

# On the Use of the Breit-Pauli Approximation in the Study of Relativistic Effects in Electron-Atom Scattering

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# ON THE USE OF THE BREIT-PAULI APPROXIMATION IN THE STUDY OF RELATIVISTIC EFFECTS IN ELECTRON-ATOM SCATTERING

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The electron-atom scattering problem is formulated by using the Breit-Pauli hamiltonian, and the Kohn variational principle is derived for this hamiltonian. Two distinct types of relativistic corrections are considered separately: (1) relativistic corrections due to the motion of the colliding electron and its interaction with the target; (2) relativistic corrections due to breakdown of  $LS$ -coupling in the target. In both of these cases it is shown that within the Breit-Pauli approximation a collision strength may be written  $\Omega^{\text{rel}}(i, j) = \Omega^{\text{nr}}(i, j) + \alpha^2 C_{\text{rel}}^{(2)}(i, j) + \alpha^4 C_{\text{rel}}^{(4)}(i, j)$ , where  $\Omega^{\text{rel}}$  is the collision strength including relativistic corrections and  $\Omega^{\text{nr}}$  is the non-relativistic collision strength. The quantities  $C_{\text{rel}}^{(2)}$  and  $C_{\text{rel}}^{(4)}$  are contributions of orders  $\alpha^2$  and  $\alpha^4$  respectively, relative to  $\Omega^{\text{nr}}$ . In the case of corrections of type (1), consistency problems render it difficult to calculate the term  $\alpha^4 C_{\text{rel}}^{(4)}$  reliably. On the other hand, strong semi-empirical evidence suggests that in the case of corrections of type (2), the  $\alpha^4$  correction can be reliably estimated within the framework of existing theory.

By means of Racah algebra it is demonstrated that fine structure interactions between colliding electron and target give no contributions of order  $\alpha^2$  provided that that  $\Omega^{\text{rel}}(i, j)$  is summed over the fine structure levels of the initial and final target terms. Breakdown of  $LS$ -coupling in the target (due to fine structure interactions among the target electrons) gives contribution of order  $\alpha^2$  to the total collision strength. However, these contributions do *not* vanish when the collision strengths are summed over the fine structure levels of the initial and final terms. Asymptotic expansions for the dependence of  $\Omega^{\text{rel}}$  upon the nuclear charge  $Z$  of the target are derived for corrections of types (1) and (2).

The present work is discussed in relation to recent work by Carse & Walker (1973) and Walker (1974), who have studied the electron-hydrogen scattering problem in a formulation based upon the Dirac equation. Practical procedures for carrying out calculations in the framework of the present theory are discussed, and one such procedure is formulated in some detail.

## 1. INTRODUCTION

In recent years a number of theoretical efforts have been directed at the investigation of relativistic effects in electron-atom scattering. These efforts may be divided into roughly four categories:

- (i) Calculations of elastic scattering cross-sections (total and partial) and electron spin polarizations in electron-heavy atom scattering. Such calculations have been reviewed by Walker (1970).

(ii) Calculations, again based upon the Dirac equation, of elastic and inelastic cross-sections and electron-spin polarizations in the scattering of electrons by hydrogen-like ions. Carse & Walker (1973) have formulated the theory of such calculations, and Walker (1974) has made calculations of the above quantities for a number of values of the nuclear charge  $Z$  in the range  $2 \leq Z \leq 100$ .

(iii) Essentially non-relativistic calculations, in which non-relativistic  $R$ -matrices in  $LS$ -coupling are transformed into a representation which enables one to work out collisional data connecting the target fine structure states. The effects of intermediate coupling in the target may be taken into account in this method. A program written by Saraph (1972) can produce fine structure collision strengths from  $LS$ -coupling  $R$ -matrices by means of this technique.

(iv) Once again, essentially non-relativistic calculations, in which the fine structure splitting of the target energies is taken into account when calculating the energy of the colliding electron. Burke & Mitchell (1974) recently reported a calculation of this type. In their study of low energy elastic scattering of electrons by caesium, they took into account the fine structure splitting of the  $6p$  state when using a two-state close-coupling approximation to calculate elastic cross-sections.

The calculations (i) and (ii) of Walker give considerable insight into the nature of relativistic effects in scattering problems. However, in these types of calculations the various relativistic effects are not separated; consequently it could be difficult to assess their importance in any particular type of cross-section. With regard to calculations in category (iii), it would be interesting to assess the  $Z$ -dependence of intermediate coupling collision strengths obtained in this manner, and to analyse the method in more depth than has been done hitherto. Finally, referring to calculations in category (iv), it would be of interest to know how the relativistic interactions between the colliding electron and the target could affect the cross-sections. Thus, in the  $e^-$ -Ce case mentioned above, the spin-orbit effect on the colliding electron in the  $p$ -wave channel could well be comparable to that on the bound  $6p$  electron.

The Breit-Pauli method has been applied widely, and with considerable success, in atomic structure problems. However, it has not yet been applied to the electron-atom scattering problem. The present paper is an initial attempt to formulate a theory of electron-atom scattering in the Breit-Pauli approximation, to understand how the various terms of the Breit-Pauli hamiltonian manifest themselves in total collision strengths and to consider the problems mentioned in the preceding paragraph.

## 2. THE BREIT-PAULI APPROXIMATION

In the Breit-Pauli approximation, the Breit-Pauli hamiltonian  $H_{B,P}$ ,

$$H_{B,P} = H_{nr} + \alpha^2 H_{rc}, \quad (1)$$

is used to describe the  $(N+1)$  electron system consisting of a  $N$ -electron ion and a colliding electron.

In (1)  $H_{nr}$  is the usual non-relativistic hamiltonian,

$$H_{nr} = \sum_{k=1}^{N+1} \left( -\nabla_k^2 - \frac{2Z}{r_k} \right) + \sum_{k>j}^{N+1} \frac{2}{r_{kj}}, \quad (2)$$

$H_{rc}$  consists of one- and two-body relativistic correction terms, and may conveniently be written:

$$\alpha^2 H_{rc} = D + B, \quad (3)$$

where

$$D = \alpha^2 \sum_{k=1}^{N+1} \left\{ -\frac{1}{4} \nabla_k^4 + \frac{Z}{r^3} - \frac{1}{4} \nabla_k^2 \left( \frac{1}{r_k} \right) \right\}, \quad (4)$$

and

$$B = B' + B''. \quad (5)$$

Here  $D$  consists of the one-body terms resulting from the reduction of the Dirac equation to Pauli form,  $B'$  consists of two-body terms which also come from the Dirac equation, whereas  $B''$  is the Breit interaction (Bethe & Salpeter 1957, § 38) expressed in its Pauli form.

The operator  $B'$  can be written as

$$B' = \sum_{k \neq j}^{N+1} \{g_{kj}(\text{d}) + g_{kj}(\text{so})\}, \quad (6)$$

where

$$\left. \begin{aligned} g_{kj}(\text{d}) &= \frac{1}{4} \alpha^2 \nabla_k^2 \left( \frac{1}{r_{kj}} \right), \\ g_{kj}(\text{so}) &= -\alpha^2 \left( \frac{\mathbf{r}_{kj}}{r_{kj}^3} \times \mathbf{p}_k \right) \cdot \mathbf{s}_k. \end{aligned} \right\} \quad (7)$$

The Breit interaction  $B''$  can be written as

$$B'' = \sum_{k \neq j}^{N+1} \{g_{kj}(\text{so}') + g_{kj}(\text{ss}') + g_{kj}(\text{css}') + g_{kj}(\text{oo}')\}, \quad (8)$$

where

$$\left. \begin{aligned} g_{kj}(\text{so}') &= -2\alpha^2 \left( \frac{\mathbf{r}_{kj}}{r_{kj}^3} \times \mathbf{p}_k \right) \cdot \mathbf{s}_j, \\ g_{kj}(\text{ss}') &= \alpha^2 \left( \frac{\mathbf{s}_k \cdot \mathbf{s}_j}{r_{kj}^3} - 3 \frac{(\mathbf{s}_k \cdot \mathbf{r}_{kj})(\mathbf{s}_j \cdot \mathbf{r}_{kj})}{r_{kj}^5} \right), \\ g_{kj}(\text{css}') &= -\frac{8\pi\alpha^2}{3} \mathbf{s}_k \cdot \mathbf{s}_j \delta^3(\mathbf{r}_{kj}), \\ g_{kj}(\text{oo}') &= -\frac{\alpha^2}{2r_{kj}} \left( \mathbf{p}_k \cdot \mathbf{p}_j + \frac{\mathbf{r}_{kj} \cdot (\mathbf{r}_{kj} \cdot \mathbf{p}_j) \mathbf{p}_k}{r_{kj}^3} \right). \end{aligned} \right\} \quad (9)$$

In equations (2)–(9) Rydbergs are used for energies and Bohr radii for  $r_j$  and  $r_{kj}$ .

The physical significance of the operators  $g_{kj}$  have been discussed extensively elsewhere (see, for example, Bethe & Salpeter 1957). Ermolaev & Jones (1973) have pointed out that the matrix of  $H_{re}$  should be evaluated by using perturbation theory† in which the zero order functions are exact non-relativistic functions. In practice, one must use the best approximate non-relativistic wavefunctions available.

### 3. FORMULATION OF THE COLLISION PROBLEM

#### 3.1. Expansion of the wavefunction

We consider an  $N$ -electron ion with nuclear charge  $Z$  and ionic charge  $z = Z - N$ . The ion Hamiltonian is  $H_I = H_I^{\text{nr}} + \alpha^2 H_{re}$ , and we formally assume that we have ion eigenfunctions such that

$$H_I \chi_i = E_i \chi_i. \quad (10)$$

If  $E_i$  is the exact relativistic energy to order  $\alpha^2 \text{Ry}$  then  $\chi_i$  will be the exact non-relativistic wavefunction (Ermolaev & Jones 1973). In this section we will use a coupling scheme such that the  $\chi_i$

† Strictly, first order perturbation theory, but in practice second order theory is frequently used. This point is discussed further in § 8.3.

are eigenfunctions of the total angular momentum  $\mathbf{J}_i = \mathbf{S}_i + \mathbf{L}_i$  of the ion and we may therefore put

$$\chi_i = \chi(\Gamma_i S_i L_i J_i M_{J_i}). \quad (11)$$

In the collision problem we consider a system with  $(N+1)$  electrons. Let  $\mathbf{x}_p = (\mathbf{r}_p, \boldsymbol{\sigma}_p)$  be the space and spin co-ordinates of electron  $p$ . We put

$$\chi_i(\bar{\mathbf{x}}_p) = \chi_i(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{p-1}, \mathbf{x}_{p+1}, \dots, \mathbf{x}_{N+1}). \quad (12)$$

We introduce orbital functions for the colliding electron,

$$\theta_i(\mathbf{x}) = \mathcal{Y}_{j_i m_i}(\hat{\mathbf{x}}) \frac{1}{r} F_i(r), \quad (13)$$

where

$$\mathcal{Y}_{j_i m_i}(\hat{\mathbf{x}}) = \sum_{\mu m} C_{\mu m}^{\frac{1}{2} l_i j_i} Y_{l_i m_i}(\hat{\mathbf{x}}) \delta(\mu, \sigma). \quad (14)$$

The function  $\delta(\mu, \sigma)$  is a spin function. The function  $\mathcal{Y}$  corresponds to the spin-orbit function  $\chi_{\kappa m}(\theta, \phi)$  defined by Grant (1970).

The  $(N+1)$  electron system is represented in terms of vector-coupled anti-symmetric functions:

$$\begin{aligned} \Theta &= \Theta_i(\Gamma_i S_i L_i J_i l_i j_i J M) \\ &= (N+1)^{-\frac{1}{2}} \sum_{p=1}^{N+1} \sum_{M_{J_i} m_i} (-1)^{p-N+1} C_{M_{J_i} m_i}^{J_i j_i J} \chi(\Gamma_i S_i L_i J_i M_{J_i} | \bar{\mathbf{x}}_p) \theta_i(l_i j_i m_i | \mathbf{x}_p). \end{aligned} \quad (15)$$

The total hamiltonian is  $H_{\text{B.P.}}$  (as defined in equation (1)). Although  $H_{\text{B.P.}}$  does not include interactions of order  $\alpha^m$  with  $m > 2$ , it is convenient to formally consider  $H_{\text{B.P.}}$  as the exact hamiltonian, the eigenvalue equation being

$$H_{\text{B.P.}} \Psi = E \Psi, \quad (16)$$

where  $E$  is the total energy. If we assume (16) is true, then we must impose the following linearization upon  $E$  and  $\Psi$ , setting  $\alpha^2 = \mu$ :

$$\left. \begin{aligned} \Psi(\mu) &= \Psi(0) + \mu \frac{\partial}{\partial \mu} \Psi(\mu) \Big|_{\mu=0}, \\ E(\mu) &= E(0) + \mu \frac{\partial}{\partial \mu} E(\mu) \Big|_{\mu=0}. \end{aligned} \right\} \quad (17)$$

It should be noted that we cannot (as for the target) choose  $\Psi$  to be the exact non-relativistic wavefunction, since it is only possible to do this for a bound state problem (to which the discussions of Ermolaev & Jones (1973) apply). In fact, it will become apparent later that the eigenfunction  $\Psi$  must contain a contribution of order  $\alpha^2$ . We represent  $\Psi$  as an expansion in the functions  $\Theta_i$

$$\Psi = \sum_i \Theta_i \quad (18)$$

### 3.2. Boundary conditions

We require that  $\Psi$  must be bounded everywhere.

