

## Close Coupling Theory of Positron Scattering from Alkali Atoms

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### *Abstract*

The close coupling equations for positron–alkali atom scattering are written as a set of coupled momentum-space Lippmann–Schwinger equations. The alkali atom is represented by a frozen-core model based upon the Hartree–Fock approximation. The interaction between the positronium and the residual ion is modified by the inclusion of a core potential. Similarly, a core term is present in the interaction describing the rearrangement process. Close coupling calculations of positron scattering from sodium are performed in a model containing multiple sodium (3s, 3p, 4s, 3d, 4p) and positronium (1s, 2s, 2p) states. Cross sections are reported for an energy range from threshold to 50 eV; the total cross sections are in agreement with experimental data.

### **1. Introduction**

Only recently have calculations of positron–hydrogen scattering that explicitly include the rearrangement channel of positronium formation been performed as a matter of routine (Hewitt *et al.* 1990; Higgins and Burke 1993; Mitroy 1993*a*, 1993*b*; Mitroy and Stelbovics 1994*a*, 1994*b*; Sarkar and Ghosh 1994). The difficulties in computing the rearrangement matrix element make calculations on the positron–hydrogen system much more difficult than those for the electron–hydrogen system. That the first above-ionisation-threshold resonance in the positron–hydrogen system was not identified until 1991 (Higgins and Burke 1991) gives an indication of the level of understanding of the positron–hydrogen system compared with that of the electron–hydrogen system. In this work, we extend a method previously used to describe positron–hydrogen scattering (Mitroy 1993*a*) so that positron–alkali atom interactions can be handled, and report the results of pilot calculations on the sodium atom.

Some experimental information is available for positron–alkali systems. The Detroit group has measured total cross sections for sodium, potassium, rubidium and caesium (Stein *et al.* 1987; Kwan *et al.* 1989, 1991).

Calculations of positron–alkali atom scattering can be divided into two classes, those excluding and those including the positronium (Ps) formation channels. Calculations using the close coupling method, but excluding Ps formation channels, have been performed at low and intermediate energies by Ward *et al.* (1988, 1989*a*, 1989*b*) and Sarkar *et al.* (1988). The justification for this class of calculation is that of ease of implementation. However, given the strong interaction between

the positronium and positron channels, the overall accuracy of this approach can be questioned. Calculations which explicitly include the positronium channels, within a restricted channel space (Abdel-Raouf 1988), or within the framework of first-order perturbation theories (Guha and Mandal 1980; Mandal and Guha 1980; Nahar and Wadehra 1987) have been reported. There has also been a calculation which included the influence of positronium formation by means of an optical potential (McCarthy *et al.* 1993). Close coupling calculations with realistic channel spaces that include the Ps channels have now been performed on lithium, sodium and potassium (Hewitt *et al.* 1992, 1993). There are some aspects of the calculations of the Daresbury group that need to be resolved. First, they do not specify the actual form of the transition operator used in the evaluation of the rearrangement matrix elements. Second, in their initial calculations on hydrogen (Hewitt *et al.* 1990) an incorrect expression was used to evaluate the interaction between the positronium and residual ion. It is unclear whether this error has also carried over to their calculations on the alkali atoms.

The present work represents a straightforward generalisation of the close coupling theory originally applied to positron–hydrogen scattering (Mitroy 1993*a*). In this method, the close coupling equations are written in terms of a set of coupled Lippmann–Schwinger equations and the basic numerical computation is the evaluation of the first Born matrix element. Some complications occur when generalising the method to alkali targets. The functional form of the transition operator for the rearrangement process has to be modified to include the interaction between the positron and the core. The matrix element for the positronium–residual ion interaction also becomes more complicated.

## 2. Details of Close Coupling Equations

The derivation of the close coupling equations for positron–alkali atom scattering is more complicated than that for positron–hydrogen atom scattering. In this work  $\mathbf{r}_0$  is the coordinate of the positron centred with respect to the proton. The set of  $N$  electron coordinates will be designated  $\mathbf{r}_i$ , where  $i \in \{1, \dots, N\}$ . The distances between the electrons (or between the electrons and the positron) will be written  $r_{ij}$ , where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . It is also necessary to introduce relative,  $\boldsymbol{\rho}_i$ , and centre of mass,  $\mathbf{R}_i$ , coordinates for the outgoing positronium species. These are defined by

$$\boldsymbol{\rho}_i = \mathbf{r}_i - \mathbf{r}_0, \quad \mathbf{R}_i = \frac{1}{2}(\mathbf{r}_i + \mathbf{r}_0) \quad (1a)$$

or

$$\mathbf{r}_i = \mathbf{R}_i + \frac{1}{2}\boldsymbol{\rho}_i, \quad \mathbf{r}_0 = \mathbf{R}_i - \frac{1}{2}\boldsymbol{\rho}_i. \quad (1b)$$

With these definitions the Jacobian of the transformation between the two coordinate systems gives

$$\int d^3r_i \int d^3r_0 = \int d^3\rho_i \int d^3R_i. \quad (2)$$

The Schrödinger equation can now be written

$$(H_e + H_{\text{atom}} - E)\Psi(\mathbf{r}_i, \mathbf{r}_0) = 0, \quad (3)$$

where  $H_e$  is the Hamiltonian operator containing the positron coordinate,

$$H_e = -\frac{1}{2}\nabla_0^2 + \frac{Z}{r_0} - \sum_i \frac{1}{r_{i0}}, \quad (4)$$

$H_{\text{atom}}$  is the  $N$ -electron Hamiltonian of the target atom,

$$H_{\text{atom}} = \sum_i \left( -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \frac{1}{2} \sum_{j \neq i} \frac{1}{r_{ij}}, \quad (5)$$

and  $E$  is the total energy of the  $(N+1)$ -body system. Since positronium formation is being considered in this work, an alternative partitioning of the Hamiltonian is possible, viz.

$$H = H_{\text{Ps}}(m) + H_{\text{ion}}(m) + H_{\text{int}}(m) \quad m \in \{1, \dots, N\}, \quad (6)$$

where  $H_{\text{ion}}(m)$  is the Hamiltonian of the residual ion with the  $m$ th electron removed,

$$H_{\text{ion}} = \sum_{i \neq m} \left( -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j, \\ i,j \neq m}} \frac{1}{r_{ij}}, \quad (7)$$

$H_{\text{Ps}}(m)$  is the interaction of the positronium molecule containing the  $m$ th electron with the residual ion,

$$H_{\text{Ps}}(m) = -\frac{1}{4}\nabla_R^2 + \frac{Z}{r_0} - \frac{Z}{r_m} - \sum_{i \neq m} \left( \frac{1}{r_{i0}} - \frac{1}{r_{im}} \right), \quad (8)$$

and  $H_{\text{int}}(m)$  is the internal Hamiltonian for a positronium molecule containing the  $m$ th electron,

$$H_{\text{int}}(m) = -\nabla_{\rho_m}^2 + \frac{1}{r_{m0}}. \quad (9)$$

The following conventions will be observed in this work. Bound states of the alkali atom will be designated  $\Psi$ , bound states of the positronium atom will be denoted by  $\Phi$ , and bound states of the residual ion will be denoted by  $\Omega$ . The individual orbital wavefunctions which constitute the alkali atom and residual ion quantum states will be designated by  $\psi$  and  $\omega$  respectively. The subscripts  $\alpha$ ,  $\beta$  and  $\gamma$  will also be used to distinguish between the manifolds of atomic, positronium and ionic states. The  $i = 1$  electron will be designated as the electron which is removed from the atom and attached to the positron when positronium is formed. Provided all wavefunctions are correctly antisymmetrised, this can be done without any loss of generality. The subscript will now be dropped from the positronium coordinates  $\rho_m$  and  $\mathbf{R}_m$  and the notation  $\mathbf{r}_{i'}$  will be used to designate that  $\Omega(\mathbf{r}_{i'})$  is a function of all the electron coordinates with the exception of the  $i = 1$  electron. The notation  $\mathbf{r}_{i' \neq m}$  will designate a function of all the electron coordinates except the  $i = m$  electron.

