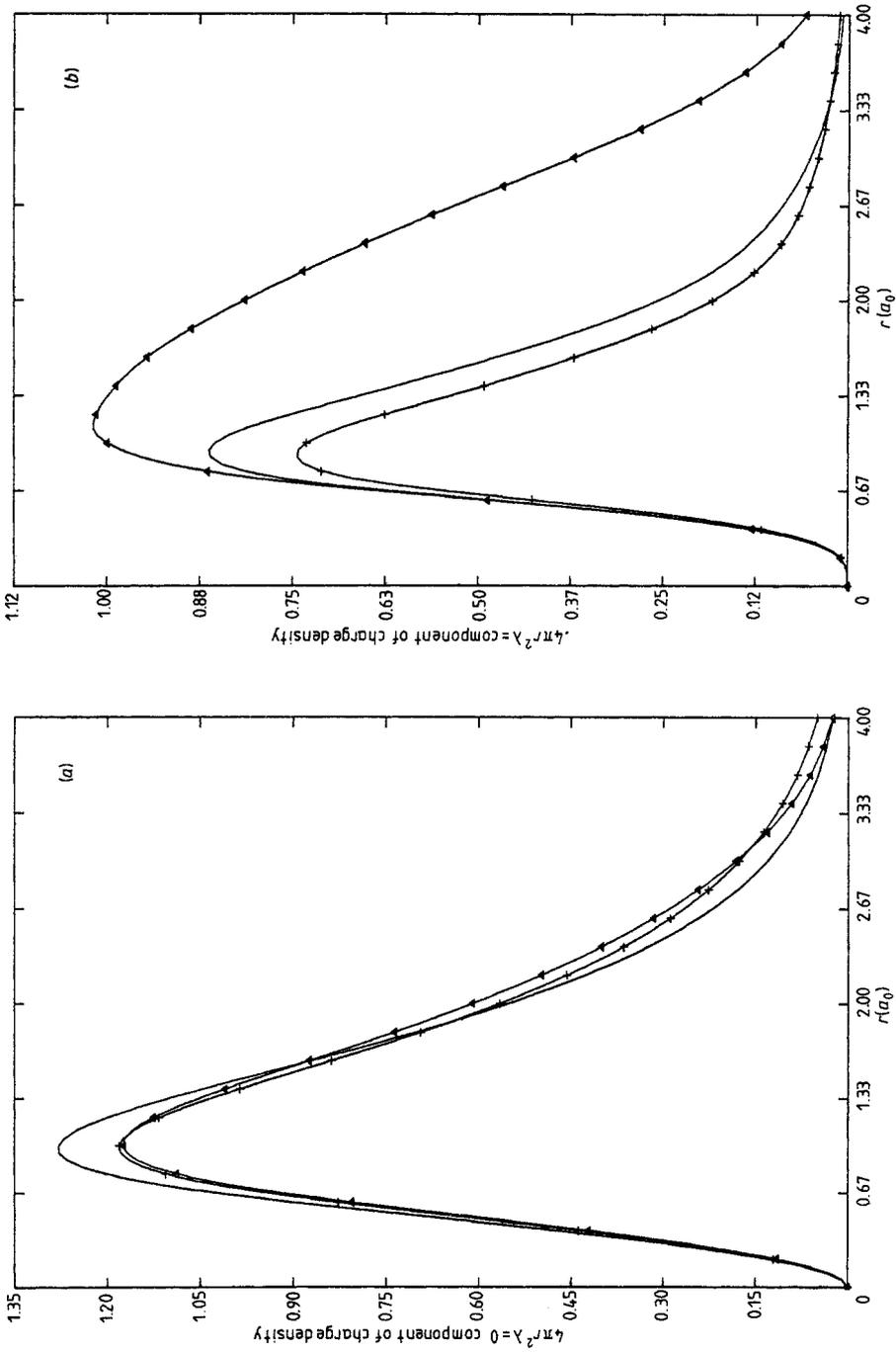
Figure 2. Radial expansion coefficients of the charge density of H_2 (see equation (10)) for (a) $\lambda = 0$, and (b) $\lambda = 2$. Three cases are shown for each coefficient: the neutral H_2 density (full curve), a polarised density (pluses) for which the distorting particle was an *electron*, and a polarised density (triangles) for which the distorting particle was a *positron*. In the latter two cases, the distorting particle was fixed along the z axis at $z = 2.5a_0$.