#### 3.2.1. Behaviour at the origin

The functions  $F_i(r)$  must be such that

$$\lim_{r \rightarrow 0} \{F_i(r)\} = 0. \quad (19)$$



It will be shown later that by using the treatment of the Breit–Pauli hamiltonian discussed subsequently, the functions  $F_i(r)$  will behave like non-relativistic functions at the origin, i.e.

$$\lim_{r \rightarrow 0} \{r^{-l_i-1} F_i(r)\} = A_i, \quad (20)$$

where  $A_i$  is a constant.

### 3.2.2. Behaviour at large radius $r$

At large  $r$ , the functions  $F_i$  have slightly different asymptotic behaviour from non-relativistic wavefunctions. They satisfy

$$\left\{ \frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2z}{r} \left( 1 + \frac{1}{2} \alpha^2 k_i^2 \right) + k_i^2 \right\} F_i(r) = 0, \quad (21)$$

where

$$k_i^2 = E - E_i + \frac{1}{4} \alpha^2 k_i^2. \quad (22)$$

For open channels, the energy (to order  $\alpha^2 R_y$ ) is positive; that is,  $k_i^2 - \frac{1}{4} \alpha^2 k_i^2 > 0$ . We assume that for open channels, the  $F_i$  take  $R$ -matrix asymptotic form:

$$F_i \underset{r \rightarrow \infty}{\sim} k_i^{-\frac{1}{2}} \{ \sin \xi_i + R_i \cos \xi_i \}, \quad (23)$$

where

$$\xi_i = \zeta_i + \tau_i, \quad (24)$$

in which

$$\zeta_i = k_i r - \frac{1}{2} l_i \pi + \frac{z'}{k_i} \ln(2k_i r) + \arg \Gamma \left( l_i + 1 - \frac{iz'}{k} \right) \quad (25)$$

and

$$z' = z \left( 1 + \frac{1}{2} \alpha^2 k_i^2 \right). \quad (26)$$

The choice of  $\tau_i$  in (24) is essentially arbitrary. The asymptotic form (21) is valid subject to the conditions

$$\frac{1}{4} \alpha^2 k_i^4 \ll k_i^2 \quad \text{that is} \quad k_i^2 \ll 4/\alpha^2 \quad (27)$$

and

$$\alpha^2 [rV(r)]^4 \ll 1, \quad (28)$$

for all  $r$  such that  $p \ll mc$  (Bethe & Salpeter 1957, § 39  $\alpha$ ). Inserting the numerical value of  $\alpha^2$  in (27) we obtain

$$k^2 \ll 75\,000 R_y.$$

### 3.3. Coupling schemes

In order to relate relativistic collision cross-sections (or collision strengths) to the corresponding non-relativistic quantities, it will be necessary to discuss the coupling schemes used for these problems.

#### 3.3.1. $LS$ -coupling

(i)  $LS$  coupling structure problem:  $F_i S_i L_i$  where  $F_i$  denotes a particular linear combination of states denoted by  $C_i \alpha_i S_i L_i$ . The symbol  $C_i$  stands for a particular configuration and  $\alpha_i$  is a degeneracy parameter which is used when more than one term  $S_i L_i$  belongs to the configuration  $C_i$ .

(ii)  $LS$ -coupling collision problem:  $F_i S_i L_i s l S L$ , where  $s, l$  represent the spin and orbital angular momenta respectively of the colliding electron, and  $S L$  refers to the total spin and orbital angular momenta of the whole system.

$LS$ -coupling is generally used for the non-relativistic problem.

#### 3.2.2. Intermediate coupling collision problem $A_i J_i s l j J$

This is almost the same as the representation used in § 3.1;  $A_i$  labels a particular linear combination of states  $|C_i \alpha_i S_i L_i J_i\rangle$ . At this stage we neglect coupling of states with different  $S_i L_i$  due to

fine structure interactions, since such coupling is equivalent to an interaction of order  $\alpha^4 R_y$  and we wish to consider interactions of order  $\alpha^2 R_y$  only. Thus, with this restriction  $A_i = \Gamma_i S_i L_i$ , but the effects of relaxing this restriction will be considered in § 8.

### 3.4. Collision strengths

We write down expressions for collision strengths in the  $LS$ -coupling and  $J_i j$  coupling representations discussed in § 3.3. The collision strengths in  $LS$ -coupling are given by

$$\Omega(\Gamma_i S_i L_i, \Gamma'_i S'_i L'_i) = \frac{1}{2} \sum_{SL} (2S+1)(2L+1) |T(\Gamma_i S_i L_i l SL; \Gamma'_i S'_i L'_i l' SL)|^2, \quad (29)$$

where the transition matrix  $T$  is given by:

$$T = 2iR(I - iR)^{-1}, \quad (30)$$

where  $I$  is the unit matrix. In  $J_i j$  coupling (§ 3.3.2)  $\Omega$  is defined to be:

$$\Omega(\Gamma_i S_i L_i J_i, \Gamma'_i S'_i L'_i J'_i) = \frac{1}{2} \sum_J (2J+1) \sum_{jj'} |T(\Gamma_i S_i L_i J_i l j J; \Gamma'_i S'_i L'_i J'_i l' j' J)|^2 \quad (31)$$

and the collision cross-section is expressed in terms of the collision strength thus:

$$Q(i, i') = \frac{1}{g_i k_i^2} \Omega(i, i') \pi a_0^2, \quad (32)$$

where  $g_i$  is the statistical weight of the initial level,  $k_i^2$  is the energy in Rydbergs of the incident electron and  $a_0$  is the Bohr radius.

## 4. THE VARIATIONAL PRINCIPLE

### 4.1. Derivation

Carse & Walker (1973) have discussed the application of the variational principle to the electron atom scattering problem in terms of the Dirac equation. Their derivation does not take into account the Breit or Møller interactions. We now formulate the variational principle within the Breit–Pauli approximation, restricting the discussion in this section to potential scattering, which illustrates most of the important features.

Consider the integral

$$I = \int \psi^\dagger (H - E) \psi \, d\tau, \quad (33)$$

in which  $\psi$  is a function of the form  $\theta$  (equation (13)) subject to the boundary conditions (20) and (23). The behaviour of the colliding particle is described by the hamiltonian  $H_{sp}$

$$H_{sp} = -\nabla^2 + V(r) + \alpha^2 \left[ \frac{1}{r} \frac{dV}{dr} \mathbf{l} \cdot \mathbf{s} - \frac{1}{4} \nabla^4 - \frac{1}{4} \nabla^2 V(r) \right], \quad (34)$$

$$H_{sp} \theta = E \theta = [k^2 - \frac{1}{4} \alpha^2 k^4] \theta, \quad (35)$$

$$V(r) = Z(r)/r \quad (36)$$

and

$$\lim_{r \rightarrow \infty} V(r) = z/r, \quad (37)$$

where  $H_{sp}$  is the Breit–Pauli hamiltonian  $H_{B,P}$ , rewritten for the potential scattering problem. Consider variations  $\delta I$  in  $I$  due to variations  $\delta \theta$  about the exact wavefunction  $\theta$ . We assume

$$\delta \theta = \mathcal{Y}_{jm}(\hat{\mathbf{x}}) (1/r) \delta F(r). \quad (38)$$



We consider a trial function  $\theta^t$  containing a radial function  $F^t$  with asymptotic form:

$$F^t \sim k^{-\frac{1}{2}}\{\sin(\xi) + \cos(\xi) R^t\} \quad (39)$$

and satisfying (19) at the origin. It follows that

$$\delta F(r) \underset{r \rightarrow 0}{\sim} 0, \quad (40)$$

$$\delta F(r) \underset{r \rightarrow \infty}{\sim} \delta R \cos \xi. \quad (41)$$

Put  $\theta^t = \theta + \delta\theta, \quad R^t = R + \delta R.$

Define  $\langle \theta | H - E | \theta \rangle^t = \langle \theta^t | H - E | \theta^t \rangle$

and consider  $\delta I = \langle \theta | H - E | \theta \rangle^t - \langle \theta | H - E | \theta \rangle. \quad (42)$

We now insert (34), (13) and (38) into (42), but before doing this we note that the matrix elements of  $f(\text{mass}) = -\frac{1}{4}\alpha^2 \nabla^4$  are taken in the following way:

$$\langle \theta | -\frac{1}{4}\alpha^2 \nabla^4 | \theta' \rangle = -\frac{1}{4}\alpha^2 \langle \nabla^2 \theta | \nabla^2 \theta' \rangle. \quad (43)$$

This is the standard method of evaluating these elements; it has been discussed by Lieber (1972). The derivation now proceeds in a similar way to the non-relativistic case. We obtain:

$$\delta I = \langle \delta\theta | H | \theta \rangle + \langle \theta | H | \delta\theta \rangle + \left[ F \frac{d}{dr} (\delta F) - \delta F \frac{dF}{dr} \right]_{r=\infty} + O(\delta\theta^2), \quad (44)$$

where the surface term results from the use of Green's theorem. Substituting  $F$  and  $\delta F$  from (39) and (41) into (44) and making use of the fact that  $\theta$  satisfies (34) we obtain

$$\delta(I - R) = 0$$

to first order in  $\delta F$ , for all variations  $\delta F$  satisfying (40) and (41). Hence:

$$R^K = R^t - \langle \theta | H - E | \theta \rangle^t, \quad (45)$$

where  $R^K$  is the Kohn-corrected  $R$ -matrix, which differs from the exact  $R$ -matrix  $R$  by terms of order  $(\delta\theta)^2$  (or  $\delta F^2$ ). As in the usual non-relativistic derivation, the surface terms in (44) come from the kinetic energy term in the non-relativistic hamiltonian. The relativistic operators do not alter the form of the variational principle: the mass-variation term does not give a surface term because of (43), whereas the other relativistic terms behave like short range potentials.

#### 4.2. Permissible trial functions

The additional terms in the hamiltonian may make the possible trial function  $F^t$  differ from the corresponding non-relativistic trial function. We consider the equation satisfied by  $\theta$  at large  $r$ . It follows from equation (37) that

$$\left. \begin{aligned} \frac{1}{r} \frac{dV}{dr} \mathbf{l} \cdot \mathbf{s} &\underset{r \rightarrow \infty}{\sim} \frac{1}{r^3}, \\ \nabla^2 V(r) &\underset{r \rightarrow \infty}{\sim} 0. \end{aligned} \right\} \quad (46)$$

These terms can therefore be neglected at sufficiently large  $r$ . Turning now to the asymptotic behaviour of  $f(\text{mass})$ , it is convenient to write equation (35) in integral form. Multiplying equation (35) from the left by  $\theta$  and integrating we obtain, after slight rearrangement,

$$\int \theta [-\nabla^2 + 2V(r) - k^2] \theta \, d\tau = \frac{1}{4}\alpha^2 \int [(\nabla^2 \theta)^2 - k^4 \theta^2] \, d\tau. \quad (47)$$

Provided the conditions (27) and (28) are satisfied, the right-hand side of (47) will be small (except near the origin), and the solution  $\theta^{(1)}$  of the equation

$$\int \theta^{(1)}[-\nabla^2 + 2V(r) - k^2] \theta^{(1)} d\tau = 0 \quad (48)$$

will be a good approximation to  $\theta$ . To obtain a better solution to (47), we substitute  $\theta^{(1)}$  into the right-hand side of (47), which leads to the equation:

$$\int \theta[-\nabla^2 + 2V(r) - k^2] \theta d\tau = \frac{1}{4}\alpha^2 \int \theta^{(1)}[4V(r)k^2 - 4V(r)^2] \theta^{(1)} d\tau. \quad (49)$$

Putting  $\theta^{(1)}$  equal to  $\theta$  on the right-hand side we get:

$$\int \theta[-\nabla^2 + 2V(r)(1 + \frac{1}{2}\alpha^2 k^2) + V(r)^2 - k^2] \theta d\tau = 0. \quad (50)$$

Hence using equation (13) we obtain the radial equation

$$\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2V(r)(1 + \frac{1}{2}\alpha^2 k^2) + \alpha^2 V(r)^2 - k^2 \right] F = 0. \quad (51)$$

The solutions of this equation will not have  $r^{l+1}$  behaviour at the origin (equation (20)), owing to presence of the short range  $V(r)^2$  term. We neglect this term, and choose our trial functions to be solutions of the equation:

$$\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2V(r)(1 + \frac{1}{2}\alpha^2 k^2) - k^2 \right] F = 0. \quad (52)$$

Equation (52) becomes equation (21) in the region of large  $r$ .