The wavefunction is expanded in an eigenfunction expansion of continuum positron and positronium states which are coupled to atomic and ionic states,

$$\Psi(\mathbf{r}_i, \mathbf{r}_0) = \sum_{\alpha} \Psi_{\alpha}(\mathbf{r}_i) F_{\alpha}(\mathbf{r}_0) + \sum_{\beta\gamma} \Omega_{\gamma}(\mathbf{r}_{i'}) \Phi_{\beta}(\boldsymbol{\rho}) G_{\beta\gamma}(\mathbf{R}). \quad (10)$$

The bound atomic  $\Psi_{\alpha}(\mathbf{r}_i)$ , positronium  $\Phi_{\beta}(\boldsymbol{\rho})$ , and ionic  $\Omega_{\gamma}(\mathbf{r}_{i'})$  states are all stationary states satisfying

$$\langle \Psi_{\alpha}(\mathbf{r}_i) | H_{\text{atom}} - \epsilon_{\alpha} | \Psi_{\alpha}(\mathbf{r}_i) \rangle = 0, \quad (11)$$

$$\langle \Phi_{\beta}(\boldsymbol{\rho}) | H_{\text{int}}(1) - \epsilon_{\beta} | \Phi_{\beta}(\boldsymbol{\rho}) \rangle = 0, \quad (12)$$

$$\langle \Omega_{\gamma}(\mathbf{r}_{i'}) | H_{\text{ion}}(1) - \epsilon_{\gamma} | \Omega_{\gamma}(\mathbf{r}_{i'}) \rangle = 0. \quad (13)$$

The Schrödinger equation now becomes

$$(E - H) \left( \sum_{\alpha} \Psi_{\alpha}(\mathbf{r}_i) F_{\alpha}(\mathbf{r}_0) + \sum_{\beta\gamma} \Phi_{\beta}(\boldsymbol{\rho}) \Omega_{\gamma}(\mathbf{r}_{i'}) G_{\beta\gamma}(\mathbf{R}) \right) = 0. \quad (14)$$

Multiplying on the left by  $\Psi_{\alpha'}(\mathbf{r}_i)$  and integrating with respect to all the  $d^3 r_i$  yields the following equation:

$$\begin{aligned} (E + \frac{1}{2} \nabla_0^2 - \epsilon_{\alpha'}) F_{\alpha'}(\mathbf{r}_0) &= \sum_{\alpha} \langle \Psi_{\alpha'} | (Z/r_0 - \sum_i 1/r_{0i}) | \Psi_{\alpha} \rangle F_{\alpha}(\mathbf{r}_0) \\ &+ \sum_{\beta\gamma} \langle \Psi_{\alpha'} | (H - E) | \Omega_{\gamma} \Phi_{\beta} G_{\beta\gamma}(\mathbf{R}) \rangle. \end{aligned} \quad (15a)$$

Similarly, a set of equations for  $G_{\beta'\gamma'}$  can also be derived

$$\begin{aligned} (E + \frac{1}{4} \nabla_{\mathbf{R}}^2 - \epsilon_{\beta'}) G_{\beta'\gamma'}(\mathbf{R}) &= \sum_{\alpha} \langle \Phi_{\beta'} \Omega_{\gamma'} | (H - E) | \Psi_0 F_{\alpha} \rangle \\ &- \sum_{m \neq 1} \sum_{\beta\gamma} \langle \Phi_{\beta'} \Omega_{\gamma'}(\mathbf{r}_{i'}) | (H - E) | \Phi_{\beta}(\boldsymbol{\rho}_{i' \neq 1}) \rangle G_{\beta\gamma}(\mathbf{R}_m) \\ &+ \sum_{\beta\gamma} \langle \Phi_{\beta'} \Omega_{\gamma'} | [Z/r_0 - Z/r_1 - \sum_{i \neq 0,1} (1/r_{i0} - 1/r_{i1})] | \Phi_{\beta} \Omega_{\gamma} \rangle G_{\beta\gamma}(\mathbf{R}) \end{aligned} \quad (15b)$$

by multiplying on the left by  $\Phi_{\beta'}(\boldsymbol{\rho}) \Omega_{\gamma'}(\mathbf{r}_{i'})$  and integrating with respect to  $d^3 r_{i'}$  and  $d^3 \boldsymbol{\rho}$ . The second term is the exchange term that results from an exchange interaction between the  $m$ th electron in the residual ion and the electron in the positronium. In order to expedite matters, the following simplifying approximations will now be made:

- (i) The wavefunctions for the atomic and residual ion states will be computed in a fixed-core model. One example of a fixed-core model is the frozen-core Hartree–Fock approximation. The atomic states are labelled by the orbital occupied by the valence electron.
- (ii) Only the electron occupying the valence orbital will be removed from the atom when positronium is formed. Hence there will only be one possible residual ion state, that of the relatively inert closed-shell core. From now on, no explicit reference will be given to the ion core except where it is needed in the calculation of a matrix element.
- (iii) The exchange interaction between the electron in the positronium and the electrons in the residual ion core will be neglected. These terms will involve 9-dimensional integrals in  $r$ -space or 6-dimensional integrals in  $p$ -space and their evaluation is expected to be very difficult.

The steps by which equations (15a) and (15b) are specialised to a particular entrance channel and then transformed into a set of momentum-space Lippmann–Schwinger equations are standard and do not need to be repeated here. The momentum-space Lippmann–Schwinger equations for a positron with momentum  $\mathbf{k}$  incident on an alkali atom in state  $\Psi_\alpha$  are

$$\begin{aligned}
 \langle \mathbf{k}'\Psi_{\alpha'}|T|\mathbf{k}\Psi_\alpha\rangle &= \langle \mathbf{k}'\Psi_{\alpha'}|V|\mathbf{k}\Psi_\alpha\rangle + \sum_{\alpha''} \int d^3k'' \frac{\langle \mathbf{k}'\Psi_{\alpha'}|V|\mathbf{k}''\Psi_{\alpha''}\rangle \langle \mathbf{k}''\Psi_{\alpha''}|T|\mathbf{k}\Psi_\alpha\rangle}{E^{(+)} - \epsilon_{\alpha''} - \frac{1}{2}k''^2} \\
 &\quad + \sum_{\beta''} \int d^3k'' \frac{\langle \mathbf{k}'\Psi_{\alpha'}|V|\mathbf{k}''\Phi_{\beta''}\rangle \langle \mathbf{k}''\Phi_{\beta''}|T|\mathbf{k}\Psi_\alpha\rangle}{E^{(+)} - \epsilon_{\beta''} - \frac{1}{4}k''^2}, \\
 \langle \mathbf{k}'\Phi_{\beta'}|T|\mathbf{k}\Psi_\alpha\rangle &= \langle \mathbf{k}'\Phi_{\beta'}|V|\mathbf{k}\Psi_\alpha\rangle + \sum_{\alpha''} \int d^3k'' \frac{\langle \mathbf{k}'\Phi_{\beta'}|V|\mathbf{k}''\Psi_{\alpha''}\rangle \langle \mathbf{k}''\Psi_{\alpha''}|T|\mathbf{k}\Psi_\alpha\rangle}{E^{(+)} - \epsilon_{\alpha''} - \frac{1}{2}k''^2} \\
 &\quad + \sum_{\beta''} \int d^3k'' \frac{\langle \mathbf{k}'\Phi_{\beta'}|V|\mathbf{k}''\Phi_{\beta''}\rangle \langle \mathbf{k}''\Phi_{\beta''}|T|\mathbf{k}\Psi_\alpha\rangle}{E^{(+)} - \epsilon_{\beta''} - \frac{1}{2}k''^2}. \tag{16}
 \end{aligned}$$

The generic term  $V$  is used to label the interaction between the different classes of channels. There are three different classes of  $V$ -matrix elements. There are the interactions between the different positron channels, namely

$$\begin{aligned}
 \langle \mathbf{k}'\Psi_{\alpha'}|V|\mathbf{k}\Psi_\alpha\rangle &= (2\pi)^{-3} \int d^3r_0 \int d^3r_i \Psi_{\alpha'}^*(\mathbf{r}_i) \exp(-i\mathbf{k}' \cdot \mathbf{r}_0) \\
 &\quad \times \left( Z/r_0 - \sum_i 1/r_{0i} \right) \Psi_\alpha(\mathbf{r}_i) \exp(i\mathbf{k} \cdot \mathbf{r}_0). \tag{17}
 \end{aligned}$$

The interactions of the positron with the valence and core electrons can be treated separately. The core potential can be defined by

$$V_{\text{core}}(r_0) = \sum_\gamma (4\ell_\gamma + 2) \int d^3r_1 \omega_\gamma^*(\mathbf{r}_1) \omega_\gamma(\mathbf{r}_1) (1/r_0 - 1/r_{01}), \tag{18}$$

where the sum over  $\gamma$  runs over all the fully occupied orbitals in the core and therefore

$$\begin{aligned} \langle \mathbf{k}' \Psi_{\alpha'} | V | \mathbf{k} \Psi_{\alpha} \rangle &= (2\pi)^{-3} \int d^3 r_0 \int d^3 r_1 \Psi_{\alpha'}(\mathbf{r}_1) \exp(-i\mathbf{k}' \cdot \mathbf{r}_0) \\ &\times [V_{\text{core}}(r_0) + 1/r_0 - 1/r_{01}] \Psi_{\alpha}(\mathbf{r}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_0). \end{aligned} \quad (19)$$