The two distortions are not identical because the electric field that brings about the distortion is *radial*. Hence the charge density that 'piles up' near the projectile in the positron case experiences a stronger field than in the electron case. If the scattering particle is reasonably far from the target, the charge cloud experiences a nearly uniform electric field. Thus, as r increases, the adiabatic polarisation potentials become identical. (All of these potentials obey equation (1) for $r > 10.0a_0$.)

3.2. Cross sections

As might be expected, using polarisation potentials as different as those of figure 1 in scattering calculations on a system that is highly sensitive to polarisation leads to strikingly different results. To illustrate this point, we compare total integrated cross sections (from the ground rotational state†, $j_0 = 0$) determined with the ADPOS and BTADE potentials in figure 3. Also shown in this figure are the most recent sets of published experimental data (Hoffman *et al* 1982, Charlton *et al* 1983).
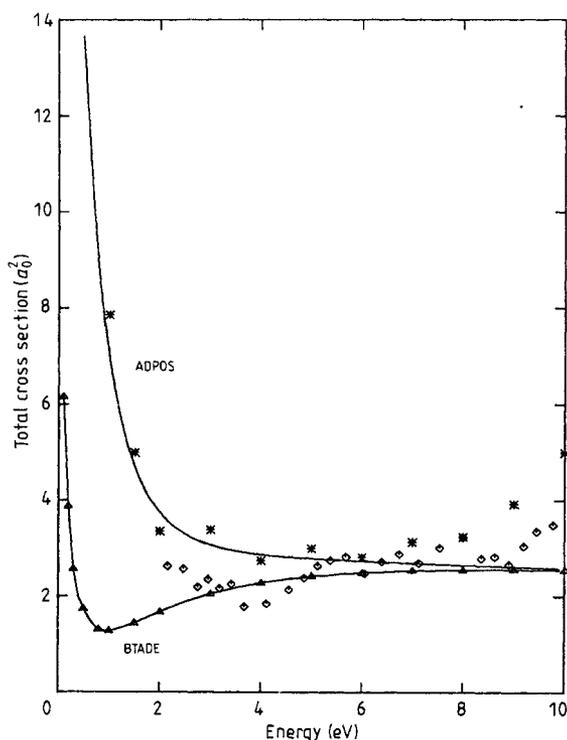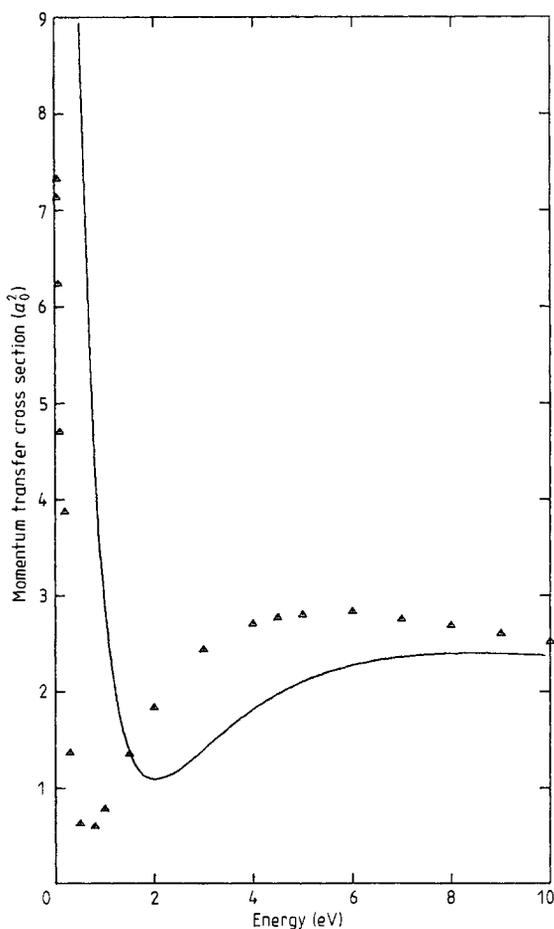

Figure 3. Total integrated cross sections for positron–H_2 scattering calculated with the ADPOS and BTADE polarisation potentials. The ADPOS potential was cut off using the function of equation (6) with $r_c = 1.8a_0$. The cross sections shown are the sum of integrated elastic scattering ($j_0 = 0 \rightarrow j = 0$) and rotational excitation ($j_0 = 0 \rightarrow j = 2$) cross sections as determined from LFCC calculations (see § 2.4). Also shown are the experimental results of Hoffman *et al* (1982) (stars) and of Charlton *et al* (1983) (diamonds).