We note that (52) may also be derived from the second order form of the Dirac equation, which has been given by Browne & Bauer (1966):

$$\frac{d^2 \mathcal{G}_\kappa}{dr^2} + \left[ \frac{1+\gamma}{2} k^2 + 2V(r) - \frac{l(l+1)}{r^2} + \alpha^2 \left\{ V(r)^2 - \frac{\kappa}{r} \frac{V'(r)}{\gamma + 1 + \alpha^2 V(r)} + \frac{1}{2} \frac{V''(r)}{\gamma + 1 + \alpha^2 V(r)} - \frac{3}{4} \frac{\alpha^2 V(r)^2}{[\gamma + 1 + \alpha^2 V(r)]^2} \right\} \right] \mathcal{G}_\kappa = 0, \quad (53)$$

where  $\gamma = (1 - \alpha^2 k^2)^{-\frac{1}{2}}$  and  $V(r)$  is the same as in equations (34)–(37). The number  $\kappa$  is related to the orbital and total momenta  $l$  and  $j$ , according to  $\kappa = -(j + \frac{1}{2})a$ , where  $a = \pm 1$  when  $l = j \mp \frac{1}{2}$  (see, for example, Grant 1970). If conditions (27) and (28) are satisfied then (53) reduces to:

$$\frac{d^2 \mathcal{G}_\kappa}{dr^2} + \left[ k^2 + \frac{1}{4}\alpha^2 k^4 + 2V(r)(1 + \frac{1}{2}\alpha^2 k^2) - \frac{l(l+1)}{r^2} + \alpha^2 W \right] \mathcal{G}_\kappa = 0, \quad (54)$$

where  $\alpha^2 W$  stands for the last term on the l.h.s. of equation (53). The correction to  $V(r)$  in (54) is the same as in (52). We note that (54) contains a term  $\frac{1}{4}\alpha^2 k^4$  which does not appear in (52): the reason for this lies in our choice of energy  $E$  in equation (35). The term  $\alpha^2 W$ , which includes spin-dependent effects, is generally small, but becomes significant near the origin. It is not identical with  $f(\text{so}) + f(\text{d})$ . Thus in their normal forms,  $f(\text{so})$  and  $f(\text{d})$  should not be included in the equation for the trial functions. Norcross (1973) has calculated trial functions in a potential which included a spin-orbit term, but he included an additional correction term in the region of the origin.†

† It should also be noted that if  $f(\text{so})$  is included in equation satisfied by the trial function, one of the principal advantages of the Breit–Pauli method is lost, namely the use of the  $J_i j$  coupling of §3.3.1, rather than  $jj$  coupling. Most target systems (even quite heavy atoms) have level structures which are described more closely by  $LS$ -coupling than by  $jj$  coupling.

4.3. *Extension to more than one particle*

The theory developed in §4.2 may be extended to more than one particle or more than one channel in a way which closely parallels the non-relativistic treatment. Let  $\Psi$  be a matrix with components  $\Psi_i$  which are solutions of (16). Let the radial functions  $F$  in  $\Psi$  have  $R$ -matrix asymptotic form. We note that both  $F$  and  $\Psi$  are both matrices because there are in general  $N_0$  linearly independent solutions for each of the  $N_0$  open channels; thus  $F_{i'}$  denotes the  $i'$ th solution in the channel labelled  $i$ . Variations in the matrix

$$\langle \Psi | H - E | \Psi \rangle$$

are considered and the proof proceeds in a similar way to that for the static potential. The Kohn corrected  $R$ -matrix is defined by the following generalization of equation (45):

$$R^K = R^t - \langle \Psi | H - E | \Psi \rangle, \quad (55)$$

where in the most general case  $H = H_{B.P.}$ . A difficulty occurs in this generalization owing to the presence of the term:

$$G(\text{oo}') = \sum_{k>j} \{g_{kj}(\text{oo}') + g_{jk}(\text{oo}')\} \quad (56)$$

in  $H$ , where  $H = H_{B.P.}$ . There is a possibility that this interaction may give rise to monopole ( $1/r$ ) terms which could lead to convergence difficulties. This point must be investigated in more detail, since it may affect the equation satisfied by the trial functions. A full expression for the matrix elements of the orbit-orbit interaction in an uncoupled representation is given in §5.2.2. It can be seen from equation (93)† and equation (B 1) of appendix B that the matrix elements

$$\langle n_\gamma l_\gamma m_\mu, k_i l_i m_i \mu_i | g_{12}(\text{oo}') + g_{21}(\text{oo}') | n_{\gamma'} l_{\gamma'} m' \mu', k_{i'} l_{i'} m_{i'} \mu_{i'} \rangle$$

contain a term

$$-\delta(\mu, \mu') \delta(\mu_i, \mu_{i'}) \delta(m + m_i, m' + m_{i'}) \sum_{\lambda=0}^{\infty} (-1)^{m-m_{i'}} c_\lambda(l_\gamma m, l_{\gamma'} m') \\ \times c_\lambda(l_i m_i, l_{i'} m_{i'}) \lambda(\lambda+1) [T^{\lambda+1}(\gamma i, \gamma' i') - T^{\lambda-1}(\gamma i, \gamma' i')], \quad (57)$$

where

$$T^\lambda(\gamma i, \gamma' i') = \frac{\alpha^2}{2\lambda+1} \int_0^\infty \int_0^\infty r_1 dr_1 r_2 dr_2 P_\gamma(r_1) F_i(r_2) \frac{r_1^\lambda}{r_1^{\lambda+1}} \frac{\partial}{\partial r_1} \left( \frac{P_{\gamma'}(r_1)}{r_1} \right) \frac{\partial}{\partial r_2} \left( \frac{F_{i'}(r_2)}{r_2} \right). \quad (58)$$

The functions  $P_\gamma$  and  $P_{\gamma'}$  are bound radial functions, and  $F_i(r_2)$ ,  $F_{i'}(r_2)$  are radial functions for the colliding electron. The integral  $T^\lambda(\gamma i, \gamma' i')$  defined by (58) is a direct integral, but clearly exchange integrals of type  $T^\lambda(i\gamma, \gamma' i')$  will occur in the matrix elements  $\langle \Psi | H - E | \Psi \rangle$  in (55). It is clear from an inspection of (57) that integrals of type  $T^0(i\gamma, i' \gamma')$  can occur when  $|l_\gamma - l_{\gamma'}| = 1$ .

Integrals of  $T^0(i\gamma, i' \gamma')$  contain terms such as:

$$\int_0^\infty P_\gamma(r_1) \frac{\partial P_{\gamma'}(r_1)}{\partial r_1} dr_1 \int_{r_1}^\infty F_i(r_2) \frac{\partial F_{i'}(r_2)}{\partial r_2} \frac{1}{r_2} dr_2.$$

We note that (i) if  $F_i(r_2)$  and  $F_{i'}(r_2)$  correspond to the same energy (i.e.  $k_i^2 = k_{i'}^2$ ) the second integral in the above product will be divergent; (ii) if  $F_i(r_2)$  and  $F_{i'}(r_2)$  are calculated at different energies, then the integral will be conditionally convergent. Suppose that we restrict ourselves to electron-hydrogen scattering for the moment. Then for elastic transitions we have  $|l_\gamma - l_{\gamma'}| = 0$  and the lowest order  $T^\lambda$  integral which can occur is  $T^1$ , which leads to dipole ( $1/r^2$ ) terms in the free-free integral. This presents no convergence problems. If  $|l_\gamma - l_{\gamma'}| = 1$ , the target state has changed,

† See §5.2.2, which deals with the orbit-orbit interaction in more detail.

and we are considering inelastic transitions (e.g. 1s–2p). The free–free integral will then be conditionally convergent. If we consider transitions such as 2s–2p which are degenerate non-relativistically then we can force convergence of the long-range integral by calculating  $F_i$  at energy  $k^2$  and  $F_{i'}$  at energy  $k^2 + \Delta E$ , where  $\Delta E$  is the energy difference due to spin–orbit coupling and quantum electrodynamic corrections (Burgess, Hummer & Tully 1970, § 2.7). Evaluation of these conditionally convergent integrals has been considered in detail by Peach (1965). The above arguments are easily extended to complex atoms.

We have thus shown that the orbit–orbit interaction gives no monopole ( $1/r$ ) terms in elastic channels. However, matrix elements corresponding to inelastic channels may contain such monopole integrals, but these are conditionally convergent and may be evaluated by known techniques. Thus, *the equations satisfied by the trial function do not need to contain any terms from the orbit–orbit interaction.*

As one would expect, similar  $1/r$  terms can occur in inelastic channels when considering the Breit interaction in a basis of four-component Dirac wavefunctions. The monopole terms come from those parts of the matrix elements of the Breit Interaction connecting two large components and two small components (D. W. Walker 1973, private communication).

The following important points should be noted:

(i) As in the corresponding non-relativistic case, the variational procedure assumes that the exact set of target states satisfying (10) is known. In practice approximate target states only will be known, which will be required to satisfy

$$(\chi_i | \chi_{i'}) = \delta_{ii'} \quad \text{and} \quad (\chi_i | H | \chi_{i'}) = E_i \delta_{ii'} \quad (59)$$

to order  $\alpha^2 R y$  in  $E_i$ , the  $\chi_i$  being non-relativistic functions. With an infinite set of states, (59) is equivalent to (10), but in practice it is only possible to use a finite set of target states. The inexactness of the target states will result in first order errors in  $R^K$ , in exact analogy with the non-relativistic case. In §§ 5, 6 and 7 we will retain the restriction of solving (59) to order  $\alpha^2 R y$  in  $E_i$ : this means that the relativistic terms of  $H_{B.P.}$  are only treated in first order of perturbation theory: in this case, solution of (59) corresponds to diagonalization of the non-relativistic part of  $H$ , and then the diagonal elements of the relativistic operators are calculated with these functions. The effect of allowing  $E_i$  to contain terms in order  $\alpha^4 R y$  and higher (i.e. intermediate coupling) will be considered in § 8.

(ii) The trial functions differ slightly from those used in the non-relativistic case (see, for example, Eissner & Seaton 1972). In the asymptotic region, the functions  $F_i$  must satisfy equation (21) rather than Eissner & Seaton's equation (2.9). If distorted wave (d.w.) trial functions are used, then the functions should satisfy equations of the form (52), with  $V$  a suitable central potential. If the coupled integro-differential equations (i.d.) method is used, then the i.d. equations should be modified in a similar manner, replacing the one-body operators  $h_i$  of Eissner & Seaton (1972),

$$h_i = -\frac{d^2}{dr^2} + \frac{l_i(l_i + 1)}{r^2} - \frac{2Z}{r}, \quad (60)$$

by operators  $h'_i$

$$h'_i = -\frac{d^2}{dr^2} + \frac{l_i(l_i + 1)}{r^2} - \frac{2Z}{r} \left( 1 + \frac{\alpha^2 k^2}{2} \right) \quad (61)$$

in the coupled equations. The d.w. and i.d. approximations are discussed in greater detail by Eissner & Seaton.

In concluding this section, several points should be stressed. Firstly, we have taken great care to choose the appropriate energy (equation (22)) and the correct asymptotic forms for the colliding electron wavefunctions. Neglect to do this will result in divergent terms which will come from the mass-variation correction. If the mass-variation term is omitted from the hamiltonian, then we will be able to use a non-relativistic energy and non-relativistic wavefunctions for the colliding electron. We have demonstrated that the orbit-orbit interaction does not modify the asymptotic form of the trial function.

It is an unsatisfactory feature of the Breit–Pauli method for continuum states that  $F^t$  cannot be a pure non-relativistic function if the hamiltonian  $H$  contains the mass-variation term: this will lead to errors.† However, such errors will probably be small compared with errors introduced due to inaccuracies in the target functions  $\chi_i$ , or as a result of deficiencies of the expansion (18) for  $\Psi$ . We also note that in practice we probably would not include the whole of  $H_{B.P.}$  in the variational procedure. For example, if we were studying electron spin-polarization effects, then we could include spin-orbit interaction between the colliding electron and the target, omitting  $f(\text{mass})$  and other non-fine structure terms, which have no bearing on electron spin-polarization.

##### 5. THE EFFECT OF RELATIVISTIC INTERACTIONS UPON COLLISION STRENGTHS

It can be shown (see appendix A) that the reactance, scattering and transition matrices  $\mathbf{R}$ ,  $\mathbf{S}$  and  $\mathbf{T}$  may be transformed from  $LS$ -coupling into  $J_i j$  coupling by using the algebraic transformation:

$$\begin{aligned} |\Gamma_i S_i L_i J_i s l j; JM\rangle &= [J_i j]^{\frac{1}{2}} \sum_{\substack{SL \\ M_S M_L}} [S, L]^{\frac{1}{2}} (-1)^{2(S_i+J_i+J)} \\ &\times \begin{Bmatrix} S_i & L_i & J_i \\ s & l & j \\ S & L & J \end{Bmatrix} C_{M_S M_L M_J}^{S L J} |\Gamma_i S_i L_i s l j S L M_S M_L\rangle, \end{aligned} \quad (62)$$

where we use the convention that  $[x, y, \dots] \equiv [(2x+1)(2y+1)\dots]$ . We will use the following notation in this section:  $\mathbf{R}_{nr}$  is a  $R$ -matrix calculated with the use of only the non-relativistic hamiltonian  $H_{nr}$  (equation (2));  $\mathbf{R}_{rel}$  is a  $R$ -matrix which contains relativistic corrections and the suffices  $nr$  and  $rel$  refer to ‘non-relativistic’ and ‘relativistic’ respectively. Rewriting (55) with  $H = H_{B.P.}$  and making use of (1) we obtain

$$\mathbf{R}_{rel}^K = \mathbf{R}_{nr}^K - \alpha^2 \langle \Psi | H_{rc} | \Psi \rangle. \quad (63)$$

The matrix  $\mathbf{R}_{nr}$  will be diagonal in  $SLM_S M_L$  and will be independent of  $M_S M_L$  (cf. Condon & Shortley 1951, p. 49). On the other hand the correction  $\alpha^2 \langle \Psi | H_{rc} | \Psi \rangle$  will not be diagonal in  $SLM_S M_L$ . Writing the  $R$ -matrix in the  $LS$ -coupling representation:

$$\begin{aligned} &R_{rel}(\Gamma_i S_i L_i s l S L M_S M_L; \Gamma'_i S'_i L'_i s' l' S' L' M'_S M'_L) \\ &= R_{nr}(\Gamma_i S_i L_i s l S L; \Gamma'_i S'_i L'_i s' l' S L) \delta(S L M_S M_L; S' L' M'_S M'_L) \\ &\quad - \alpha^2 \langle \Psi(\Gamma_i S_i L_i s l S L M_S M_L) | H_{rc} | \Psi(\Gamma'_i S'_i L'_i s' l' S' L' M'_S M'_L) \rangle, \end{aligned} \quad (64)$$

where here and subsequently we omit the superscript  $K$ . We now consider the effect of different types of terms in  $H_{rc}$ .