There are two classes of interactions between the positronium and residual ion, a direct-type interaction and an exchange-type interaction involving the positronium channels. The direct interaction is

$$\begin{aligned} \langle \mathbf{k}' \Phi_{\beta'} | V | \mathbf{k} \Phi_{\beta} \rangle &= (2\pi)^{-3} \int d^3 \rho \int d^3 R \Phi_{\beta'}^*(\rho) \exp(-i\mathbf{k}' \cdot \mathbf{R}) \\ &\times [V_{\text{core}}(r_0) - V_{\text{core}}(r_1) + 1/r_0 - 1/r_1] \Phi_{\beta}(\rho) \exp(i\mathbf{k} \cdot \mathbf{R}). \end{aligned} \quad (20)$$

The evaluation of this interaction in  $r$ -space requires a two-dimensional integration or a partial wave expansion of  $V_{\text{core}}(r_0) - V_{\text{core}}(r_1)$  and  $1/r_0 - 1/r_1$  into the  $(\rho, \mathbf{R})$  coordinate system. The expansion of  $1/r_0 - 1/r_1$  into the  $(\rho, \mathbf{R})$  coordinates can be done by using standard results; however, the expansion of the core term is more problematical. The core term is best handled in momentum space. As mentioned earlier, the exchange interaction between the electron in the positron and the core electrons will be neglected.

Finally, there are the rearrangement matrix elements

$$\begin{aligned} \langle \mathbf{k}' \Phi_{\beta'} | V | \mathbf{k} \Psi_{\alpha} \rangle &= (2\pi)^{-3} \int d^3 r_0 \int d^3 r_i \Omega(\mathbf{r}_i) \Phi_{\beta'}^*(\rho) \exp(-i\mathbf{k}' \cdot \mathbf{R}) \\ &\times (H - E) \Psi_{\alpha}(\mathbf{r}_i) \exp(i\mathbf{k} \cdot \mathbf{r}_0). \end{aligned} \quad (21)$$

We make the approximation that  $H_{\text{atom}} \Psi_{\alpha}(\mathbf{r}_i) = (\epsilon_{\text{core}} + \epsilon_{\alpha}) \Psi_{\alpha}(\mathbf{r}_i)$ , where  $\epsilon_{\text{core}}$  is the energy of the closed-shell core. The single-particle HF energy of the valence electron is  $\epsilon_{\alpha'}$  and the single-electron orbital characterising the state is  $\psi_{\alpha}(\mathbf{r}_1)$ . With these definitions, the interaction is

$$\begin{aligned} \langle \mathbf{k}' \Phi_{\beta'} | V | \mathbf{k} \Psi_{\alpha} \rangle &= (2\pi)^{-3} \int d^3 r_0 \int d^3 r_1 \int d^3 r_i \Omega(\mathbf{r}_i) \Phi_{\beta'}^*(\rho) \exp(-i\mathbf{k}' \cdot \mathbf{R}) \\ &\times (H_e + \epsilon_{\text{core}} + \epsilon_{\alpha} - E) \Psi_{\alpha}(\mathbf{r}_i) \exp(i\mathbf{k} \cdot \mathbf{r}_0), \end{aligned} \quad (22)$$

which reduces to

$$\begin{aligned} \langle \mathbf{k}' \Phi_{\beta'} | V | \mathbf{k} \Psi_{\alpha} \rangle &= (2\pi)^{-3} \int d^3 r_0 \int d^3 r_1 \Phi_{\beta'}^*(\rho) \exp(-i\mathbf{k}' \cdot \mathbf{R}) \\ &\times [\tfrac{1}{2} \mathbf{k}^2 + V_{\text{core}}(r_0) + 1/r_0 - 1/r_{01} + \epsilon_{\text{core}} + \epsilon_{\alpha} - E] \\ &\times \psi_{\alpha}(\mathbf{r}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_0). \end{aligned} \quad (23)$$

The partitioning of the Hamiltonian into  $H_{\text{Ps}} + H_{\text{ion}} + H_{\text{int}}$  gives an identical answer:

$$\begin{aligned} \langle \mathbf{k}' \Phi_\beta | V | \mathbf{k} \Psi_\alpha \rangle &= (2\pi)^{-3} \int d^3 r_0 \int d^3 r_1 \int d^3 r_{i'} \Omega(\mathbf{r}_{i'}) \Phi_\beta^*(\boldsymbol{\rho}) \exp(-i\mathbf{k}' \cdot \mathbf{R}) \\ &\times (H_{\text{Ps}} + H_{\text{int}} + \epsilon_{\text{core}} - E) \Psi_\alpha(\mathbf{r}_i) \exp(i\mathbf{k} \cdot \mathbf{r}_0). \end{aligned} \quad (24)$$

Since  $H_{\text{ion}} \Omega(\mathbf{r}_{i'}) = \epsilon_{\text{core}} \Omega(\mathbf{r}_{i'})$  and  $H_{\text{int}} \Phi_\beta(\boldsymbol{\rho}) = \epsilon_\beta \Phi_\beta(\boldsymbol{\rho})$ , we get

$$\begin{aligned} \langle \mathbf{k}' \Phi_\beta | V | \mathbf{k} \Psi_\alpha \rangle &= (2\pi)^{-3} \int d^3 r_0 \int d^3 r_1 \int d^3 r_{i'} \Omega(\mathbf{r}_{i'}) \Phi_\beta^*(\boldsymbol{\rho}) \exp(-i\mathbf{k}' \cdot \mathbf{R}) \\ &\times \left( \epsilon_\beta + \frac{1}{4} \mathbf{k}'^2 - Z/r + \sum_{i \neq 1} 1/r_{1i} + V_{\text{core}}(r_0) + 1/r_0 + \epsilon_{\text{core}} - E \right) \\ &\times \psi_\alpha(\mathbf{r}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_0). \end{aligned} \quad (25)$$

Since  $\Phi_\beta(\boldsymbol{\rho})$  is a positronium eigenstate, the  $-1/r_{01}$  factor can be removed from equation (24). In a similar manner, equation (25) can be simplified by replacing  $(-Z/r_1 + \sum_{i \neq 1} 1/r_{1i}) \Psi_\alpha(\mathbf{r}_1)$ . These substitutions yield

$$\begin{aligned} \langle \mathbf{k}' \Phi_\beta | V | \mathbf{k} \Psi_\alpha \rangle &= (2\pi)^{-3} \int d^3 r_0 \int d^3 r_1 \int d^3 r_{i'} \Phi_{\beta'}^*(\boldsymbol{\rho}) \exp(-i\mathbf{k}' \cdot \mathbf{R}) \\ &\times \left[ \frac{1}{2} \mathbf{k}'^2 + \nabla_\rho^2 + \epsilon_\alpha + \epsilon_\beta + \epsilon_{\text{core}} + V_{\text{core}}(r_0) + 1/r_0 - E \right] \\ &\times \psi_\alpha(\mathbf{r}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_0) \end{aligned} \quad (26a)$$

or

$$\begin{aligned} \langle \mathbf{k}' \Phi_{\beta'} | V | \mathbf{k} \Psi_\alpha \rangle &= (2\pi)^{-3} \int d^3 \rho \int d^3 R \Phi_{\beta'}^*(\boldsymbol{\rho}) \exp(-i\mathbf{k}' \cdot \mathbf{R}) \\ &\times \left[ \frac{1}{4} \mathbf{k}'^2 + \frac{1}{2} \nabla_1^2 + \epsilon_\alpha + \epsilon_\beta + \epsilon_{\text{core}} + V_{\text{core}}(r_0) + 1/r_0 - E \right] \\ &\times \psi_\alpha(\mathbf{r}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_0). \end{aligned} \quad (26b)$$

These different expressions are sometimes referred to as the post and prior forms of the matrix element. In the present context, where the interaction Hamiltonian is sandwiched between plane waves, it is irrelevant which form is adopted, since the two forms yield equivalent matrix elements.