† We include in the total cross sections σ_{tot} only contributions from $j_0 = 0 \rightarrow j = 0$ (elastic) and $j_0 = 0 \rightarrow j = 2$. Cross sections for $|\Delta j| > 2$ make negligible contributions to σ_{tot} at energies under consideration (cf, Baille *et al* 1974).

The two polarisation potentials clearly lead to qualitatively different cross sections. In contrast to the BTADE results, the ADPOS cross sections do not exhibit a minimum and rise much more rapidly with decreasing energy. (We shall return to the question of the minimum in σ_{tot} in § 3.3.) Since the positronium formation channel is not taken into account in our formulation, the calculated cross sections do not exhibit the rise at about 8.0 eV that is seen in the experimental results due to this channel. However, below this energy it is possible to obtain good agreement between experiment and theory using the cut-off adiabatic positron–H_2 potential. (In the ADPOS potential used here we chose $r_c = 1.8a_0$ (see figure 6 for a study of the sensitivity of these results to r_c).

Significant differences are also seen in the total momentum transfer cross sections σ_{mom}, calculated with the BTADE and ADPOS potentials, shown in figure 4. Both potentials produce a low-energy minimum in σ_{mom} although at different energies.

Figure 4. Total momentum transfer cross sections for positron–H_2 scattering calculated with the ADPOS (full curve) and BTADE (triangles) polarisation potentials. The ADPOS potential was cut-off with the function of equation (6) with $r_c = 1.8a_0$. The cross sections shown are the sum of momentum transfer cross sections for elastic scattering ($j_0 = 0 \rightarrow j = 0$) and rotational excitation ($j_0 = 0 \rightarrow j = 2$) cross sections as determined from LFCC calculations (see § 2.4).

Since the ADPOS potential gives the best overall agreement with experimental total cross sections, we used it to determine total differential cross sections. These are shown (at selected energies) in figure 5. Their variation with energy is qualitatively similar to that observed in positron–He scattering (cf figure 5 of Massey *et al* 1966). These results may be useful in the absolute normalisation of experimental data (Hoffmann *et al* 1982).
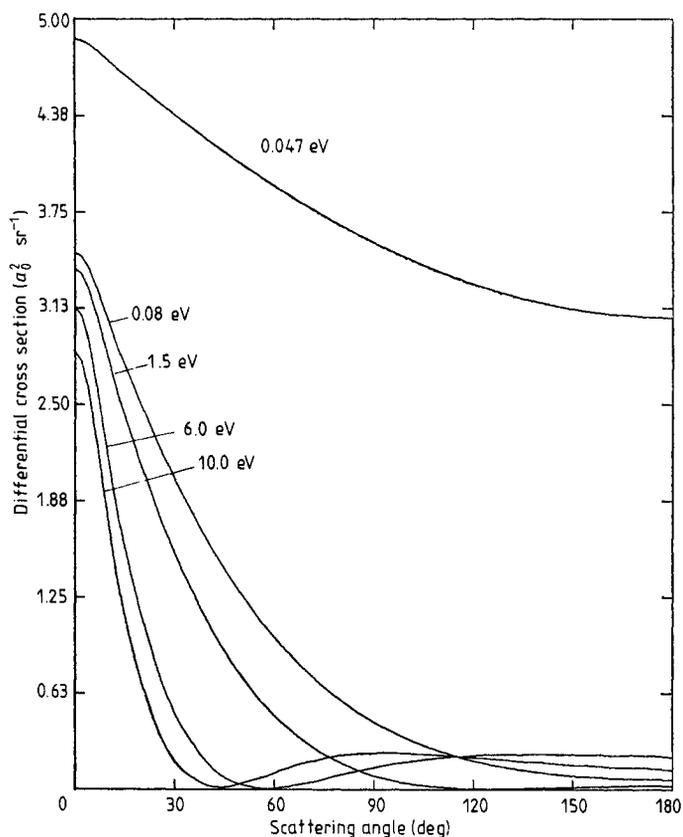

Figure 5. Total differential cross sections for positron–H₂ scattering at selected energies. These results were calculated with the ADPOS polarisation potential using the cut-off function of equation (6) with $r_c = 1.8$. The cross sections shown are the sum of differential elastic scattering ($j_0 = 0 \rightarrow j = 0$) and rotational excitation ($j_0 = 0 \rightarrow j = 2$) cross sections as determined from LFCC calculations (see § 2.4).