† Bethe & Salpeter (1957, § 39) give reasons for using non-relativistic wavefunctions with the Breit–Pauli hamiltonian.



5.1. *Effect of fine structure interactions*

The fine structure (f.s.) interactions consist of the spin-orbit interaction  $f_k(\text{so})$ , the mutual spin-orbit interaction  $g_{kj}(\text{so})$ , the spin-other-orbit interaction  $g_{kj}(\text{so}')$  and the spin-spin interaction  $g_{kj}(\text{ss}')$ . We will not consider the spin-spin contact interaction  $g_{kj}(\text{css}')$  as a fine structure interaction since it is a scalar force (de-Shalit & Talmi 1963, p. 174), and thus commutes with both  $\mathbf{S}$  and  $\mathbf{L}$ . The interactions  $f_k(\text{so})$ ,  $g_{kj}(\text{so})$  and  $g_{kj}(\text{so}')$  are vector interactions (de-Shalit & Talmi (1963), p. 204, give the most general form of a vector interaction, of which spin-orbit type interactions are special cases). In the case of the spin-spin interaction, Innes (1953) has shown that it may be written thus:

$$g_{kj}(\text{ss}') = -6 \sum_{\mu} (-1)^{\mu} \{S_k S_j\}_{\mu}^2 \{\mathbf{R}\mathbf{R}\}_{-\mu}^2, \quad (65)$$

where  $\{\}_{\mu}^2$  stands for the component  $\mu$  of a spherical tensor of degree 2. The tensor  $\{\mathbf{R}\mathbf{R}\}_{-\mu}^2$  will not be defined here (Jones (1971 *a*) has defined  $\mathbf{R}$  in a form consistent with the units used in this paper). The spin-spin interaction is thus a tensor interaction (de-Shalit & Talmi 1963, p. 144). The f.s. interactions can thus all be expressed as a product of tensors of degree  $k$ :

$$\alpha^2 T_0(k) = \alpha^2 \mathbf{R}_k \cdot \mathbf{S}_k, \quad (66)$$

where  $k = \begin{cases} 1 & \text{for spin-orbit, mutual spin-orbit and spin-other-orbit interactions,} \\ 2 & \text{for the spin-spin interaction,} \end{cases}$

$\mathbf{R}_k$  is an orbital angular momentum operator and  $\mathbf{S}_k$  is a spin angular momentum operator.

Clearly, there can be no two-particle f.s. interactions with  $k > 2$ , since one cannot construct a tensor of higher degree than two from the spin operators of two particles. Thus any discussion of the scattering problem based upon the interaction  $T_0(k)$  will apply to any fine structure interaction obtained from any order of quantum electrodynamics. We therefore consider an interaction of type  $T_0(k)$ , putting  $H_{\text{rc}} = T_0(k)$  in (64). Using the transformation (62) we obtain

$$\begin{aligned} & R_{\text{rel}}(\Gamma_i S_i L_i J_i s l j J M; \Gamma'_i S'_i L'_i J'_i s' l' j' J M) \\ &= [J_i, J'_i, j, j']^{\frac{1}{2}} \sum_{SL, S'L'} [S, S', L, L']^{\frac{1}{2}} \begin{Bmatrix} S_i & L_i & J_i \\ s & l & j \\ S & L & J \end{Bmatrix} [R_{\text{nr}}(\Gamma_i S_i L_i s l S L; \Gamma'_i S'_i L'_i s' l' S L) \\ &\quad \times \delta(S L M_s M_L; S' L' M'_s M'_L) - \alpha^2 \sum_{\substack{M_S M_L \\ M'_S M'_L}} C_{M_S M_L}^S C_{M'_S M'_L}^{S'} C_{M_S M_L}^J C_{M'_S M'_L}^{J'} \\ &\quad \times \langle \Psi(\Gamma_i S_i L_i s l S L M_s M_L) | \mathbf{R}_k \cdot \mathbf{S}_k | \Psi(\Gamma'_i S'_i L'_i s' l' S' L' M'_s M'_L) \rangle \begin{Bmatrix} S'_i & L'_i & J'_i \\ s' & l' & j' \\ S' & L' & J \end{Bmatrix}, \quad (67) \end{aligned}$$

where we have eliminated the summation over azimuthal quantum numbers in the first part of this expression by means of the orthogonality property of the Clebsch-Gordon coefficients. We recognize that the second part of (67) contains a quantity:

$$-\alpha^2 \langle \Psi(\Gamma_i S_i L_i s l S L J M) | \mathbf{R}_k \cdot \mathbf{S}_k | \Psi(\Gamma'_i S'_i L'_i s' l' S' L' J M) \rangle,$$

which may be written immediately as

$$-\alpha^2 (-1)^{S+L'+J} \begin{Bmatrix} S & S' & k \\ L' & L & J \end{Bmatrix} [S, L]^{\frac{1}{2}} \langle \Gamma_i S_i s S | \mathbf{S}_k | \Gamma'_i S'_i s' S' \rangle \langle \Gamma_i L_i l L | \mathbf{R}_k | \Gamma'_i L'_i l' L' \rangle$$



(Brink & Satchler 1968, appendix VI). Hence equation (67) now becomes

$$\begin{aligned}
 & R_{\text{rel}}(\Gamma_i S_i L_i J_i s l j J M; \Gamma'_i S'_i L'_i J'_i s l' j' J M) \\
 &= [J_i, J'_i, j, j']^{\frac{1}{2}} \sum_{SL, S'L'} \left[ [S, L, S', L']^{\frac{1}{2}} \begin{Bmatrix} S_i & L_i & J_i \\ s & l & j \\ S & L & J \end{Bmatrix} [R_{\text{nr}}(\Gamma_i S_i L_i s l S L; \Gamma'_i S'_i L'_i s l S L) \right. \\
 &\quad \times \delta(S L M_S M_L; S' L' M'_S M'_L) - \alpha^2 (-1)^{S+L+J} [S, L]^{\frac{1}{2}} \begin{Bmatrix} S & S' & k \\ L' & L & J \end{Bmatrix} \\
 &\quad \left. \times \text{RME}(\Gamma_i S_i L_i s l S L; \Gamma'_i S'_i L'_i l' S' L') \right] \begin{Bmatrix} S'_i & L'_i & J'_i \\ s' & l' & j' \\ S' & L' & J \end{Bmatrix}, \quad (68)
 \end{aligned}$$

where†

$$\begin{aligned}
 \text{RME}(\Gamma_i S_i L_i s l S L, \Gamma'_i S'_i L'_i l' S' L') &= \langle \Gamma_i S_i s S \| \mathbf{S}_k \| \Gamma'_i S'_i s S' \rangle \langle \Gamma'_i L'_i l L \| \mathbf{R}_k \| \Gamma'_i L'_i l' L' \rangle \\
 &= \langle \Gamma_i S_i L_i s l S L \| \mathbf{R}_k \cdot \mathbf{S}_k \| \Gamma'_i S'_i L'_i l' S' L' \rangle. \quad (69)
 \end{aligned}$$

We will first consider the case when all  $R_{ij}$  are small, when we can approximate:

$$\mathbf{T} = -2i\mathbf{R}. \quad (70)$$

It will be shown later that the results of this section will be valid even when this restriction is relaxed. With (70) we have:

$$\Omega(\Gamma_i S_i L_i J_i, \Gamma'_i S'_i L'_i J'_i) = \frac{1}{2} \sum_{wjj'} 4(2J+1) |R(\Gamma_i S_i L_i l j J; \Gamma'_i S'_i L'_i l' j' J)|^2 \quad (71)$$

and substituting (68) in (71) we obtain:

$$\begin{aligned}
 & \Omega^{\text{rel}}(\Gamma_i S_i L_i J_i; \Gamma'_i S'_i L'_i J'_i) \\
 &= \frac{1}{2} \sum_{wjj'} 4(2J+1) |R_{\text{nr}}(\Gamma_i S_i L_i J_i s l j J; \Gamma'_i S'_i L'_i J'_i s l' j' J)|^2 \\
 &\quad - \frac{1}{2} \alpha^2 \sum_{jj'w} [J, J_i, J'_i, j, j'] \sum_{\substack{SLS'L' \\ S'L'S''L''}} 4[S, L, S', L', S'', L'', S''', L''']^{\frac{1}{2}} \\
 &\quad \times \begin{Bmatrix} S_i & L_i & J_i \\ \frac{1}{2} & l & j \\ S & L & J \end{Bmatrix} \begin{Bmatrix} S'_i & L'_i & J'_i \\ \frac{1}{2} & l' & j' \\ S' & L' & J \end{Bmatrix} \begin{Bmatrix} S_i & L_i & J_i \\ \frac{1}{2} & l & j \\ S'' & L'' & J \end{Bmatrix} \begin{Bmatrix} S'_i & L'_i & J'_i \\ \frac{1}{2} & l' & j' \\ S''' & L''' & J \end{Bmatrix} \\
 &\quad \times \left\{ \delta(S L M_S M_L, S' L' M'_S M'_L) [S'', L'']^{\frac{1}{2}} R_{\text{nr}}(\Gamma_i S_i L_i s l S L; \Gamma'_i S'_i L'_i s l' S' L) \right. \\
 &\quad \times \text{RME}(\beta S'' L'', \beta' S''' L''') (-1)^{S''+L''+J} \begin{Bmatrix} S'' & S''' & k \\ L'' & L''' & J \end{Bmatrix} \\
 &\quad + \delta(S'' L'' M''_S M''_L, S''' L''' M'''_S M'''_L) [S, L]^{\frac{1}{2}} R_{\text{nr}}(\Gamma_i S_i L_i s l S'' L''; \Gamma'_i S'_i L'_i s l' S''' L''') \\
 &\quad \times \text{RME}(\beta S L, \beta' S' L') (-1)^{S+L+J} \begin{Bmatrix} S & S' & k \\ L' & L & J \end{Bmatrix} \\
 &\quad \left. - \alpha^2 [S, L, S'', L'']^{\frac{1}{2}} \text{RME}(\beta S L; \beta' S' L') \text{RME}(\beta S'' L''; \beta' S''' L''') \right\} \\
 &\quad \times (-1)^{S+S''+L'+L''+2J} \begin{Bmatrix} S & S' & k \\ L' & L & J \end{Bmatrix} \begin{Bmatrix} S'' & S''' & k \\ L'' & L''' & J \end{Bmatrix}, \quad (72)
 \end{aligned}$$

where

$$\beta = \Gamma_i S_i L_i s l \quad \text{and} \quad \beta' = \Gamma'_i S'_i L'_i s l'$$

† We use a quasi-FORTRAN notation for the reduced matrix element RME.

and  $R_{\text{nr}}(\Gamma_i S_i L_i J_i s l j J; \Gamma'_i S'_i L'_i J'_i s' l' j' J)$  is obtained from  $R_{\text{nr}}(\Gamma_i S_i L_i s l S L; \Gamma'_i S'_i L'_i s l S L)$  by means of the usual algebraic transformation of  $LS$ -coupling  $R$ -matrices to  $J_i j$  coupling (equation (A 9) of appendix A).

It can now be seen that (72) has the form:

$$\Omega^{\text{rel}}(\Gamma_i S_i L_i J_i; \Gamma'_i S'_i L'_i J'_i) = \Omega^{\text{nr}}(\Gamma_i S_i L_i J_i; \Gamma'_i S'_i L'_i J'_i) + \alpha^2 C_{\text{rel}}^{(2)}(\Gamma_i S_i L_i J_i; \Gamma'_i S'_i L'_i J'_i) + \alpha^4 C_{\text{rel}}^{(4)}(\Gamma_i S_i L_i J_i; \Gamma'_i S'_i L'_i J'_i), \quad (73)$$

where  $C_{\text{rel}}^{(2)}$  and  $C_{\text{rel}}^{(4)}$  are the coefficients of  $\alpha^2$  and  $\alpha^4$  respectively in equation (72). It would be consistent to neglect the terms in order  $\alpha^4$ , since  $H_{\text{B.P.}}$  contains no terms of higher order than  $\alpha^2 R y$ ; clearly terms in order  $\alpha^4 R y$  in the hamiltonian would contribute to  $C_{\text{rel}}^{(4)}$ . This comment also applied to calculations based upon the Dirac equation, where again the hamiltonian contains no terms of higher order than  $\alpha^2 R y$ . In the Dirac equation formalism it is difficult to separate out the  $\alpha^2$  contribution to the  $R$ -matrix, making it difficult to omit the contribution  $C_{\text{rel}}^{(4)}$ . It would be easier, but still somewhat inconvenient to omit this contribution in a Breit–Pauli calculation. The possible effects of this  $\alpha^4$  contribution will be investigated in § 7.