For purposes of practical computation, it is convenient to write these matrix elements in a form amenable to calculations in momentum space. The direct interaction for positron scattering, equation (19), becomes

$$\begin{aligned} \langle \mathbf{k}' \Psi_{\alpha'} | V | \mathbf{k} \Psi_{\alpha} \rangle &= \frac{1}{2\pi^2 |\mathbf{k} - \mathbf{k}'|^2} \left( \delta_{\alpha' \alpha} - \int d^3 r \psi_{\alpha'}(\mathbf{r}) \psi_{\alpha}(\mathbf{r}) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] \right) \\ &+ \delta_{\alpha' \alpha} \sum_{\gamma} \frac{4\ell_{\gamma} + 2}{2\pi^2 |\mathbf{k} - \mathbf{k}'|^2} \left( 1 - \int d^3 r \omega_{\gamma}^*(\mathbf{r}) \omega_{\gamma}(\mathbf{r}) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] \right), \end{aligned} \quad (27)$$

which can be written in more detail as

$$\begin{aligned} \langle \mathbf{k}' \Psi_{\alpha'} | V | \mathbf{k} \Psi_{\alpha} \rangle &= \frac{1}{2\pi^2 |\mathbf{k} - \mathbf{k}'|^2} \left[ \delta_{\alpha' \alpha} \delta_{\lambda 0} - \sum_{\lambda \mu} i^{\lambda} (-1)^{m_{\alpha'} + \mu} \right. \\ &\times X_{\alpha' \alpha}^{\lambda}(|\mathbf{k} - \mathbf{k}'|) C_{-\mu}^{\lambda}(\mathbf{k} - \mathbf{k}') \hat{\ell}_{\alpha} \hat{\ell}_{\alpha'} \hat{\lambda}^2 \begin{pmatrix} \ell_{\alpha} & \lambda & \ell_{\alpha'} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & \ell_{\alpha} & \ell_{\alpha'} \\ \mu & m_{\alpha} & -m_{\alpha'} \end{pmatrix} \left. \right] \\ &+ \delta_{\alpha' \alpha} \delta_{\lambda 0} V_{\text{core}}(|\mathbf{k} - \mathbf{k}'|), \end{aligned} \quad (28)$$

where

$$X_{\alpha' \alpha}^{\lambda}(K) = \int_0^{\infty} dr r^2 \psi_{\alpha'}(r) \psi_{\alpha}(r) j_{\lambda}(Kr), \quad (29)$$

$C_{-\mu}^{\lambda}(\mathbf{k} - \mathbf{k}')$  is a spherical tensor, and  $\hat{\lambda} = (2\lambda + 1)^{\frac{1}{2}}$ . The momentum-space core potential is

$$V_{\text{core}}(K) = (2\pi)^{-3} \int d^3 r V_{\text{core}}(r) \exp[-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}], \quad (30)$$

which reduces to

$$V_{\text{core}}(K) = (2\pi^2)^{-1} \int_0^{\infty} dr r^2 V_{\text{core}}(r) j_0(Kr). \quad (31)$$

In practice, the core potential is evaluated using

$$V_{\text{core}}(K) = \sum_{\gamma} \frac{4\ell_{\gamma} + 2}{2\pi^2 K^2} \left[ 1 - \int_0^{\infty} dr r^2 \omega_{\gamma}(r) \omega_{\gamma}(r) j_0(Kr) \right], \quad (32)$$

The direct interaction for positronium proton scattering is

$$\begin{aligned} \langle \mathbf{k}' \Phi_{\beta'} | V | \mathbf{k} \Phi_{\beta} \rangle &= \left( V_{\text{core}}(|\mathbf{k} - \mathbf{k}'|) + \frac{1}{2\pi^2 |\mathbf{k} - \mathbf{k}'|^2} \right) \\ &\times \int d^3 \rho \Phi_{\beta'}^*(\rho) \{ \exp[\frac{1}{2}i(\mathbf{k}' - \mathbf{k}) \cdot \rho] - \exp[-\frac{1}{2}i(\mathbf{k}' - \mathbf{k}) \cdot \rho] \}. \end{aligned} \quad (33)$$



In more detail, we have

$$\begin{aligned} \langle \mathbf{k}' \Phi_{\beta'} | V | \mathbf{k} \Phi_{\beta} \rangle &= \left( V_{\text{core}}(K) + \frac{1}{2\pi^2 K^2} \right) [1 - (-1)^\lambda] \sum_{\lambda\mu} i^\lambda (-1)^{m_{\beta'} + \mu} \\ &\times Y_{\beta'\beta}^\lambda(K) C_{-\mu}^\lambda(\mathbf{k} - \mathbf{k}') \hat{\ell}_\beta \hat{\ell}_{\beta'} \hat{\lambda}^2 \begin{pmatrix} \ell_\beta & \lambda & \ell_{\beta'} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & \ell_\beta & \ell_{\beta'} \\ \mu & m_\beta & -m_{\beta'} \end{pmatrix}, \end{aligned} \quad (34)$$

where

$$Y_{\beta'\beta}^\lambda(K) = \int_0^\infty d\rho \rho^2 \Phi_{\beta'}(\rho) \Phi_\beta(\rho) j_\lambda(\tfrac{1}{2}K\rho). \quad (35)$$

It is clear from equation (34) that the matrix element is non-zero only when  $\lambda$  is odd, hence the direct interaction of the positronium with the residual ion core can only connect states of different parity. This matrix element is identical to the positronium proton matrix element with the addition of the term  $V_{\text{core}}(\mathbf{k})$ .

The positronium formation interaction is most conveniently written in terms of products of momentum-space wavefunctions. The hydrogen and positronium momentum-space wavefunctions,  $\psi(\mathbf{p})$  and  $\phi(\mathbf{p})$ , are defined by

$$\begin{aligned} \psi_\alpha(\mathbf{p}) &= (2\pi)^{-\frac{3}{2}} \int d^3r \psi_\alpha(\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}), \\ \phi_\beta(\mathbf{p}) &= (2\pi)^{-\frac{3}{2}} \int d^3\rho \phi_\beta(\rho) \exp(-i\mathbf{p} \cdot \rho). \end{aligned} \quad (36)$$

The inverse Fourier transforms are just

$$\begin{aligned} \psi_\alpha(\mathbf{r}) &= (2\pi)^{-\frac{3}{2}} \int d^3p \Psi_\alpha(\mathbf{p}) \exp(i\mathbf{p} \cdot \mathbf{r}), \\ \phi_\beta(\rho) &= (2\pi)^{-\frac{3}{2}} \int d^3p \phi_\beta(\mathbf{p}) \exp(i\mathbf{p} \cdot \rho). \end{aligned} \quad (37)$$

In terms of explicit quantities, the momentum-space wavefunction for  $\psi_\alpha(\mathbf{p})$  is

$$\psi_\alpha(\mathbf{p}) = i^{\ell_\alpha} (-1)^{\ell_\alpha} Y_{\ell_\alpha m_\alpha}(\mathbf{p}) \psi_\alpha(p), \quad (38)$$

where the  $Y_{\ell m}(\mathbf{p})$  in (38) is a spherical harmonic and the spherically symmetric component of the wavefunction is defined by

$$\psi_\alpha(p) = (2/\pi)^{\frac{1}{2}} \int_0^\infty dr r^2 \psi_\alpha(r) j_{\ell_\alpha}(pr). \quad (39)$$

With these definitions, the matrix element for Ps formation reduces to

$$\begin{aligned} \langle \mathbf{k}' \Phi_\beta | V | \mathbf{k} \Psi_\alpha \rangle &= \left( \frac{1}{2} \mathbf{k}^2 - |\mathbf{k} - \frac{1}{2} \mathbf{k}'|^2 + \epsilon_\alpha + \epsilon_{\text{core}} + \epsilon_\beta - E \right) \Psi_\alpha(\mathbf{k}' - \mathbf{k}) \phi_\beta^* \left( \frac{1}{2} \mathbf{k}' - \mathbf{k} \right) \\ &+ \int d^3 q \psi_\alpha(\mathbf{k}' - \mathbf{q}) \phi_\beta^* \left( \frac{1}{2} \mathbf{k}' - \mathbf{q} \right) [V_{\text{core}}(|\mathbf{q} - \mathbf{k}|) + 1/(2\pi^2 |\mathbf{q} - \mathbf{k}|^2)], \end{aligned} \quad (40a)$$

or

$$\begin{aligned} \langle \mathbf{k}' \Phi_\beta | V | \mathbf{k} \Psi_\alpha \rangle &= \left( \frac{1}{4} |\mathbf{k} - \mathbf{k}'|^2 + \epsilon_\alpha + \epsilon_{\text{core}} + \epsilon_\beta - E \right) \Psi_\alpha(\mathbf{k}' - \mathbf{k}) \phi_\beta^* \left( \frac{1}{2} \mathbf{k}' - \mathbf{k} \right) \\ &+ \int d^3 q \Psi_\alpha(\mathbf{k}' - \mathbf{q}) \phi_\beta^* \left( \frac{1}{2} \mathbf{k}' - \mathbf{q} \right) [V_{\text{core}}(|\mathbf{q} - \mathbf{k}|) + 1/(2\pi^2 |\mathbf{q} - \mathbf{k}|^2)]. \end{aligned} \quad (40b)$$

Equation (40), which is the most compact form of the interaction matrix element, involves a three-dimensional integral. This is evaluated by using a slight modification of the method developed by Mitroy (1993a) for positron–hydrogen scattering.