As expected, differential cross sections exhibit a dramatic sensitivity to the choice of polarisation potential. For example, BTADE differential cross sections (not shown) are less strongly peaked in the forward direction but show more scattering at $\theta_q > 90°$ than do the ADPOS results in figure 5.

We also calculated rotational excitation cross sections with the ADPOS and BTADE potentials. These cross sections also showed considerable sensitivity to the polarisation potential at scattering energies greater than about 0.1 eV. (Below this energy, they are entirely determined by the permanent quadrupole interaction.) However, since the ADPOS rotational excitation cross sections are given to within a few per cent by the

first Born approximation for scattering energies up to about 8.0 eV, they need not be presented here (see Baille *et al* 1974, Pande and Singh 1978).

In assessing the cross sections presented thus far, it is important to keep in mind that the ADPOS potential contains an adjustable parameter, the cut-off radius r_c. The choice of r_c determines approximately the extent to which non-adiabatic effects modify the adiabatic polarisation potential. In figure 6(a), we present a study of the sensitivity of σ_{tot} to this parameter. All of the curves in this figure are based on V_{AD}^+.
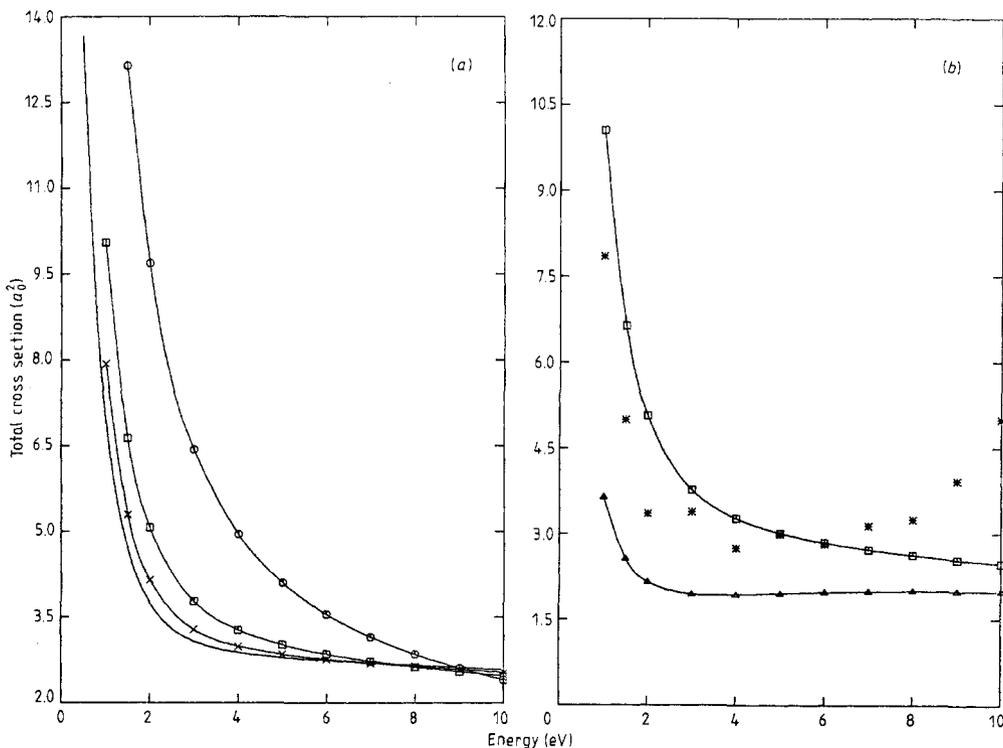
Figure 6. Studies of the sensitivity of total integrated positron–H_2 cross sections to: (a) the cut-off parameter in the cut-off function of equation (6); (b) the use of an electron or a positron as the distorting particle. In (a), results are shown for three cut-off ADPOS potentials, with cut-off radii $r_c = 1.5a_0$ (squares), $1.7a_0$ (crosses), and $1.8a_0$ (full curve), and for the fully adiabatic ADPOS potential of equation (3) (circles). In (b) cross sections are shown for *identically* cut-off ADPOS (squares) and ADELEC (diamonds) polarisation potentials (with $r_c = 1.5a_0$). Also shown are the experimental data of Hoffman *et al* (1982) (stars).