It is impossible to simplify (72) any further without carrying out summations over  $J_i$  and  $J'_i$  (i.e. over the target levels). If we do this, we can make use of the orthogonality properties of the  $9j$  symbols (Brink & Satchler 1968, appendix III) to obtain:

$$\begin{aligned} \sum_{J_i, J'_i} \Omega^{\text{rel}}(\Gamma_i S_i L_i J_i; \Gamma'_i S'_i L'_i J'_i) &= \Omega^{\text{nr}}(\Gamma_i S_i L_i; \Gamma'_i S'_i L'_i) - \frac{1}{2} \alpha^2 \sum_{SL S' L'} \sum_{jj' W} 4(2J+1) \left\{ 2\delta(S L M_S M_L, S' L' M'_S M'_L) \right. \\ &\quad \times (-1)^{S+L'+J} [S, L]^{\frac{1}{2}} \begin{Bmatrix} S & S' & k \\ L' & L & J \end{Bmatrix} R_{\text{nr}}(\beta S L; \beta' S' L') \text{RME}(\beta S L; \beta' S' L') \\ &\quad \left. - \alpha^2 [S, L] \begin{Bmatrix} S & S' & k \\ L' & L & J \end{Bmatrix}^2 |\text{RME}(\beta S L; \beta' S' L')|^2 \right\}. \end{aligned} \quad (74)$$

The  $6j$  symbols satisfy the sum rule:

$$\sum_g (-1)^{2g} (2g+1) \begin{Bmatrix} a & a & f \\ b & b & g \end{Bmatrix} = \delta_{f0} [a, b]^{\frac{1}{2}}. \quad (75)$$

Using (75) and also the  $6j$ -symbol orthogonality relations, we obtain:

$$\begin{aligned} \sum_{J_i, J'_i} \Omega^{\text{rel}}(\Gamma_i S_i L_i J_i; \Gamma'_i S'_i L'_i J'_i) &= \Omega^{\text{nr}}(\Gamma_i S_i L_i; \Gamma'_i S'_i L'_i) - \frac{1}{2} \alpha^2 \delta(k, 0) \sum_{\substack{jj' W \\ SL}} 8[S, L] R_{\text{nr}}(\beta S L; \beta' S L) \text{RME}(\beta S L; \beta' S L) \\ &\quad + \frac{1}{2} \alpha^4 \sum_{\substack{jj' W \\ SL S' L'}} 4[S, L] \frac{1}{[k]} |\text{RME}(\beta S L; \beta' S' L')|^2. \end{aligned} \quad (76)$$

A similar proof applies when we use a unitarized  $T$ -matrix (30) rather than the non-unitarized  $T$ -matrix (70). The proof is accomplished more elegantly if we define  $T$  in terms of the scattering matrix  $S$ :

$$T = I - S. \quad (77)$$

The wavefunction of the colliding electron must have  $S$ -matrix asymptotic form, in which case the principle still takes the form (55), but with  $S^{\text{K}}$  and  $S^{\text{t}}$  replacing  $R^{\text{K}}$  and  $R^{\text{t}}$  respectively. For inelastic scattering we have

$$|T_{ij}|^2 = |S_i|^2 \quad (i \neq j). \quad (78)$$

Similar arguments to those which lead to (76) give us

$$\begin{aligned} \sum_{J_i, J_i'} \Omega^{\text{rel}}(\Gamma_i S_i L_i J_i; \Gamma_i' S_i' L_i' J_i') \\ = \Omega^{\text{nr}}(\Gamma_i S_i L_i; \Gamma_i' S_i' L_i') - \frac{1}{2} \alpha^2 \delta(k, 0) \sum_{\substack{j j' \\ S L}} 2[S, L] \operatorname{Re}[S_{\text{nr}}^*(\beta S L; \beta' S L) \operatorname{RME}(\beta S L; \beta' S L)] \\ + \frac{1}{4} \alpha^4 \sum_{\substack{j j' \\ S L S' L'}} [S, L] \frac{1}{[k]} |\operatorname{RME}(\beta S L; \beta' S' L')|^2. \end{aligned} \quad (79)$$

If we consider elastic scattering we obtain

$$\begin{aligned} \sum_{J_i, J_i} \Omega^{\text{rel}}(\Gamma_i S_i L_i J_i; \Gamma_i S_i L_i J_i) \\ = \Omega^{\text{nr}}(\Gamma_i S_i L_i; \Gamma_i S_i L_i) - \frac{1}{2} \alpha^2 \delta(k, 0) \sum_{j i S L} 2[S, L] \operatorname{Re}[\operatorname{RME}(\beta S L; \beta S L) \\ + S_{\text{nr}}^*(\beta S L; \beta S L) \operatorname{RME}(\beta S L; \beta S L)] + \frac{1}{4} \alpha^4 \sum_{j i S L} [S, L] \frac{1}{[k]} |\operatorname{RME}(\beta S L; \beta S L)|^2. \end{aligned} \quad (80)$$

We have proved that, to order  $\alpha^2$ , the f.s. interactions of order  $\alpha^2 \text{Ry}$  make no contributions to elastic or inelastic collision strengths which have been summed over the fine structure levels of the initial and final target terms. However, the collision strengths will also contain terms in  $\alpha^4$ , which appear as a consequence of the f.s. interaction of order  $\alpha^2 \text{Ry}$ . These terms do *not* vanish when a sum over the target fine structure is made. The proof will also apply to f.s. interactions of any order  $\alpha^m \text{Ry}$  ( $m > 2$ ). Examples of such higher order f.s. interactions may be found among the quantum electrodynamic corrections of order  $\alpha^3 \text{Ry}$  (Ermolaev 1973) and the corrections of order  $\alpha^4 \text{Ry}$  (Daley, Douglas, Hambro & Kroll 1972).

The above theorem will not apply to differential cross-sections and electron-spin polarizations, which will in general contain non-vanishing contributions of order  $\alpha^2$ . The calculations of Burke & Mitchell (1974) do not take account of relativistic effects involving the colliding electron. It follows from the above theorem that their calculations of elastic cross-sections will be correct to order  $\alpha^2$ . However, their results for differential cross-sections and spin-polarizations may be in error due to their omission of spin-orbit interactions of the colliding electron in the field of the target.

As one would expect, the effect of f.s. interactions does not necessarily vanish to order  $\alpha^2$  when one considers collision strengths between fine structure levels. Two effects come in here:

(i) Spin-orbit, spin-spin, etc., interactions of the colliding electron with the target, i.e. phenomena which directly involve the colliding electron.

(ii) Mixing of target terms due to breakdown of  $LS$ -coupling. Saraph (1972) refers to this as 'term-coupling', an expression which we will adopt in this paper. Term-coupling will be discussed in § 8, but it suffices to note here that this type of effect does not vanish when one sums over the target f.s. levels.

### 5.2. Effect of other interactions

The interactions  $f_k(\text{d})$ ,  $f_k(\text{mass})$ ,  $g_{kj}(\text{d})$ ,  $g_{kj}(\text{css}')$  and  $g_{kj}(\text{oo}')$  can all be evaluated in  $LS$ -coupling. The interaction  $f_k(\text{d})$  makes no contribution to *inelastic* collision strengths, since it is a one-body interaction. For a similar reason,  $f_k(\text{mass})$  makes no direct contribution to inelastic collision strengths, but there will be a small indirect contribution, since  $f_k(\text{mass})$  modifies slightly the asymptotic form of the colliding electron wavefunction (see equations (21) and (52)).

Of the remaining two-body interactions we note that  $g_{kj}(\text{d})$  comes directly from reduction of the Dirac equation to Pauli form, whereas  $g_{kj}(\text{css}')$  and  $g_{kj}(\text{oo}')$  both come from the Breit interaction. In order to gain some insight into the relativistic effects on inelastic collision cross-sections, we

consider the effect of including  $g_{kj}(\text{d})$  only in the hamiltonian. We note that this will allow us to compare the predictions of our theory with the calculated results of Walker (1974) since Walker uses the Dirac equation only. He thus effectively includes  $g_{kj}(\text{so})$  and  $g_{kj}(\text{d})$  in his calculations.† However, according to the results of § 5.1, the effects of mutual spin orbit interaction  $g_{kj}(\text{so})$  can be eliminated by summing over the target fine structure, thus leaving  $g_{kj}(\text{d})$  as the only contributor.

With only  $g_{kj}(\text{d})$  (and/or  $g_{kj}(\text{css}')$  and  $g_{kj}(\text{oo}')$ ) included in the hamiltonian, we can solve the whole problem in  $LS$ -coupling, without any need to carry out transformations of the type (62). We will use similar notation to that of Eissner & Seaton (1972).

### 5.2.1. Two-body Darwin term

Firstly we write down the matrix elements of  $g_{kj}(\text{d})$  between uncoupled wavefunctions, each consisting of a product of a bound state wavefunction:

$$\langle n_\gamma l_\gamma \mu m \rangle \equiv \phi(n_\gamma l_\gamma \mu m | \mathbf{x}) = Y_{l_\gamma m}(\hat{\mathbf{r}}) \frac{1}{r} P_{n_\gamma l_\gamma}(r) \delta(\mu, \sigma) \quad (81)$$

with a continuum wavefunction  $\theta_i(\hat{\mathbf{x}})$  of the same form:

$$\langle k_i l_i \mu_i m_i \rangle \equiv \theta_i(l_i \mu_i m_i | \mathbf{x}) = Y_{l_i m_i}(\hat{\mathbf{r}}) \frac{1}{r} F_i(r) \delta(\mu_i, \sigma). \quad (82)$$

The matrix element has been given by Jones (1971 *b*)

$$\begin{aligned} & \langle n_\gamma l_\gamma \mu m, k_i l_i \mu_i m_i | g_{12}(\text{d}) | n'_\gamma l'_\gamma \mu' m', k_i l_i \mu_i m_i \rangle \\ &= -\alpha^2 \delta(\mu, \mu') \delta(\mu_i, \mu'_i) \delta(m + m_i, m' + m'_i) \sum_\lambda (-1)^{m - m'_i} c_\lambda(l_\gamma m, l'_\gamma m') c_\lambda(l_i m_i, l'_i m'_i) \\ & \quad \times [\lambda] X_2(F_i F'_i P_\gamma P'_\gamma), \end{aligned} \quad (83)$$

$$\left. \begin{aligned} \text{where} \quad c_\lambda(lm, l'm') &= \frac{[l, l']^{\frac{1}{2}}}{[\lambda]} C_{000}^{l'l\lambda} C_{-m m' -m}^{l' m' \lambda} \\ \text{and} \quad X_2(F_i F'_i P_\gamma P'_\gamma) &= \int_0^\infty \frac{1}{r^2} F_i(r) F'_i(r) P_\gamma(r) P'_\gamma(r) dr. \end{aligned} \right\} \quad (84)$$

The algebraic coefficient involved in (83) differs by a factor of  $(2\lambda + 1)$  from that involved in the Coulomb interaction. Hence one may take into account the two-body Darwin term by adding to each two-body Coulomb radial integral a correction:

$$-\alpha^2(2\lambda + 1) X_2(F_i F'_i P_\gamma P'_\gamma).$$

We may now write down the matrix element  $\langle \Psi | H - E | \Psi \rangle$  with the help of theory developed elsewhere (see, for example, Eissner & Seaton 1972), where  $\Psi$  now represents the wavefunction of the whole system in  $LS$  coupling. The function  $\Psi$  is defined by (18) with  $\Theta_i$  now defined by:

$$\begin{aligned} \Theta_i &= \Theta(I_i S_i L_i l_i S L M_s M_L) \\ &= (N + 1)^{-\frac{1}{2}} \sum_{p=1}^{N+1} (-1)^{p-N+1} C_{M S_i \frac{1}{2} \mu_i M_S}^{S_i \frac{1}{2} S} C_{M L_i \frac{1}{2} m_i M_L}^{L_i \frac{1}{2} L} \chi_i(I_i S_i L_i | \mathbf{x}_p) \theta_i(l_i \mu_i m_i | \mathbf{x}_p). \end{aligned} \quad (85)$$

† In the calculations of Walker (1974), all three one-body terms  $f_k(\text{mass})$ ,  $f_k(\text{d})$  and  $f_k(\text{so})$  are automatically included in the hamiltonian when calculating the wavefunctions. He expresses his cross-sections in terms of  $R$ -matrix elements whose phase are referred to those of his Coulomb-Dirac trial functions. Thus to first order, Walker subtracts out the effects of  $f_k(\text{mass})$ ,  $f_k(\text{d})$  and  $f_k(\text{so})$ , but in his formulation, they will make second and higher order contributions to  $\langle \Psi | H - E | \Psi \rangle$ .