The present method exploits the fact that the  $\Psi_\alpha(\mathbf{k}' - \mathbf{q}) \phi_\beta^*(\frac{1}{2} \mathbf{k}' - \mathbf{q})$  product is only a function of  $\mathbf{k}'$  and  $\mathbf{q}$ , while the  $V_{\text{core}}(|\mathbf{q} - \mathbf{k}|) + 1/(2\pi^2 |\mathbf{q} - \mathbf{k}|^2)$  factor is only a function of  $\mathbf{k}$  and  $\mathbf{q}$ . Therefore, even though the entire integrand is a function of  $\mathbf{k}$ ,  $\mathbf{k}'$  and  $\mathbf{q}$ , it can be factorised into two parts and partial wave expansions of each of the parts can be done separately. Doing this leads to calculations which are manageable. The presence of the additional  $V_{\text{core}}(|\mathbf{q} - \mathbf{k}|)$  term in the kernel slows down the evaluation of the matrix elements, but does not otherwise lead to any major modifications in the calculation. One comment on the calculations of Hewitt *et al.* (1993) must be made: it is not clear whether they include core terms in the evaluation of the equations (33) and (40).

### 3. Partial Wave Analysis

The matrix elements are reduced to partial wave form by

$$\begin{aligned} V_{\alpha' L' \alpha L}^{(J)}(k', k) &= \sum_{m_\alpha' m_\alpha M M'} \int d\hat{\mathbf{k}} \int d\hat{\mathbf{k}}' Y_{L' M'}^*(\hat{\mathbf{k}}') \langle L' M' \ell_\alpha' m_\alpha' | J M J \rangle \\ &\times \langle \mathbf{k}' \alpha' | V | \alpha \mathbf{k} \rangle \langle L M \ell_\alpha m_\alpha | J M \rangle Y_{L M}(\hat{\mathbf{k}}), \end{aligned} \quad (41)$$

where  $\langle L M \ell_\alpha m_\alpha | J M \rangle$  is a Clebsch–Gordan coefficient. In writing down equation (41) all considerations of spin coupling have been ignored since the absence of an exchange interaction leads to the singlet and triplet partial wave  $T$ -matrix elements being identical. Performing the reductions, the following expressions are realised:

$$\begin{aligned}
V_{\alpha'L'\alpha L}^{(J)}(k', k) &= \sum_{\lambda'\tau} i^\lambda (-1)^{\tau+\lambda'+\lambda+J} \hat{\lambda}^3 \hat{\lambda}'^2 \hat{\ell}_\alpha \hat{\ell}_{\alpha'} \hat{L} \hat{L}' \\
&\times \left[ \frac{(2\lambda)!}{(2\tau)!(2\lambda-2\tau)!} \right]^{\frac{1}{2}} k^{\lambda-\tau} k'^\tau X_{\alpha'\alpha}^{\lambda'\lambda}(k', k) \\
&\times \begin{pmatrix} L' & \lambda' & \lambda-\tau \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & \tau & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_{\alpha'} & \lambda & \ell_\alpha \\ 0 & 0 & 0 \end{pmatrix} \\
&\times \left\{ \begin{matrix} \lambda & L' & L \\ \lambda' & \lambda-\tau & \tau \end{matrix} \right\} \left\{ \begin{matrix} \ell_{\alpha'} & L' & J \\ L & \ell_\alpha & \lambda \end{matrix} \right\}, \tag{42}
\end{aligned}$$

The  $X_{\alpha'\alpha}^{\lambda'\lambda}(k', k)$  is an angular integral defined by

$$\begin{aligned}
X_{\alpha'\alpha}^{\lambda'\lambda}(k', k) &= 2\pi \int_{-1}^1 du P_{\lambda'}(u) [\delta_{\lambda 0} \delta_{\alpha\alpha'} - X_{\alpha'\alpha}^\lambda(K)] / 2\pi^2 K^{\lambda+2} \\
&+ \delta_{\lambda 0} \delta_{\alpha\alpha'} 2\pi \int_{-1}^1 du P_{\lambda'}(u) V_{\text{core}}(K), \tag{43}
\end{aligned}$$

where  $P_{\lambda'}(u)$  is a Legendre polynomial,  $\mathbf{k} = |\mathbf{k} - \mathbf{k}'|$  and  $u = \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}$ .

The interaction between the different positronium channels is non-zero only when the levels have different parities. When this occurs, the matrix element is very similar to the interaction between the different hydrogen channels,

$$\begin{aligned}
V_{\beta'L'\beta L}^{(J)}(k', k) &= \sum_{\lambda\lambda'\tau} i^\lambda (-1)^{\tau+\lambda+\lambda'+J} \hat{\lambda}^3 \hat{\lambda}'^2 \hat{\ell}_\beta \hat{\ell}_{\beta'} \hat{L} \hat{L}' \\
&\times \left[ \frac{(2\lambda)!}{(2\tau)!(2\lambda-2\tau)!} \right]^{\frac{1}{2}} k^{\lambda-\tau} k'^\tau Y_{\beta'\beta}^{\lambda'\lambda}(k', k) [1 - (-1)^\lambda] \\
&\times \begin{pmatrix} L' & \lambda' & \lambda-\tau \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & \tau & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_{\beta'} & \lambda & \ell_\beta \\ 0 & 0 & 0 \end{pmatrix} \\
&\times \left\{ \begin{matrix} \lambda & L' & L \\ \lambda' & \lambda-\tau & \tau \end{matrix} \right\} \left\{ \begin{matrix} \ell_{\beta'} & \ell_\beta & J \\ L & L' & \lambda \end{matrix} \right\}, \tag{44}
\end{aligned}$$

where

$$Y_{\beta'\beta}^{\lambda'\lambda}(k', k) = \int_{-1}^1 du \frac{2\pi}{K^\lambda} \left[ V_{\text{core}}(K) + \frac{1}{2\pi^2 K^2} \right] P_{\lambda'}(u) Y_{\beta'\beta}^\lambda(K), \tag{45}$$

and where the definitions of  $\mathbf{k}$  and  $u$  are the same as those used for equation (43). The numerical evaluation of the integrals of equations (43) and (45) to yield  $X_{\alpha'\alpha}^{\lambda'\lambda}(k', k)$  and  $Y_{\beta'\beta}^{\lambda'\lambda}(k', k)$  is done using a composite Gauss-Legendre quadrature mesh. This technique is highly reliable and has received extensive use in numerous calculations of electron-atom scattering.

The matrix element for positronium formation is considerably more complicated, involving as it does an additional integration. The specific form of this matrix element that is most amenable to large-scale computation seems to be

$$\begin{aligned}
 V_{\beta L' \alpha L}^{(J)}(k', k) &= \sum_{\lambda \tau_\alpha \tau_\beta c j k} i^{\ell_\alpha + \ell_\beta} (-1)^{L+J+c+\ell_\alpha} \hat{\lambda}^2 \hat{\lambda}'^2 \hat{\ell}_\alpha \hat{\ell}_\beta \hat{L} \hat{L}' \\
 &\times \left[ \frac{(2\ell_\alpha)! (2\ell_\beta)!}{(2\tau_\alpha)! (2\tau_\beta)! (2\ell_\alpha - 2\tau_\alpha)! (2\ell_\beta - 2\tau_\beta)!} \right]^{\frac{1}{2}} \left(\frac{1}{2}\right)^{\ell_\beta - \tau_\beta} k'^{\ell_\alpha + \ell_\beta - \tau_\alpha} \\
 &\times \begin{pmatrix} j & \lambda & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & \lambda & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda_\alpha - \tau_\alpha & j & \lambda_\beta - \tau_\beta \\ 0 & 0 & 0 \end{pmatrix} \\
 &\times \begin{pmatrix} \tau_\alpha & k & \tau_\beta \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} L & c & L' \\ j & \lambda & k \end{matrix} \right\} \\
 &\times \left\{ \begin{matrix} \ell_\beta & L' & J \\ L & \ell_\alpha & c \end{matrix} \right\} \left\{ \begin{matrix} k & c & j \\ \tau_\alpha & \ell_\alpha & \ell_\alpha - \tau_\alpha \\ \tau_\beta & \ell_\beta & \ell_\beta - \tau_\beta \end{matrix} \right\} [Z_{1,\beta\alpha}^{\lambda,\tau}(k', k) + Z_{2,\beta\alpha}^{\lambda,\tau}(k', k)], \quad (46)
 \end{aligned}$$

where  $\tau = \tau_\alpha + \tau_\beta$ . This matrix element involves two separate integrals. The first integral is over the angle between  $\mathbf{k}$  and  $\mathbf{k}'$ , viz.