The *purely adiabatic* potential, in which $r_c = 0$ and non-adiabatic effects are completely neglected, is too strong to qualitatively reproduce the shape of the experimental cross sections shown in figure 3. This observation emphasises the importance of non-adiabatic effects for low-energy positron–molecule scattering. Applying the cut-off function $C(r_q)$ weakens V_{AD}^+, decreasing the total cross section. Increasing r_c in this function 'flattens' σ_{tot}, causing it to rise more sharply with decreasing energy. Encouragingly, the sensitivity of this cross section to r_c is not great.

A concern of the present study that is unrelated to non-adiabatic effects is the importance of the higher order (sign-dependent) perturbation terms in $V_{AD}^{\pm}$. In figure 6(b) we compare total positron–H₂ cross sections calculated with identically cut-off ADELEC and ADPOS potentials. The differences between these curves, therefore, arise solely from the sign of the charge of the (fixed) projectile.

Figure 6(b) illustrates the strong sensitivity of σ_{tot} to the sign of q in V_{pol}. The ADELEC cross section is much flatter than the ADPOS curve and does not agree as well with the experimental data. Worse yet, variation of r_c in the ADELEC potential does not noticeably improve the overall agreement with experiment. For example, decreasing r_c induces a sharper rise in the total cross section below about 3.0 eV, improving the agreement with experiment at low energies. However, this adjustment lowers σ_{tot} above 3.0 eV, moving the theoretical curve *away* from the experimental results. These results tend to support the findings of Darewych (1982) and of Horbatsch and Darewych (1983) that a cut-off *electron* polarisation potential is inadequate for positron collisions, although we note that the latter studies were based on the asymptotic form (1) rather than on V_{AD}^{+}.

3.3. A Ramsauer–Townsend minimum?

One of the most distinctive differences between the BTADE and ADPOS cross sections in figure 3 is the minimum in the former curve at about 0.9 eV. The recent experimental data of Hoffman *et al* (1982) do not show a low-energy minimum (see also Coleman *et al* 1974, 1976). However, there is some indication of such a structure (at about 3.8 eV) in the results of Charlton *et al* (1980, 1983). The theoretical cross sections of Lodge *et al* (1971), Baille *et al* (1974), Hara (1974) and Sur and Ghosh (1982), all of which were based on *electron*–H₂ polarisation potentials, exhibit a minimum in the total cross section, although the energy at which this minimum occurs and the rapidity of the decrease of σ_{tot} with increasing energy differ significantly among these results.

Because of disagreements among existing experimental data and uncertainties about the proper inclusion of polarisation in theoretical calculations, we consider the question of whether or not there is a Ramsauer–Townsend minimum in the total positron–H₂ cross section to be unanswered at present. Unfortunately, the need for a parameter in the ADPOS potential prohibits us from making a definitive statement on this question.

However, some light can be shed on the situation by breaking down the total cross section into partial contributions according to system symmetry (cf, equation (8)). In figure 7(a), the ADPOS total cross sections and contributions to it from the dominant symmetries in the energy range under consideration (Σ_g, Σ_u and Π_u) are shown.

The Σ_g symmetry is dominant below about 2.0 eV, and is responsible for the sharp rise in σ_{tot} at low energies. Above this energy, several symmetries make important contributions to σ_{tot}. The Σ_g cross section is nearly zero at roughly 3.8 eV. However, this energy is large enough that the contributions from the Σ_u and Π_u symmetries effectively 'wash out' this minimum from the total cross section, which is free of structure. For a Ramsauer–Townsend minimum to be present in σ_{tot}, the minimum in the Σ_g cross section would have to occur at a significantly lower energy.