In general the antisymmetrized target functions  $\chi_i$  are constructed from the bound state orbitals of (81). The matrix element of the hamiltonian is given by:

$$\langle \Psi | H - E | \Psi \rangle = \sum_{ii'} (F_i | (h_i - k_i^2) \delta_{ii'} + W_{ii} | F_i), \quad (86)$$

where  $h_i$  is defined by equation (60)† and

$$\int_0^\infty F_i W_{ii'} F_{i'} dr = 2 \sum_\nu \{ f_{ii'}^{(\nu)} \bar{R}_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) - g_{ii'}^{(\nu)} \bar{R}_\lambda(F_i P_\gamma, P_{\gamma'} F_{i'}) \}, \quad (87)$$

where 
$$\bar{R}_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) = R_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) - \alpha^2(2\lambda + 1) X_2(F_i F_{i'} P_\gamma P_{\gamma'}) \quad (88)$$

with 
$$R_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) = \int_0^\infty F_i y_\lambda(P_\gamma P_{\gamma'} | r) F_{i'} dr. \quad (89)$$

The  $y_\lambda$  function of equation (89) is defined by:

$$y_\lambda(AB|r) = r^{-\lambda-1} \int_0^\infty A(x) B(x) x^\lambda dx + r^\lambda \int_0^\infty A(x) B(x) x^{\lambda-1} dx. \quad (90)$$

The coefficients  $f_{ii'}^{(\nu)}$  and  $g_{ii'}^{(\nu)}$  are algebraic. The index  $\nu$  merely labels the algebraic coefficients  $f_{ii'}$  and  $g_{ii'}$  for a pair of channels  $(i, i')$ , and the sum over  $\nu$  in (87) contains a finite number of terms. The quantities  $\lambda$ ,  $\gamma$  and  $\gamma'$  in (87) depend upon  $i$ ,  $i'$  and  $\nu$ .

We have shown that one may take into account the two-body Darwin term by adding a correction to the radial integrals which appear in the usual set of coupled integro-differential equations obtained in the non-relativistic case. For  $1s-2s$  (or in general  $1s-ns$ ) transitions in electron-hydrogen-like inelastic scattering, the approximation thus obtained will be equivalent to that of Walker (1974). The reason for this is that Walker omits the Breit interaction from his calculations, and thus his Dirac calculations only account for the Darwin two-body and mutual spin-orbit terms. The latter vanishes to order  $\alpha^2$  in the case  $1s-2s$  (this follows from § 5.1), leaving only the two-body Darwin term. For  $1s-2p$  excitations in the same system, the theory described here will give collision strengths  $\Omega(1s-2p)$  which are equivalent to the sum of Walker's results for  $\Omega(1s-2p_{\frac{1}{2}})$  and  $\Omega(1s-2p_{\frac{3}{2}})$ .

### 5.2.2. Spin-spin contact and orbit-orbit terms

It may be shown that the matrix element of  $-(8\pi/3) \mathbf{s}_k \cdot \mathbf{s}_l \delta^3(\mathbf{r}_{kl})$  is equal to that of  $2\pi\delta^3(\mathbf{r}_{kl})$  provided that the wavefunction is antisymmetric with respect to the interchange of the  $k$ th and  $l$ th electrons (de-Shalit & Talmi 1963, p. 218). The wavefunctions  $\Psi$  and  $\Theta_i$  used here are antisymmetric with respect to interchange of any of the  $N+1$  electrons. Hence in our problem we may write

$$g_{kl}(css') = -2g_{kl}(d). \quad (91)$$

The arguments of the previous section now apply, so it follows that we may include the spin-spin contact interaction in our calculations by adding to each two-body Coulomb radial integral a correction:

$$+ 2\alpha^2(2\lambda + 1) X_2(F_i F_{i'} P_\gamma P_{\gamma'}).$$

This corresponds to a result derived by Feneuille (1968) for the atomic structure problem.

If we include both two-body Darwin and spin-spin contact terms in  $H$ , then the matrix elements of  $H - E$  will be given by equations (86), (87), (89) and (90) but with  $\bar{R}_\lambda$  replaced by  $\bar{\bar{R}}_\lambda$

† For convenience we have omitted  $f_k(\text{mass})$ ; at this stage we study the effect of the two-body Darwin term only.



where

$$\begin{aligned} \bar{R}_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) &= R_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) + \alpha^2(2\lambda + 1) X_2(F_i F_{i'} P_\gamma P_{\gamma'}) \\ &= \bar{R}_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) + 2\alpha^2(2\lambda + 1) X_2(F_i F_{i'} P_\gamma P_{\gamma'}). \end{aligned} \quad (92)$$

Thus addition of the spin-spin contact term (which comes from the Breit hamiltonian, not from the Dirac equation, that is,  $B''$  rather than  $B'$  (equation (5)) could have a large effect upon the relativistic corrections. The results of Walker (1974) for quantities such as  $\Omega(1s_{\frac{1}{2}}-2s_{\frac{1}{2}})$  could be substantially altered if the Breit interaction were to be included in the hamiltonian which he used.

Inclusion of the orbit-orbit interaction in  $H$  is more difficult. Once again, we find that part of  $g_{12}(oo')$  may be written in a similar form to the Coulomb interaction, but with a different radial part (Eissner, Jones & Nussbaumer 1974). The matrix elements of  $g_{12}(oo')$  in an uncoupled representation are given by

$$\begin{aligned} &\langle n_\gamma l_\gamma \mu m, k_i l_i \mu_i m_i | g_{12}(oo') + g_{21}(oo') | n_{\gamma'} l_{\gamma'} \mu' m', k_{i'} l_{i'} \mu_{i'} m_{i'} \rangle \\ &= \delta(\mu, \mu') \delta(\mu_i, \mu_{i'}) \delta(m + m_i, m' + m_{i'}) \sum_{\lambda > 0} (-1)^{m-m_i} c_\lambda(l_\gamma m, l_{\gamma'} m') c_\lambda(l_i m_i, l_{i'} m_{i'}) Z_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) \\ &\quad - 2 \sum_{\lambda=0}^{\infty} (-1)^{m-m_i} d_\lambda(l_\gamma m, l_{\gamma'} m') d_\lambda(l_i m_i, l_{i'} m_{i'}) \frac{1}{(\lambda+1)(\lambda+2)} \\ &\quad \times \{ (l_\gamma + l_{\gamma'} + \lambda + 2)(l_{\gamma'} - l_\gamma + \lambda + 1)(l_\gamma - l_{\gamma'} + \lambda + 1)(l_\gamma + l_{\gamma'} - \lambda)(l_i + l_{i'} + \lambda + 2) \\ &\quad \times (l_{i'} - l_i + \lambda + 1)(l_i - l_{i'} + \lambda + 1)(l_i + l_{i'} - \lambda) \}^{\frac{1}{2}} \\ &\quad \times \{ N^\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) + N^\lambda(F_i P_\gamma, F_{i'} P_{\gamma'}) \}, \end{aligned} \quad (93)$$

where  $Z_\lambda$  consists of a linear combination of various types of integrals, and the quantities  $N^\lambda$  are the usual magnetic integrals. The quantities  $Z_\lambda$  and  $N^\lambda$  are defined in appendix B. The coefficients  $d_\lambda$  resemble the  $c_\lambda$  coefficients, and are defined by:

$$d_\lambda(lm, l'm') = \{ [l, l'] \}^{\frac{1}{2}} C_{00}^{l'l} C_{-m m'}^{l' \lambda} C_{-m m'}^{l \lambda+1}. \quad (94)$$

The first term of (93) has the same angular part as the Coulomb interaction, and thus one can take account of this part by adding a correction  $Z_\lambda$  to the radial integrals  $R_\lambda$  or  $\bar{R}_\lambda$ . The algebraic factor in the second term of (93) is different from that in the Coulomb interaction, and the algebra of this term must be evaluated separately. Thus  $W_{ii'}$  must be redefined:

$$\begin{aligned} \int_0^\infty F_i W_{ii'} F_{i'} dr &= 2 \sum_{\nu} \{ f_{ii'}^{(\nu)} R_\lambda^c(P_\gamma F_i, P_{\gamma'} F_{i'}) - g_{ii'}^{(\nu)} R_\lambda^c(F_i P_\gamma, P_{\gamma'} F_{i'}) \} \\ &\quad + 2 \sum_{\nu} \{ f_{ii'}^{(\nu)}(oo') N^\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) - g_{ii'}^{(\nu)}(oo') N^\lambda(F_i P_\gamma, P_{\gamma'} F_{i'}) \}, \end{aligned} \quad (95)$$

where  $f_{ii'}^{(\nu)}(oo')$  and  $g_{ii'}^{(\nu)}(oo')$  are algebraic coefficients for the non-Coulombic part of  $g_{kj}(oo')$ . They are analogous to the coefficients  $f_{ii'}^{(\nu)}$  and  $g_{ii'}^{(\nu)}$  and may be calculated in a similar way. The radial integrals  $R_\lambda^c$  contain corrections from the interactions  $g_{kj}(d)$ ,  $g_{kj}(css')$  and  $g_{kj}(oo')$ , and they are defined by

$$R_\lambda^c(P_\gamma F_i, P_{\gamma'} F_{i'}) = R_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}) + \alpha^2(2\lambda + 1) X_2(F_i F_{i'} P_\gamma P_{\gamma'}) + [1 - \delta(\lambda, 0)] Z_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'}). \quad (96)$$

In (96) it should be remembered that  $Z_\lambda(P_\gamma F_i, P_{\gamma'} F_{i'})$  has a factor  $\alpha^2$  absorbed within it, so that both corrections to  $R_\lambda$  are of order  $\alpha^2 R_\gamma$ .



## 6. SCALING PROPERTIES OF COLLISION STRENGTHS

## 6.1. Derivation of scaling properties

It may be shown (see, for example, Burgess *et al.* 1970) that non-relativistic collision strengths have the following asymptotic behaviour along the target isoelectronic sequence

$$\Omega \sim \text{const}/Z^2, \quad (97)$$

where for each  $Z$ ,  $\Omega$  is calculated for the same reduced energy  $K^2$  of the colliding electron

$$K^2 = k^2/Z^2, \quad (98)$$

$k^2$  being the energy of the incident electron in Rydbergs, referred to the target ground state energy. In this section, we examine how relativistic effects can modify the asymptotic behaviour (97). To do this, we change the radial variable from  $r$  to  $\rho = Zr$  for the target radial wavefunctions, and define reduced target radial functions

$$\mathcal{P}_{nl}(\rho) = Z^{-\frac{1}{2}}P_{nl}(r). \quad (99)$$

For the colliding electron we change the radial variable from  $r$  to  $\xi = zr$ , and define a reduced free wavefunction to be

$$\mathcal{F}_i(\xi) = z^{\frac{1}{2}}F(r). \quad (100)$$

For inelastic transitions, the  $R$ -matrix will scale in the same way as  $\langle \Psi | H - E | \Psi \rangle$ . For simplicity we will only include  $g_{kl}(d)$  in  $H$ , but the form of the expansions obtained will be the same when other interactions from the Breit–Pauli hamiltonian are included.

Substituting (99) and (100) into (87) and using scaled radial variables we obtain

$$\begin{aligned} (\mathcal{F}_i | \mathcal{W}_{ii'} | \mathcal{F}_i) = 2 \sum_{\nu} \left\{ f_{ii'}^{(\nu)} \left[ \frac{Z}{z^2} \mathcal{R}_{\lambda}^{\rho}(\mathcal{P}_{\gamma} \mathcal{F}_i, \mathcal{P}_{\gamma'} \mathcal{F}_{i'}) - \frac{Z^2 \alpha^2}{z} \mathcal{X}_{\frac{1}{2}}^{\rho}(\mathcal{P}_{\gamma} \mathcal{F}_i, \mathcal{P}_{\gamma'} \mathcal{F}_{i'}) \right] \right. \\ \left. - g_{ii'}^{(\nu)} \left[ \frac{Z}{z^2} \mathcal{R}_{\lambda}^{\rho}(\mathcal{P}_{\gamma} \mathcal{F}_i, \mathcal{P}_{\gamma'} \mathcal{F}_{i'}) - \frac{Z^2 \alpha^2}{z} \mathcal{X}_{\frac{1}{2}}^{\rho}(\mathcal{P}_{\gamma} \mathcal{F}_i, \mathcal{P}_{\gamma'} \mathcal{F}_{i'}) \right] \right\}. \quad (101) \end{aligned}$$

In equation (101), the scripted integrals  $\mathcal{R}_{\lambda}^{\rho}$  and  $\mathcal{X}_{\frac{1}{2}}^{\rho}$  are the reduced forms of  $R_{\lambda}$  and  $X_{\frac{1}{2}}$ . The superscript indicates that the integration is carried out with respect to  $\rho$ . Hence using (86) and (101) in (55) we obtain

$$\mathcal{R}_{ii'} = \frac{Z}{z^2} \mathcal{A}_{ii'} + \frac{Z^2 \alpha^2}{z} \mathcal{B}_{ii'} \quad (102)$$

$$\text{where } \left. \begin{aligned} \mathcal{A}_{ii'} &= 2 \sum_{\nu} [f_{ii'}^{(\nu)} \mathcal{R}_{\nu}^{\rho}(\mathcal{P}_{\gamma} \mathcal{F}_i, \mathcal{P}_{\gamma'} \mathcal{F}_{i'}) - g_{ii'}^{(\nu)} \mathcal{R}_{\nu}^{\rho}(\mathcal{F}_i \mathcal{P}_{\gamma}, \mathcal{P}_{\gamma'} \mathcal{F}_{i'})], \\ \mathcal{B}_{ii'} &= -2 \sum_{\nu} [f_{ii'}^{(\nu)} + g_{ii'}^{(\nu)}] \mathcal{X}_{\frac{1}{2}}^{\rho}(\mathcal{P}_{\gamma} \mathcal{F}_i, \mathcal{P}_{\gamma'} \mathcal{F}_{i'}). \end{aligned} \right\} \quad (103)$$

In (102)  $\mathcal{R}_{ii'}$  is a scaled reactance matrix element. It follows that if we insert  $\mathcal{R}$ -matrix elements of form (102) into the expression (29) for  $\Omega$ , first using approximation (70) we obtain

$$\Omega \underset{\text{large } Z}{\sim} A/Z^2 + \alpha^2 B + \alpha^2 Z^2 C \quad (104)$$

$$\text{or } Z^2 \Omega \sim A + \alpha^2 Z^2 B + \alpha^4 Z^4 C. \quad (105)$$

Expressions (104) or (105) hold subject to

$$\alpha^2 Z^4 \ll 1, \quad (106)$$

which is the condition for the validity of the Breit–Pauli method (see § 3.2). The expansions are thus approximately valid in a region of large  $Z$ , rather than in the  $Z = \infty$  limit as in the non-relativistic case.