$$Z_{1,\beta\alpha}^{\lambda,\tau}(k', k) = \frac{1}{2} k^\tau \int_{-1}^1 du \left( \frac{1}{2} k^2 + \frac{1}{2} K_1^2 + \epsilon_{\text{core}} + \epsilon_\alpha + \epsilon_\beta - E \right)$$

or  $\times \Psi_\alpha(K_1) \phi_\beta(K_2) P_\lambda(u)$

$$\begin{aligned}
 Z_{2,\beta\alpha}^{\lambda,\tau}(k', k) &= \frac{1}{2} k^\tau \int_{-1}^1 du \left( \frac{1}{4} k'^2 + \frac{1}{2} K_2^2 + \epsilon_{\text{core}} + \epsilon_\alpha + \epsilon_\beta - E \right) \\
 &\times \Psi_\alpha(K_1) \phi_\beta(K_2) P_\lambda(u), \quad (47)
 \end{aligned}$$

with  $K_1 = |\mathbf{k} - \mathbf{k}'|$  and  $K_2 = |\mathbf{k} - \frac{1}{2}\mathbf{k}'|$ . No problems are encountered in the numerical evaluation of (47) since the integrations are similar to those encountered previously, e.g. in (43) and (45). The second term in (46) is

$$Z_{2,\beta\alpha}^{\lambda,\tau L}(k', k) = \frac{1}{8\pi^3} \int_0^\infty dq q^{2+\tau} H_{\beta\alpha}^\lambda(k', q) [V_{\text{core},L}(k, q) + V_L(k, q)], \quad (48)$$

where  $V_L(k, q)$  is just the partial wave component of the momentum-space form of the Coulomb potential, i.e.

$$V_L(k, q) = 2\pi \int_{-1}^1 du |q - k|^2 P_L(u); \quad u = \hat{\mathbf{q}} \cdot \hat{\mathbf{k}} \quad (49a)$$

$$= \frac{2\pi}{qk} Q_L[\frac{1}{2}(q/k + k/q)] \quad (49b)$$

and  $V_{\text{core},L}(k,q)$  is the Legendre coefficient of  $V_{\text{core}}(|\mathbf{q} - \mathbf{k}|)$ ,

$$V_{\text{core},L}(k,q) = 2\pi \int_{-1}^1 du \, 2\pi^2 V_{\text{core}}(|\mathbf{q} - \mathbf{k}|) P_L(u); \quad u = \hat{\mathbf{q}} \cdot \hat{\mathbf{k}}. \quad (50)$$

In expression (49b),  $Q_L[\frac{1}{2}(q/k+k/q)]$  is a Legendre function of the second kind. The functions  $V_{\text{core},L}(k,q)$  are computed and stored for all combinations of  $k$  and  $q$  prior to the evaluation of (48). The Legendre functions  $Q_L[\frac{1}{2}(q/k+k/q)]$  are computed as they arise in the integrand. The  $H_{\beta\alpha}^\lambda(k',q)$  are just projections of the product of the spherically symmetric part of the momentum-space wavefunctions, e.g.

$$H_{\beta\alpha}^\lambda(k',q) = 2\pi \int_{-1}^1 du \, \phi_\beta(|\frac{1}{2}\mathbf{k}' - \mathbf{q}|) \Psi_\alpha(|\mathbf{k}' - \mathbf{q}|) P_\lambda(u), \quad (51)$$

with  $u = \hat{\mathbf{q}} \cdot \hat{\mathbf{k}}'$  in this case. Care has to be taken to ensure that the numerical computations involved in the evaluation of (48) are done reliably and efficiently. That the functions  $H_{\beta\alpha}^\lambda(k',q)$  are functions of  $k'$  but not of  $k$  is of crucial importance. The functions  $H_{\beta\alpha}^\lambda(k',q)$  can be computed and stored for all possible combinations of  $\lambda, \beta, \alpha$  and  $k'$  prior to performing the final integration over  $q$ . This leads to a substantial decrease in the time needed to compute the matrix elements for all combinations of  $k$  and  $k'$ .

An additional difficulty is associated with (48), namely the presence of the Coulomb singularity. The argument of  $Q_L[\frac{1}{2}(q/k+k/q)] \rightarrow 1$  as  $q \rightarrow k$  and so a logarithmic singularity occurs at  $q = k$ . This singularity is handled by a subtraction technique. The basic integral that has to be done is of the type

$$I_L(k',k) = \int_0^\infty dq \, H(k',q) \{R(k,q) + Q_L[\frac{1}{2}(q/k+k/q)]\}. \quad (52)$$

This is rewritten as

$$I_L(k',k) = \int_0^\infty dq \left( H(k',q) Q_L[\frac{1}{2}(q/k+k/q)] - F(q) Q_0[\frac{1}{2}(q/k+k/q)] \right) + \int_0^\infty dq \, H(k',q) R(k,q) + \int_0^\infty dq \, F(q) Q_0[\frac{1}{2}(q/k+k/q)]. \quad (53)$$

By normalising  $F(q)$  so that

$$F(k) = H(k',k), \quad (54)$$

the logarithmic singularity in the first term in (53) is removed because  $Q_L(x) - Q_0(x) \rightarrow \text{constant}$  as  $x \rightarrow 1$ . The second term is finite everywhere and does not present a problem. The utility of this method depends on choosing a form for  $F(q)$  that permits the analytic evaluation of the third term of (53). In practice,  $F(q)$  is chosen to be a constant, and the subtraction is confined to the particular element of the Gaussian mesh in which the singularity occurs. More details can be found in Mitroy (1993a).

All quantities in this calculation are evaluated in terms of the momentum-space wavefunction or the momentum-space form of the potential. The momentum-space wavefunctions are computed by taking the Fourier transforms of the coordinate-space potentials and wavefunctions. Given that the atomic and positronium wavefunctions are expressed in terms of Slater-type orbitals, the conversion from coordinate space to momentum space can be performed analytically.

To facilitate numerical calculations, the kernel matrix is converted into purely real numbers by dividing each individual matrix element by  $i^{L-L'}$ . When this is done, the partial wave form of the Lippmann-Schwinger equation is

$$\begin{aligned}
 T_{\alpha'L'\alpha L}^{(J)}(k', k) &= V_{\alpha'L'\alpha L}^{(J)}(k', k) + \sum_{\alpha''} \int d^3k'' \frac{V_{\alpha'L'\alpha''L''}^{(J)}(k', k'') T_{\alpha''L''\alpha L}^{(J)}(k'', k)}{E^{(+)} - \epsilon_{\alpha''} - \frac{1}{2}k''^2} \\
 &\quad + \sum_{\beta''} \int d^3k'' \frac{V_{\alpha'L'\beta''L''}^{(J)}(k', k'') T_{\beta''L''\alpha L}^{(J)}(k'', k)}{E^{(+)} - \epsilon_{\beta''} - \frac{1}{4}k''^2}, \\
 T_{\beta'L'\alpha L}^{(J)}(k', k) &= V_{\beta'L'\alpha L}^{(J)}(k', k) + \sum_{\alpha''} \int d^3k'' \frac{V_{\beta'L'\alpha''L''}^{(J)}(k', k'') T_{\alpha''L''\alpha L}^{(J)}(k'', k)}{E^{(+)} - \epsilon_{\alpha''} - \frac{1}{2}k''^2} \\
 &\quad + \sum_{\beta''} \int d^3k'' \frac{V_{\beta'L'\beta''L''}^{(J)}(k', k'') T_{\beta''L''\alpha L}^{(J)}(k'', k)}{E^{(+)} - \epsilon_{\beta''} - \frac{1}{4}k''^2}. \quad (55)
 \end{aligned}$$

Apart from the fact that energy denominators arising from intermediate positronium states ( $\beta''$ ) have a  $\frac{1}{4}k''^2$  factor instead of the usual  $\frac{1}{2}k''^2$  factor, these equations are identical to those occurring in electron-atom scattering. Hence, techniques introduced to solve these equations for electron-atom scattering (McCarthy and Stelbovics 1983) can be adopted with minimal modification.

#### 4. Calculation Details

The positron-sodium system has one unusual feature in that the ground state of positronium has a larger binding energy than that of sodium. Consequently, the transition to positronium in its ground state is a superelastic transition and the cross section can be expected to diverge as  $E^{-\frac{1}{2}}$  as  $E \rightarrow 0$ .

The valence states of the sodium atom are computed in a fixed-core model. The core interaction consists of two parts. There is the static-exchange interaction with the  $\text{Na}^+$  core. The  $\text{Na}^+$  wavefunction is obtained from a calculation of the  $\text{Na } 3s \text{ } ^2\text{S}^e$  ground state. A semi-empirical core polarisation potential (Norcross and Seaton 1974) is then added to the core Hamiltonian. The details of the wavefunctions are identical to those used in a previous  $R$ -matrix calculation of electron-sodium scattering at low energy (Zhou *et al.* 1990).