This is precisely what happens when the BTADE potential is used. The Σ_g cross section produced by this potential is nearly zero at about 0.9 eV, at which energy this contribution is the dominant one. This minimum therefore appears in the total cross section shown in figure 3. This result shows the Σ_g partial cross section to be particularly
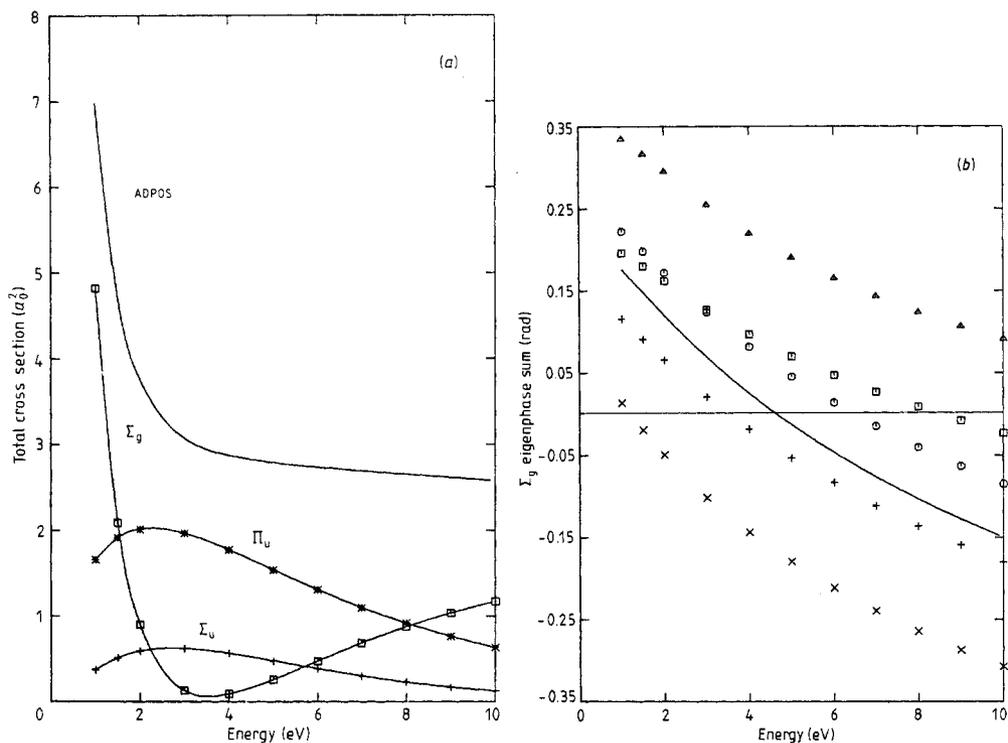
Figure 7. Investigation of the low-energy minimum in the positron–H_2 total cross sections. (a) Partial cross sections (see equation (8)) in the Σ_g (squares), Σ_u (pluses) and Π_u (stars) symmetries, together with their sum, the total cross section. (b) Σ_g eigenphase sums for various polarisation potentials: fully adiabatic ADPOS (triangles) and ADELEC (squares), cut-off ADPOS with $r_c = 1.5a_0$ (circles) and with $r_c = 1.8a_0$ (full curve), cut-off ADELEC with $r_c = 1.5a_0$ (pluses) and BTADE (crosses). Note that the ADPOS with $r_c = 1.8a_0$ was used in calculating the results of figures 3, 4 and 5.

sensitive to short-range features of the polarisation potential. This sensitivity is strikingly illustrated by the Σ_g eigenphase sum, δ_{sum} (Σ_g). This quantity equals zero at an energy very near that at which the corresponding partial cross section is zero. In figure 7(b), Σ_g eigenphase sums are compared for several polarisation potentials.

Clearly, this important scattering parameter is critically sensitive to how non-adiabatic effects are incorporated in the model potential. For example, one can change the energy at which the Σ_g cross section passes through zero by adjusting the cut-off radius in the ADPOS potential. Increasing the cut-off radius from $1.5a_0$ to $1.8a_0$ in this potential lowers the energy at which $\delta_{sum}(\Sigma_g)$ equals zero. Use of a *much* larger value of r_c in the ADPOS potential could induce a zero in $\delta_{sum}(\Sigma_g)$ at a low enough energy that the resulting total cross section would exhibit a Ramsauer–Townsend minimum. However, such a calculation would be unlikely to shed much light on the question of whether the feature is actually present in the positron–H_2 system.

The eigenphase sums in figure 7(b) also exhibit great sensitivity to the sign of q in the adiabatic potential. For example, identically cut-off ADPOS and ADELEC potentials produce zeros at quite different energies, the latter occurring at a much lower energy (for the same value of r_c) than the former.

4. Conclusions

We have explored several facets of polarisation in positron–molecule scattering, using as a first example positron–H_2 scattering in the rigid-rotor approximation. At issue are the importance of higher order perturbation terms in the adiabatic polarisation potential—terms which are sensitive to the sign of the charge of the projectile—and, secondarily, non-adiabatic effects in V_{pol}. We have also examined the validity of using electron–molecule polarisation potentials in positron–molecule scattering calculations.

We have demonstrated that, because of differences in the way electrons and positrons distort the H_2 charge cloud, V_{pol} and, more importantly, σ_{tot}, exhibit considerable sensitivity to the sign of the charge of the projectile. This fact indicates the importance of perturbation terms of higher than second order in the adiabatic polarisation potential. Non-adiabatic effects are also important, and the cross sections are rather sensitive to how they are taken into account.