The result (105) is quite general; it can be verified that all terms of the Breit–Pauli hamiltonian will give contributions to scaled inelastic collision strengths which are of the form  $\alpha^2 Z^2 B + \alpha^4 Z^4 C$ . This can be done by examining the scaling properties of the various radial integrals arising in the matrix elements of  $H_{B.P.}$ .

### 6.2. Discussion

The following comments may be made in the light of the asymptotic expansion (105):

(i) In § 5.1 we pointed out that it is inconsistent on theoretical grounds to retain the term in  $\alpha^4$  arising from f.s. interactions between colliding electron and target. Furthermore, there is no semi-empirical evidence for retaining this term. However, one can justify the retention of  $\alpha^4$  terms arising in intermediate-coupling calculations of collision strengths.†

(ii) It was noted that in § 5.2.2 that results obtained with the two-body Darwin term only in the hamiltonian may differ considerably from results calculated taking into account both the two-body Darwin term and the spin–spin contact interaction. It can now be seen that the effect of including the extra interaction  $g_{kl}(css')$  will be to change the sign of the term in  $\alpha^2$  of equation (105).

(iii) It is reasonable to assume that  $A$ ,  $B$  and  $C$  are all of the same order of magnitude, since they are all functions of radial integrals  $\mathcal{R}_\lambda$ ,  $\mathcal{X}_2$ , etc.‡ For a hydrogenic ion with  $Z = 25$  (Mn xxv) it then follows that the terms in  $\alpha^2 Z^2$  and  $\alpha^4 Z^4$  will make contributions of about 3% and 0.1% respectively. Walker's calculations for Mn xxv give total corrections of about 3% for the 1s–2s and 1s–2p transitions, and about 5% for 2s–2p, at a reduced energy of  $K^2 = 1$ . Walker finds slightly larger ( $\sim 10\%$ ) corrections for elastic transitions.

## 7. EFFECT OF BREAKDOWN OF $LS$ -COUPLING IN THE TARGET

We discuss here the method used by Saraph (1972) in which fine structure collision strengths are obtained from  $LS$ -coupled  $R$ -matrices. Flower & Pineau des Forêts (1973) and Mason (1974) have used the method in calculating collision strengths for certain high ionization stages of Fe, where  $LS$ -coupling breaks down appreciably. The aim of this section is to:

- (1) list all necessary formulae;
- (2) state precautions which should be taken in such calculations;
- (3) look at contributions of order  $\alpha^2$  and  $\alpha^4$  to both  $R$ -matrices and collision strengths;
- (4) examine the dependence of the fine structure collision strengths upon  $Z$  or  $z$ , and to find the analogue of expansion (105).

In connexion with point (3) we will justify the retention of the  $\alpha^4$  contribution for  $LS$ -coupling breakdown effects.

### 7.1. Formulae

We assume that we have a set of  $LS$ -coupling  $R$ -matrix elements:

$$R(F_i S_i L_i l S L; F'_i S'_i L'_i l' S L)$$

† See also the comments in § 8.3.2.

‡ Magnetic and similar integrals occurring in the Breit–Pauli method commonly have the factor  $\alpha^2$  absorbed into them. We do not do this here, so one would expect all integrals  $\mathcal{R}_\lambda$ ,  $\mathcal{X}_2$ ,  $\mathcal{N}^\lambda$ , etc., to be of the same order of magnitude for given  $\lambda$  ( $\mathcal{N}^\lambda$  is a scaled magnetic integral  $N^\lambda$ ).

These  $R$ -matrices are then transformed into  $J_i j$  coupling by means of the algebraic transformation:

$$R(\Gamma_i S_i L_i J_i l j J; \Gamma'_i S'_i L'_i J'_i l' j' J) = [j, j', J_i, J'_i]^{\frac{1}{2}} \sum_{S, L} [S, L] \begin{Bmatrix} S_i & L_i & J_i \\ \frac{1}{2} & l & j \\ S & L & J \end{Bmatrix} R(\Gamma_i S_i L_i l S L; \Gamma'_i S'_i L'_i l' S L) \begin{Bmatrix} S'_i & L'_i & J'_i \\ \frac{1}{2} & l' & j' \\ S & L & J \end{Bmatrix}. \quad (107)$$

A further transformation is now made to intermediate coupling

$$R(\Delta_i J_i l j J; \Delta'_i J'_i l' j' J) = \sum_{\substack{\Gamma_i S_i L_i \\ \Gamma'_i S'_i L'_i}} f_{J_i}(\Delta_i, \Gamma_i S_i L_i) R(\Gamma_i S_i L_i J_i l j J, \Gamma'_i S'_i L'_i l' j' J) f_{J'_i}(\Delta'_i, \Gamma'_i S'_i L'_i), \quad (108)$$

where 
$$f_{J_i}(\Delta_i, \Gamma_i S_i L_i) = \sum_{C_i \alpha_i} a^{S_i L_i}(\Gamma_i, C_i \alpha_i) b^{J_i}(\Delta_i, C_i \alpha_i S_i L_i). \quad (109)$$

In (109) the coefficients  $a^{S_i L_i}$  and  $b^{J_i}$  are expansion coefficients of the configuration-mixing wavefunctions and the intermediate-coupling wavefunctions respectively, i.e.

$$|\Gamma_i S_i L_i\rangle = \sum_{C_i \alpha_i} a^{S_i L_i}(\Gamma_i, C_i \alpha_i) |C_i \alpha_i S_i L_i\rangle, \quad (110)$$

and 
$$|\Delta_i J_i\rangle = \sum_{C_i \alpha_i S_i L_i} b^{J_i}(\Delta_i, C_i \alpha_i S_i L_i) |C_i \alpha_i S_i L_i J_i\rangle. \quad (111)$$

In expansions (109) and (110) and (111) it is understood that the coefficients  $a^{S_i L_i}$ ,  $b^{J_i}$  and  $f_{J_i}$  all refer to wavefunctions of the same parity. Expressions (107), (108) and (109) are derived in Appendix A.

It should be noted that in general the  $f_{J_i}$  coefficients are not the same as the set of mixing coefficients obtained when the Breit–Pauli hamiltonian matrix of the target is diagonalized. However, in the special case of single configuration calculations it follows from (109) that

$$f_{J_i}(\Delta_i, \Gamma_i S_i L_i) = b^{J_i}(\Delta_i, C_i \alpha_i S_i L_i), \quad (112)$$

where  $\Gamma_i = C_i \alpha_i$  in absence of configuration mixing. Calculation of the  $f_{J_i}$  involves three steps:

(i) Calculation of the configuration mixing coefficients  $a^{S_i L_i}(\Gamma_i, C_i \alpha_i)$  by diagonalizing the submatrices of  $S_i L_i$  and parity of the target hamiltonian.

(ii) Calculation of the coefficients  $b^{J_i}(\Delta_i, C_i \alpha_i S_i L_i)$  by diagonalizing the target energy submatrices belonging to the same  $J_i$  and parity with some or all of the f.s. interactions of the Breit–Pauli hamiltonian included in the calculation of the energy submatrices.

(iii) Substitution in (109) to obtain  $f_{J_i}$ .

## 7.2. Consistency of phases

The derivation of expressions (111), (112) and (113) implicitly assumes that the representation  $\Gamma_i$  used in the calculation of the  $R$ -matrices should be consistent with the representations  $\Delta_i$  and  $\Gamma'_i$  used in the calculation of the  $f_{J_i}$ . This means that the calculations of the collision problem, the  $LS$ -coupling target problem and the intermediate-coupling target problem should be based upon the same non-relativistic target functions. Thus, *the same algebraic methods should be used to calculate the  $R$ -,  $a^{S_i L_i}$ - and  $b^{J_i}$ -matrices.* If, for example the Slater determinant expansion method discussed in § 8.2.2 is employed, precautions should be taken to ensure that the same Slater determinant expansions of the target states are used in the calculation of  $R$ ,  $a$  and  $b$  matrices. It also follows that mixing of different algebraic methods may give unreliable results; for example, the use of fractional percentage techniques in the calculation of  $R$ , but the use of Slater determinant expansion techniques in calculating the  $f_{J_i}$  (or the  $a^{S_i L_i}$  and  $b^{J_i}$ ).

A program package satisfying these phase consistency requirements is now available at University College London (Eissner 1972). A program written by Eissner may be used to produce  $R$ -matrices in the distorted wave approximation. The program of Jones (1970, 1971*a*, *b*, Eissner *et al.* 1974)† produces  $f_{J_i}$  coefficients consistent with  $R$ -matrices from Eissner's program.

### 7.3. Dependence of transformed $R$ -matrices and fine structure collision strengths upon $\alpha^2$ and $Z$

#### 7.3.1. Dependence upon $\alpha^2$

In order to avoid unnecessary complication we will examine this problem for the special case of collisional excitations among the  $1s^2^1S$  and  $1s2p^1,^3P$  states of a helium-like target. The results obtained will display all principal features of the problem.

Consider first the excitation  $1s^2^1S_0 \rightarrow 1s2p^3P_1$ . We will represent initial and final states by one configuration only.‡ In intermediate coupling, the  $2^3P_1$  and  $2^1P_1$  levels mix (the 'singlet-triplet mixing' of Ermolaev & Jones (1972)) and we may write

$$\left. \begin{aligned} \psi(\Delta = 1, 2^3P_1) &= b(1, 1) \phi(2^3P_1) + b(1, 2) \phi(2^1P_1), \\ \psi(\Delta = 2, 2^1P_1) &= b(2, 1) \phi(2^3P_1) + b(2, 2) \phi(2^1P_1), \end{aligned} \right\} \quad (113)$$

where  $b = b(\Delta, i)$ , and  $i = 1$  for  $2^3P_1$ ,  $i = 2$  for  $2^1P_1$  and  $\Delta = 1, 2$  correspond to the labels on the intermediate coupling eigenfunctions  $\psi$ . The label  $\Delta = 1$  represents the eigenfunction  $\psi$  corresponding to the lowest eigenvalue in this case. The  $\psi$  are linear combinations of orthonormal non-relativistic wavefunctions  $\phi(^3P_1)$  and  $\phi(^1P_1)$ . We omit  $J_i$  in the labelling of the  $b$ 's, since only the  $J = 1$  states couple; the matrices of  $b$  for  $J = 0$  and  $J = 2$  consists of single unit elements. Owing to our neglect of configuration mixing, the  $f_{J_i}$  and  $b^{J_i}$  coefficients will be equal (i.e. equation (112) applies). For the purposes of this discussion it will be clearer if we denote intermediate-coupling and  $LS$ -coupling  $R$ -matrices by  $R^{IC}$  and  $R^{LS}$  respectively. A similar convention will be adopted for collision strengths. It then follows from (108) that

$$\begin{aligned} R^{IC}(1^1S_0 ljJM; 2^3P_1 l'j'JM) \\ = b(1, 1) R^{LS}(1^1S_0 ljJM; 2^3P_1 l'j'JM) + b(1, 2) R^{LS}(1^1S_0 ljJM; 2^1P_1 l'j'JM). \end{aligned} \quad (114)$$

Obviously, if both initial and final states were affected by intermediate coupling, additional terms quadratic in the  $b$ 's would appear.

The  $\alpha^2$ -dependence of  $R^{IC}$  can now be obtained by means of perturbation theory for the coefficients  $b$ . The matrix of  $b(i, j)$  is normally calculated by diagonalizing the energy matrix including fine structure interactions. Ermolaev & Jones (1972) have pointed out that this is approximately equivalent to the application of second order perturbation theory: thus the shift  $E_{\text{pert}}(1)$  of the energy of the target level 1 due to the perturbation  $\alpha^2 H_{\text{pert}}$  is given by

$$E_{\text{pert}}(1) = \alpha^2 \langle 1 | H_{\text{pert}} | 1 \rangle + \alpha^4 \sum_{\text{all } n \neq 1} \frac{\langle 1 | H_{\text{pert}} | n \rangle \langle n | H_{\text{pert}} | 1 \rangle}{E_1 - E_n}. \quad (115)$$

With the restriction that the summation over states  $n$  is restricted to include only those states resulting from the set of configurations included in the calculation. In our example of the helium-like  $2^3P_1$  state, this means that only the nearest state which is  $2^1P_1$  (i.e.  $n = 2$ ) is included. Second

† This program will shortly be published in *Computer Physics Communications* as part of a joint publication with Dr W. Eissner, Dr H. Nussbaumer and Dr P. J. Storey.