The following labelling convention is used in this work. The label  $\text{CC}(m, n)$  represents a close coupling calculation in which  $m$  sodium states and  $n$  positronium states are explicitly coupled together. A number of different sets of close coupling calculations have been done.

$\text{CC}(4, 0)$ . In this approximation the  $\text{Na}(3s)$ ,  $\text{Na}(3p)$ ,  $\text{Na}(4s)$  and  $\text{Na}(5p)$  states are explicitly coupled. These calculations use the same channel space of

Hewitt *et al.* (1993) and were done so that direct comparisons between the two calculations could be made.

*CC(5,0)*. In this approximation the lowest five states of sodium, the Na(3s), Na(3p), Na(4s), Na(3d) and Na(5p) states, are explicitly coupled. These calculations are similar to the calculations of Ward *et al.* (1989a) and Sarkar *et al.* (1988).

*CC(5,3)*. This includes the lowest five states of sodium, Na(3s), Na(3p), Na(4s), Na(3d) and Na(4p), and the lowest three positronium states, Ps(1s), Ps(2s) and Ps(2p).

*UBA(5,3)*. This is an approximate solution of the Lippmann–Schwinger equation with the real part of Green’s function omitted.

Table 1. Elastic and excitation cross sections (in  $\pi a_0^2$  for  $e^+ - \text{Na}$ ) scattering

Model	Energy (eV)					
	3	5	7	10	20	50
	3s–3s					
CC(4,0) <sup>A</sup>	74.6	43.6	30.1	18.5	8.41	4.15
CC(4,0) <sup>B</sup>		54.24		19.78	8.84	4.75
CC(4,0)	77.2	45.3	29.8	18.9	8.93	4.60
CC(5,0) <sup>C</sup>	110.2	54.13	33.04	19.84	8.98	4.67
CC(5,0)	111.4	56.1	33.9	20.0	9.04	4.58
CC(4,3) <sup>A</sup>	82.0	50.3	31.2	21.2	7.50	
CC(5,3)	72.8	48.6	25.4	18.6	8.24	4.70
	3s–3p					
CC(4,0) <sup>A</sup>	36.3	64.9	70.5	68.4	50.7	27.5
CC(4,0) <sup>B</sup>		72.4		65.8	46.5	26.5
CC(4,0)	32.7	62.4	69.3	67.2	50.2	27.4
CC(5,0) <sup>C</sup>	66.11	69.99	65.91	59.21	44.61	25.67
CC(5,0)	65.7	69.9	66.5	59.4	45.1	26.1
CC(4,3) <sup>A</sup>	9.09	24.9	34.0	38.2	42.0	
CC(5,3)	7.08	23.5	32.7	36.8	40.2	25.5
	3s–4s					
CC(4,0) <sup>A</sup>		2.41	1.66	1.28	0.993	0.601
CC(4,0)		2.32	1.89	1.34	0.805	0.517
CC(5,0) <sup>C</sup>		9.61	5.42	2.48	0.81	0.47
CC(5,0)		9.72	5.51	2.49	0.794	0.501
CC(4,3) <sup>A</sup>		1.54	1.97	1.13	0.566	
CC(5,3)		1.43	2.16	0.576	0.421	0.462
	3s–3d					
CC(4,0) <sup>B</sup>		7.18		11.53	6.81	2.09
CC(5,0) <sup>C</sup>		7.49	10.64	11.04	6.27	1.81
CC(5,0)		7.40	10.63	11.2	6.50	1.88
CC(5,3)		2.46	5.60	5.41	3.72	1.76
	3s–4p					
CC(4,0) <sup>A</sup>		0.711	1.97	2.43	1.64	0.784
CC(4,0)		0.828	1.81	2.33	1.86	0.810
CC(5,0) <sup>C</sup>		3.49	6.55	6.24	3.11	0.99
CC(5,0)		3.82	6.67	6.34	3.11	0.987
CC(4,3) <sup>A</sup>		1.89	1.62	1.91	0.630	
CC(5,3)		0.576	1.02	1.98	1.19	0.859

<sup>A</sup> Hewitt *et al.* (1993).

<sup>B</sup> Sarkar *et al.* (1988).

<sup>C</sup> Ward *et al.* (1989a).

The calculations of Hewitt *et al.* (1993) are similar to the present CC(5,3) with the exception that they omit the Na(3d) state from the CC expansion. Since the present method encounters no problems with  $l = 2$  states, there is no point in compromising the accuracy of the calculation by omitting the 3d orbital.

The numerical details of the calculation were as follows. At the lowest energy (3 eV), a 40 point quadrature mesh was used to discretise the kernel. At higher energies, 48 point meshes were used to discretise the kernel. We have done calculations with different meshes at a few energies to assess the numerical precision of the calculations. From these calculations, we would estimate that the elastic, resonant Na(3s)  $\rightarrow$  Na(3p) excitation and ground-state positronium formation cross sections are generally accurate to better than 5%. The cross sections for the weaker transitions have an accuracy of about 10%. The rearrangement matrix elements were explicitly included in the kernel for  $J \leq 18$ . The small contributions to the positronium formation cross section (<5%) coming from higher partial waves were included by extrapolating the partial wave sum, assuming that the partial cross sections scale like a power series. The  $T$ -matrices used in the calculation of the cross sections correspond to full solutions of the CC equations for  $J \leq 40$  except at the highest energy (50 eV) where the calculations were extended to  $J = 50$ . At the higher energies, the partial wave sum for the inelastic transitions had to be completed using the extrapolation procedure described earlier.

## 5. Excitation of Sodium

Cross sections for elastic scattering and excitation of sodium are given in Table 1. Comparison of the present CC(5,0) cross section with the cross sections of Ward *et al.* (1989a) gives an estimate of the numerical accuracy of the present calculations. For most transitions, and at most energies, the two calculations agree to within a couple of per cent. The agreement between the two sets of calculations is as good as can be expected, given that details of the sodium wavefunctions are different for the two calculations.

Comparison with the notionally equivalent CC(4,0) calculation of Hewitt *et al.* (1993) shows differences of the order of 10% in a number of cases. These discrepancies are too numerous and too large to be attributed purely to differences in the sodium wavefunctions. The most likely cause for the discrepancies is the use of an integral equation numerical quadrature by Hewitt *et al.* (1993) that is not sufficiently dense at the important parts of the kernel. The  $T$ -matrix elements for weak transitions are often more sensitive to the details of the numerical analysis.

It is apparent from the comparison of the CC(5,0) and CC(5,3) cross sections that the rearrangement channels have a major effect on the collision dynamics. At energies below 10 eV the elastic cross section undergoes a 10–20% decrease when the positronium channels are included.

For the inelastic transitions to the excited sodium levels, the inclusion of the positronium channels exerts an even larger effect. The cross sections for excitation of the 3p, 4s, 3d and 4p levels are all greatly reduced, with the effect being largest at low energies. For instance, the cross section for the 3s  $\rightarrow$  3p resonant transition is reduced from 69.9 to  $23.3 \pi a_0^2$  at 5 eV and from 65.7 to  $7.25 \pi a_0^2$  at 3 eV when the positronium channels are included in the calculation.



We suspect that the suppression of excitation cross sections to the low-lying atomic levels by the positronium channels may be a universal feature of positron-alkali atom collisions. This trend is also evident in positron excitation cross sections reported by Hewitt *et al.* (1992, 1993) for lithium and potassium.

**Table 2.** Cross sections (in  $\pi a_0^2$ ) for positronium formation in the Ps(1s), Ps(2s) and Ps(2p) states for  $e^+$ -Na scattering

Model	Energy (eV)					
	3	5	7	10	20	50
Ps(1s)						
FBA <sup>A</sup>		49.1		15.2	2.82	
FBA	119.3	60.3	33.2	14.8	1.40	0.0137
UBA(5,3)	33.1	12.0	7.20	4.47	0.787	0.0157
CC(4,3) <sup>B</sup>	49.0	19.7	10.9	5.01	0.924	
CC(5,3)	26.8	20.0	12.8	5.34	0.819	0.0464
Ps(2s)						
FBA		23.8	9.84	3.56	0.631	0.0057
UBA(5,3)		1.78	1.88	1.28	0.212	0.0042
CC(4,3) <sup>B</sup>		4.57	4.34	3.08	1.53	
CC(5,3)		0.819	2.47	2.77	0.564	0.0106
Ps(2p)						
FBA		43.8	49.9	23.9	2.37	0.0056
UBA(5,3)		6.00	6.27	4.54	0.795	0.0051
CC(4,3) <sup>B</sup>		5.03	10.2	9.42	2.42	
CC(5,3)		2.49	5.86	7.10	1.56	0.0231

<sup>A</sup> Post form of FBA, Guha and Mandal (1980).      <sup>B</sup> Hewitt *et al.* (1983).