Using a cut-off fully adiabatic *positron*–H_2 polarisation potential, we have obtained rather good agreement with recent experimental total cross sections (at energies where the positronium formation channel appears to be unimportant). However, the presence of the adjustable cut-off radius in this model renders it less than satisfactory. Theoretical cross sections are rather sensitive to the value of this parameter. However, no *ab initio* prescription for its determination can be given at present, and without such a prescription, even qualitative questions—like the presence or absence of a Ramsauer–Townsend minimum—cannot be resolved by theory. Therefore, we view the present ADPOS calculations as only a first step towards a viable theory of polarisation in positron–molecule scattering.

Further progress would seem to require a more rigorous, parameter-free, computationally tractable theory of non-adiabatic effects in positron scattering. An exact treatment for a simple system, such as positron–H_2, (e.g., using an optical potential) would provide valuable benchmarks for future study.

A further difficulty arises for scattering energies above about 5.0 eV, where various rearrangement channels (e.g., positronium formation, dissociation, and electronic excitation) properly should be included in the theory. Doing so may exacerbate the problems caused by polarisation. Positronium formation is a correlation effect, like polarisation, and, if the coupling between the positron formation channel and, say, the elastic channel is strong, the former may significantly influence the total cross sections. Indeed, since positronium is highly polarisable (Humberston 1979), any theory that includes positronium formation should treat all correlation effects, including polarisation very accurately.

Finally, it is important to determine if the sensitivity seen in the present positron–H_2 study to higher order perturbation terms and to how the dynamic polarisation terms are approximated is exhibited in other positron–molecule systems. The availability of recent experimental data and theoretical work recommends the positron–N_2 and positron–CO_2 systems for immediate further study of this question.

References

Arthurs A M and Dalgarno A 1960 *Proc. R. Soc.* A **256** 540–54
Baille P, Darewych J W and Lodge J G 1974 *Can. J. Phys.* **52** 667–77
Bhattacharyya P K and Ghosh A S 1975 *Phys. Rev.* A **12** 1881–4
Burke P G and Chandra N 1972 *J. Phys. B: At. Mol. Phys.* **5** 1696–705
Burke P G and Taylor A J 1966 *Proc. Phys. Soc.* **88** 549–63
Callaway J, LaBahn R W, Pu R T and Duxler W M 1969 *Phys. Rev.* **168** 12–21
Canter K F and Mills A P Jr 1982 *Can. J. Phys.* **60** 551–64
Castillejo L, Percival I C and Seaton M J 1960 *Proc. R. Soc.* A **254** 259–66
Chang E S and Fano U 1972 *Phys. Rev.* A **6** 173–87
Charlton M, Griffith T C, Heyland G R and Wright G L 1980 *J. Phys. B: At. Mol. Phys.* **13** L353–6
—— 1983 *J. Phys. B: At. Mol. Phys.* **16** 323–41
Coleman P G, Griffith T C and Heyland G R 1974 *Appl. Phys.* **4** 80–90
—— 1981 *J. Phys. B: At. Mol. Phys.* **14** 2509–17
Collins L A, Norcross D W and Schmid G B 1980 *Comput. Phys. Commun.* **21** 79–90
Dalgarno A, Drake G F W and Victor G A 1968 *Phys. Rev.* **176** 194–9
Darewych J W 1982 *J. Phys. B: At. Mol. Phys.* **15** L415–9
Darewych S W and Baille P 1974 *J. Phys. B: At. Mol. Phys.* **7** L1–4
Darewych S W, Baille P and Hara S 1974 *J. Phys. B: At. Mol. Phys.* **7** 2047–54
Drachman R J and Temkin A 1972 *Case Studies in Atomic Physics* vol 2 ed W E McDaniel and M R C McDowell (Amsterdam: North-Holland) pp 401–7
Eades R A, Truhlar D G and Dixon D A 1979 *Phys. Rev.* A **20** 867–78
Feldt A N, Gibson T L and Morrison M A 1983 *Bull. Am. Phys. Soc.* **28** 811
Ghosh A S, Sil N C and Mandal P 1983 *Phys. Rep.* **87** 313–406
Gibson T L and Morrison M A 1982 *J. Phys. B: At. Mol. Phys.* **15** L221–8
—— 1983 *Phys. Rev.* A in press
Gillespie E S and Thompson D G 1975 *J. Phys. B: At. Mol. Phys.* **8** 2858–68
Griffith T C 1979 *Adv. At. Mol. Phys.* **15** 135–66
Hara S 1969 *J. Phys. Soc. Japan* **27** 1262–8
—— 1972 *J. Phys. B: At. Mol. Phys.* **5** 589–98
—— 1974 *J. Phys. B: At. Mol. Phys.* **13** 1748–55
Hoffman K R, Dababneh M S, Hsieh Y-F, Kauppila W E, Pol V, Smart J H and Sein T S 1982 *Phys. Rev.* A **25** 1393–401
Horbatsch M and Darewych J W 1983 *J. Phys. B: At. Mol. Phys.* **16** 4059–64
Horbatsch M, Darewych J W and McEachran R P 1983 *J. Chem. Phys.* **78** 5564–6
Humberston J W 1979 *Adv. At. Mol. Phys.* **15** 101–34
Jain A 1983 *J. Chem. Phys.* **78** 6579–83
Jain A and Thompson D G 1982 *J. Phys. B: At. Mol. Phys.* **15** L631–7
—— 1983a *J. Phys. B: At. Mol. Phys.* **16** 2593–607
—— 1983b *J. Phys. B: At. Mol. Phys.* **16** 3077–98
—— 1983c *J. Phys. B: At. Mol. Phys.* **16** L347–54
—— 1983d *J. Phys. B: At. Mol. Phys.* **16** 1113–23
Jean Y C and Schrader D W 1978 *Phys. Rev.* A **18** 2030–40
Kauppila W E and Stein T S 1982 *Can. J. Phys.* **60** 471–93
Khan P and Ghosh A S 1983 *Phys. Rev.* A **27** 1904–9
Kleinman C J, Hahn Y and Spruch L 1969 *Phys. Rev.* **165** 53–62
Lane N F 1980 *Rev. Mod. Phys.* **52** 29–120
Lane N F and Henry R J W 1968 *Phys. Rev.* **173** 183–93
Lodge J G, Darewych J W and McEachran R P 1971 *Can. J. Phys.* **49** 13–9

McEachran R P, Morgan D L, Ryman A G and Stauffer A D 1977 *J. Phys. B: At. Mol. Phys.* **10** 663–77

McEachran R P and Stauffer A D 1983 *J. Phys. B: At. Mol. Phys.* **16** 255–74

Massey H S W 1982 *Can. J. Phys.* **60** 461–70

Massey H S W, Lawson J and Thompson D G 1966 *Quantum Theory of Atoms, Molecules, and the Solid State* ed P Lowdin (New York: Academic) pp 203–5

Morgan L A 1982 *J. Phys. B: At. Mol. Phys.* **15** L25–9

Morrison M A 1979 *Electron–Molecule and Photon–Molecule Collisions* ed T Rescigno, V McKoy and B Schneider (New York: Plenum) pp 15–50

—— 1980 *Comput. Phys. Commun.* **21** 63–77

—— 1983 *Aust. J. Phys.* **36** 239–86

Morrison M A, Feldt A N and Austin D 1983 *Phys. Rev. A* in press

Morrison M A and Hay P J 1979 *Phys. Rev. A* **20** 740–8

Mukherjee A and Sural D P 1982 *J. Phys. B: At. Mol. Phys.* **15** 1121–30

Onda K and Temkin A 1983 *Phys. Rev. A* **28** 621

Pande A K and Singh R S 1978 *J. Phys. B: At. Mol. Phys.* **11** 1633–41

Ray A, Ray P R and Saha B C 1980 *J. Phys. B: At. Mol. Phys.* **13** 4509–19

Schrader D M and Svetic R E 1982 *Can. J. Phys.* **60** 517–42

Sin Fai Lam L T 1982 *J. Phys. B: At. Mol. Phys.* **15** 143–53

Stein T S and Kauppila W E 1982 *Adv. At. Mol. Phys.* **18** 53–96

Sur S and Ghosh A S 1982 *Can. J. Phys.* **60** 597–600

Temkin A 1957 *Phys. Rev.* **107** 1004–12

Truhlar D G, Dixon D A and Eades R A 1979 *J. Phys. B: At. Mol. Phys.* **12** 1913–9

Varracchio E F and Girardeau M D 1983 *J. Phys. B: At. Mol. Phys.* **16** 1097–112

Willis S L and McDowell M R C 1982 *J. Phys. B: At. Mol. Phys.* **15** L31–5