## 6. Positronium Formation

Cross sections for positronium formation in the Ps(1s), Ps(2s) and Ps(2p) states are given in Table 2. Cross sections are reported in the first Born approximation (FBA), the unitarised Born approximation (UBA), the CC(4,3) (Hewitt *et al.* 1993) and CC(5,3) approximations.

The agreement between the present FBA cross section with the previous FBA calculations is not good. This is not surprising since the transition operator used in the two calculations is different. Guha and Mandal (1980) omitted the kinetic energy terms from the interaction Hamiltonian.

Comparison of the FBA, UBA(5,3) and CC(5,3) reveals that the UBA(5,3) is a reasonable approximation to the CC(5,3) cross section, and the FBA is a poor approximation to the CC(5,3) cross section. The FBA overestimates the positronium formation cross sections for the Ps(1s), Ps(2s) and Ps(2p) levels by factors of 2 to 10 at energies below 10 eV. The UBA cross sections are generally correct to within a factor of 2 in this energy range.

The most notable feature of Table 2 is the large size of the positronium formation cross sections at low energies. At an incident energy of 3 eV, the electron transfer cross section to the Ps(1s) state is  $27.4 \pi a_0^2$ . Since this is a superelastic transition, the  $J=0$  partial cross section can be expected to increase like  $E^{-\frac{1}{2}}$  as  $E \rightarrow 0$ . As the S-wave cross section is only  $0.524 \pi a_0^2$ , it is clear that the energy has to decrease a lot more before the asymptotic region

is reached. To keep the large size of the positronium formation cross section in perspective, it should be recalled that the maximum size of this cross section for positron–hydrogen scattering is only about  $4.0 \pi a_0^2$  (Mitroy and Stelbovics 1994*b*).

At higher energies the opposite is true. The positronium formation cross section decreases rapidly and at the highest energy (50 eV), the net cross section for positronium formation in all states is only  $0.081 \pi a_0^2$ . This is much smaller than the net Ps formation cross section for positron–hydrogen scattering, which is  $0.55 \pi a_0^2$  at 54.42 eV (Mitroy and Stelbovics 1994*b*).

At the qualitative level, the present CC(5,3) and the CC(4,3) calculations of Hewitt *et al.* (1993) are in agreement. Both report large positronium formation cross sections which decrease rapidly as the energy increases. However, the detailed differences between the two calculations cannot be attributed to the slightly different channel spaces. A CC(4,3) calculation, using the same channel space as Hewitt *et al.*, was performed at an incident energy of 5 eV. This gave cross sections of 19.7, 1.25 and  $3.33 \pi a_0^2$  for the Ps(1s), Ps(2s) and Ps(2p) cross sections respectively. These cross sections are sufficiently close to the CC(5,3) cross sections, and sufficiently different from the Hewitt *et al.* cross sections, to indicate that the differences are due in large part to numerical aspects or possibly to a different interaction Hamiltonian, and are not the result of a slightly different channel space.

## 7. Total Cross Section

The only experimental information available on positron–sodium scattering is that from the experiment of Kwan *et al.* (1991), who reported total cross sections for sodium. This is an attenuation experiment, and so cannot discriminate against elastic scattering in the forward direction. Consequently, the experimental data will systematically underestimate the actual cross section by an amount equal to

$$\Delta\sigma_T = 2\pi \int_0^\alpha \sigma_{\text{el}}(\theta) \sin\theta \, d\theta, \quad (56)$$

where positrons undergoing elastic collisions up to an angle  $\alpha$  are assumed to be detected. At low energies, the large size of the elastic cross section in the forward direction will make  $\Delta\sigma_T$  a considerable fraction of the total cross section. For a direct comparison between theory and experiment it is necessary to apply a correction to the theoretical or experimental total cross sections. In this work, we have chosen to add a correction to the experimental cross sections by using the present CC(5,3) differential cross sections to evaluate  $\Delta\sigma_T$  for the cutoff angles listed in Table I of Kwan *et al.* (1991). At energies of 2.7, 7.7, 17.7, 27.7, 37.6, 48.3 and 57.9 eV,  $\Delta\sigma_T$  was 18.5, 8.4, 4.0, 2.8, 1.7, 1.4 and  $1.1 \pi a_0^2$ . Only at the low energies of 2.7 and 7.7 eV does the correction make a difference of 10% or greater to the empirical cross section. It should be mentioned that much larger corrections occur at low energies when the CC(5,0) differential cross sections are used.

Total cross sections from the present CC(5,0) calculation, the CC(4,3) model of Hewitt *et al.* (1993) and the present CC(5,3) calculation are depicted in Fig. 1.

We have performed calculations at additional energies to supplement those given in Tables 1 and 2. The present CC(5,0) model and the earlier calculation of Ward *et al.* (1989a) can be regarded as giving equivalent cross sections for all practical purposes. Comparison of the CC(5,3) and CC(5,0) cross sections shows that inclusion of the positronium formation channels leads to a large drop in the total cross section at lower energies. This drop in the cross section improves the agreement with the adjusted data of Kwan *et al.* (1989). At higher energies the difference between the CC(5,3) and CC(5,0) cross sections becomes much smaller. To summarise, the agreement between the CC(5,3) cross section and the experimental data of Kwan *et al.* (1991) is almost perfect, although the large size of the errors bars means this is not a very stringent test.

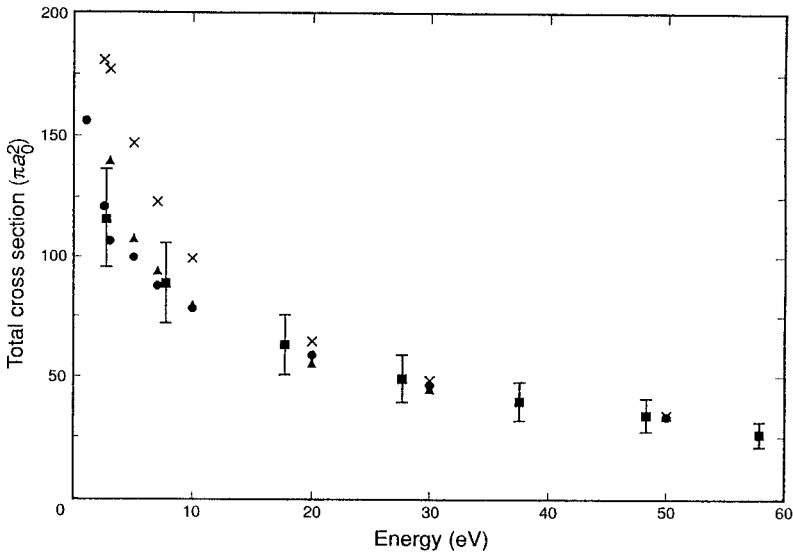


Fig. 1. Total cross sections for positron-sodium scattering. The adjusted measurements of Kwan *et al.* (1991) (■) are compared with the present CC(5,0) (x) and CC(5,3) (●) cross sections. Also depicted are the cross sections (▲) of Hewitt *et al.* (1993).

## 8. Conclusion

In this work we have generalised the theory of positron-hydrogen scattering to positron scattering from alkali atoms. Treating the alkali atom as a single-electron target simplifies the interaction kernel sufficiently to make calculations with explicit coupling between the positronium and positron channels possible. In making these simplifications, the exchange interaction between the electron in the positronium and the electrons in the residual ion has been omitted from the calculation.

Although the present calculations are different in detail from those of Hewitt *et al.* (1993), both calculations report a suppression of the resonant Na(3s)  $\rightarrow$  Na(3p) transition when the positronium formation channels are included in the channel space. The cross sections for excitation to the Na(4s), Na(3d) and Na(4p) states

are also reduced at low energies by the inclusion of the positronium channels. This is contrary to the speculation by Kwan *et al.* (1991) that inelastic cross sections for positron impact excitation at low energies are larger than those for electron impact excitation. The peak values of the positronium formation cross sections for the Ps(1s), Ps(2s) and Ps(2p) states are found to be much larger at low energy than the corresponding cross sections for positron–hydrogen scattering. At higher energies however, the positronium formation cross sections are much smaller than those for positron–hydrogen scattering. Given the small size of the Ps formation cross sections, and the good agreement between the CC(5,0) and CC(5,3) cross sections for sodium excitations at 50 eV, we would suggest that for incident positron energies of 50 eV or greater it should be possible to omit the positronium channels from the calculation.

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