‡ This is a good approximation for highly ionized members of this sequence; see Ermolaev, Jones & Phillips (1972), who compare their elaborate calculations of energies with energies calculated from the simple  $Z$ -expansions of Doyle (1969), for selected ions in a wide range of  $Z$ .

order perturbation theory will be a good approximation to the diagonalization procedure provided that

$$H_{1n} = \langle 1 | H_{\text{pert}} | n \rangle \ll (E_1 - E_2) \quad (116)$$

for all the states  $n$  included in the approximation. Now the second order energy can be obtained from the first order perturbed wavefunction. Hence if the condition (116) holds, the eigenvectors of the hamiltonian matrix for  $J = 1$  will correspond to the first order perturbed wavefunctions.

$$\left. \begin{aligned} \psi(\Delta = 1, 2^3P_1) &= \phi(2^3P_1) + \alpha^2 \frac{H_{12}}{E_1 - E_2} \phi(2^1P_1), \\ \psi(\Delta = 2, 2^1P_1) &= \phi(2^1P_1) - \alpha^2 \frac{H_{12}}{E_1 - E_2} \phi(2^3P_1), \end{aligned} \right\} \quad (117)$$

where the functions  $\phi$  are non-relativistic basis functions which are orthonormal. In (117) the functions  $\psi$  are not normalized to unity, but they may be normalized by multiplying the equations (117) by a factor.

$$C = \left\{ 1 + \alpha^4 \left( \frac{H_{12}}{E_1 - E_2} \right)^2 \right\}^{-\frac{1}{2}}. \quad (118)$$

Thus 
$$\psi(\Delta = 1, 2^3P_1) = C \left[ \phi(2^3P_1) + \alpha^2 \frac{H_{12}}{E_1 - E_2} \phi(2^1P_1) \right], \quad (119)$$

with a similar expression for  $\psi(\Delta = 2, 2^1P_1)$ . We may now write down explicit expressions for the  $b$ -coefficients:

$$\left. \begin{aligned} b(1, 1) &= C; & b(2, 2) &= C, \\ b(1, 2) &= C\alpha^2 \frac{H_{12}}{E_1 - E_2}; & b(2, 1) &= -C\alpha^2 \frac{H_{12}}{E_1 - E_2}. \end{aligned} \right\} \quad (120)$$

Substituting expression (120) in (114) we obtain:

$$\begin{aligned} R^{\text{IC}}(1^1S_0 l j J M; 2^3P_1 l' j' J M) \\ = C R^{\text{LS}}(1^1S_0 l j J M; 2^3P_1 l' j' J M) + C\alpha^2 \frac{H_{12}}{E_1 - E_2} R^{\text{LS}}(1^1S_0 l j J M; 2^1P_1 l' j' J M). \end{aligned} \quad (121)$$

For convenience we now use approximation (70) for the  $T$ -matrix, obtaining the collision strength from (71). (Use of approximation (70) does not affect the generality of the results: the transformation (108) also applies to the  $S$ -matrix—the transformed  $S$ -matrix could then be substituted in the more general expression (77) to yield the  $T$ -matrix.) We obtain:

$$\begin{aligned} \Omega^{\text{IC}}(1^1S_0; 2^3P_1) &= C^2 \left\{ \Omega^{\text{LS}}(1^1S_0; 2^3P_1) + \alpha^4 \left( \frac{H_{12}}{E_1 - E_2} \right)^2 \Omega^{\text{LS}}(1^1S_0; 2^1P_1) \right. \\ &\quad \left. + \alpha^2 \frac{2H_{12}}{E_1 - E_2} D(1^1S_0; 3P_1, 1P_1) \right\}, \end{aligned} \quad (122)$$

where  $D$  is a cross term defined by

$$D(1^1S_0; 3P_1, 1P_1) = \sum_{w'j'} 4[J] R^{\text{LS}}(1^1S_0 l j J M; 2^3P_1 l' j' J M) R^{\text{LS}}(1^1S_0 l j J M; 2^1P_1 l' j' J M). \quad (123)$$

Eliminating  $C^2$  from (122) with the help of (118) we obtain

$$\begin{aligned} \Omega^{\text{IC}}(1^1S_0; 2^3P_1) &= \Omega^{\text{LS}}(1^1S_0; 2^3P_1) \\ &\quad + \alpha^4 \frac{H_{12}^2}{(E_1 - E_2)^2} \{ \Omega^{\text{LS}}(1^1S_0; 2^1P_1) - \Omega^{\text{LS}}(1^1S_0; 2^3P_1) \} \\ &\quad + \alpha^2 \frac{H_{12}}{E_1 - E_2} D(1^1S_0; 3P_1, 1P_1) + O(\alpha^6). \end{aligned} \quad (124)$$



Two important points now arise:

(i) Is it valid to retain the term in  $\alpha^4$ , since the target hamiltonian does not contain any interactions of this order?

(ii) How do phase inconsistencies of the type discussed in § 7.2 affect  $\Omega^{\text{IC}}$ ?

With reference to point (i) we note that there is a large body of semi-empirical evidence to support the retention of the  $\alpha^4$  term in  $\Omega^{\text{IC}}$ . Recently Ermolaev & Jones (1972) carried out a study of the fine structure of  $1snp$  state in ions of the helium iso-electronic sequence. They concluded, after comparing the results of their calculations of f.s. splittings in  $1s2p$  states with the quite accurate experimental values, that the singlet-triplet correction seems to account for the major part of the  $\alpha^4 R_y$  correction to the f.s. energies. It would appear that, in this case at any rate, all other corrections of order  $\alpha^4 R_y$  which Daley *et al.* (1972) considered give only a small contribution to the f.s. separations. Further semi-empirical justification for the use of second order treatments of the Breit-Pauli hamiltonian can be found in studies of other systems. For example Condon & Shortley use 'second order spin-orbit interaction' to obtain the correct transition from  $LS$ -coupling to  $jj$ -coupling expected from experiment. Jones (1971*a*) explained the inversion of certain f.s. levels in Fe VI by means of a second order treatment of spin-orbit interaction; Nussbaumer (1974) has found similar effects in Fe XIII. Thus there is fairly strong support for the use of second order perturbation theory in calculating breakdown in  $LS$ -coupling for the target problem. Validity of second order perturbation theory for the energy implies the validity of using first order perturbed wavefunctions, such as those of (117) or (119). Consequently, if it is valid to use such a wavefunction for the calculation of a  $R$ -matrix, one must retain all terms arising from it, including the term in  $\alpha^4$  together with the higher order terms  $O(\alpha^6)$  which arise from the normalization. This state of affairs should be contrasted with that relating to the calculation of relativistic effects explicitly involving the colliding electron (§ 6.2).

Turning to point (ii), it suffices to note that changes of phase in the calculation of the algebra of the target can result in phase changes in the off-diagonal matrix element  $H_{12}$  or the cross term  $D$ . It is therefore essential that both  $H_{12}$  and  $D$  are calculated from the same target vector coupling coefficients to avoid errors in the  $\alpha^2$  term of equation (124). The terms in  $\alpha^2$  and  $\alpha^4$  of (124) are likely to be of the same order of magnitude. In cases of interest, these two terms may dominate  $\Omega^{\text{IC}}$ . Thus any change in the relative sign of these two terms could alter the collision strength by a considerable amount.

Two further points should be noted: firstly, if we use the mixing coefficients to estimate  $\Omega^{\text{IC}}$  from the relation

$$\Omega^{\text{IC}}(1^1S_0; 2^3P_1) \sim b(1, 1)^2 \Omega^{\text{LS}}(1^1S_0; 2^3P_1) + b(1, 2)^2 \Omega^{\text{LS}}(1^1S_0; 2^1P_1), \quad (125)$$

then it will only give a very rough estimate of the change in collision strength due to intermediate coupling, since it neglects the cross-term in  $\alpha^2$ . This cross-term is likely to be significant when intermediate coupling effects are important. Secondly, by contrast with the effects discussed in § 5.1, term-coupling can effect collision strengths (to order  $\alpha^2$  and higher) even when the collision strengths are summed over the fine structure of the initial and final states.

### 7.3.2. Dependence upon $Z$

The dependence of  $\Omega^{\text{IC}}$  upon  $Z$  may be obtained by examining the  $Z$ -dependence of the various terms on the right-hand side of (124). For this, we need to know the  $Z$ -dependence of  $\Omega^{\text{LS}}$ ,  $D$ ,  $H_{12}$  and  $E_1 - E_2$ . We note that  $\Omega^{\text{LS}}$  has the asymptotic behaviour (97). It may be easily



verified that the term  $D$  (equation (124)) has the same asymptotic behaviour. In order to account for intermediate coupling effects, the matrix elements  $H_{12}$  must include at least spin-orbit interaction. It follows that  $H_{12}$  has the scaling property†

$$H_{12} \propto (Z-S)^4, \quad (126)$$

where  $S$  is a screening parameter (in our helium-like example  $1s2p$ ,  $S$  is the screening parameter for the  $2p$  electron).† The energy difference  $E_1 - E_2$  is essentially the difference between two energies belonging to the same configuration, and the  $Z$ -dependence will be approximately

$$E_1 - E_2 \propto (Z-S) \quad (127)$$

(see, for example, Layzer (1959) or Edlén (1964)). At sufficiently high  $Z$ , relativistic terms of the type  $\alpha^2(Z-S)^4$  will start to become significant on the right-hand side of (127), but the term in  $(Z-S)$  will still be the leading term.

Inserting these scaling properties into (124) it follows that the asymptotic form of  $\Omega^{\text{IC}}$  for large  $Z$  and fixed effective energy  $K^2$  of the colliding electron is

$$\Omega^{\text{IC}} \sim \frac{A'}{Z^2} + \frac{B'\alpha^2(Z-S)^3}{Z^2} + \frac{C'\alpha^4(Z-S)^6}{Z^2} + O(\alpha^6). \quad (128)$$

At sufficiently high  $Z$ ,  $Z-S \sim Z$  and we may write

$$\Omega^{\text{IC}} \sim \frac{A'}{Z^2} + B'\alpha^2 Z + C'\alpha^4 Z^4 + O(\alpha^6). \quad (129)$$

Expansion (129) is valid for  $Z$  large, but not so large as to violate condition (106). Thus as with expansion (105), we must not interpret (129) as an expansion valid in the limit  $Z \rightarrow \infty$ . However, it is impossible to write down any expansion valid in the limit  $Z \rightarrow \infty$  within any relativistic approximation which assumes a point nucleus (see Ermolaev & Jones (1973) for a brief discussion of range of validity of bound state solutions of the Dirac equation; inspection of equations (9), (10) and (11) of Walker (1974) will also show that  $s_{\frac{1}{2}}$  and  $p_{\frac{1}{2}}$  free wavefunctions are not physically meaningful for  $Z \geq 137$ ). Also, in the limit  $Z \rightarrow \infty$  intractable problems involving higher order quantum electrodynamic corrections will occur.

For fixed  $K^2$ ,  $A'$ ,  $B'$  and  $C'$  in (129) are constants; they have primes to distinguish them from quantities  $A$ ,  $B$  and  $C$  of expansion (104). Contrasting (129) and (104), we note that in (129) the terms in  $\alpha^2$  and  $\alpha^4$  contain higher powers of  $Z$  than the corresponding terms of (104), so that intermediate coupling effects become important at lower values of  $Z$  than relativistic effects involving the colliding electron. Also, in (104) the coefficients,  $A$ ,  $B$  and  $C$  will be of the same order of magnitude, whereas in cases of interest  $B'$  and  $C'$  may be an order or several orders of magnitude greater than  $A'$ , for example when  $A'$  corresponds to a scaled exchange collision strength as in (125).

Although the expansion (129) has been derived for a helium-like target, similar expansions hold for more complex systems, including transitions where both initial and final states are affected by intermediate coupling.

† The other f.s. interactions scale as  $(Z-S)^3$  (see, for example, Jones 1971.) Note also that  $H_{12}$  is a matrix element of some subset of  $H_{re}$  (equation (3)), which has the factor  $\alpha^2$  left out of it by definition. Thus equation (126) does not include a factor of  $\alpha^2$  on the right hand side, since  $\alpha^2$  has already appeared as the perturbation parameter in (115) and the following equations.

8. PRACTICAL PROCEDURES FOR THE CALCULATION OF  $R$ -MATRICES8.1. *Calculations which use the  $jJ$ -coupling representation throughout*

The most obvious procedure for the calculation of  $R$ -matrices within the framework of the present theory would involve setting up channel lists of the form  $\Gamma_i S_i L_i J_i l_j J$  and then carrying out the complete calculation in this representation. This method has the following disadvantages:

(i) The  $jJ$ -coupling channel list will be longer than the corresponding  $LS$ -coupling list by a factor of roughly four. This will require more storage for channel lists and various other quantities. Also, within a Breit–Pauli approximation the set of quantum numbers  $\Gamma_i S_i L_i J_i l_j J$  overspecify the system, since the colliding electron wavefunctions for  $j = l \pm \frac{1}{2}$  ( $l \neq 0$ ) are identical.

(ii) In the region where the Breit–Pauli approximation is valid the non-relativistic contribution  $\mathbf{R}_{nr}$  to  $\mathbf{R}_{rel}$  will dominate. Non-relativistic  $R$ -matrices are most conveniently calculated in  $LS$ -coupling.

This method has the advantage that the target energies include fine structure splittings, and thus the energy of the colliding electron will take into account the target fine structure. This is important in cases such as that considered by Burke & Mitchell (1974), when the scattering phase is varying rapidly with the energy (at a resonance, for example). However, it is not necessary to use the full  $jJ$ -coupling method to take this type of effect into account, as we will discuss in § 8.2. In the author's opinion, the disadvantages of this method considerably outweigh any advantages which it might have.

8.2. *Transformation methods based upon  $LS$ -coupling reduced matrix elements*8.2.1. *General description of the procedure*

This method is more elegant than that of § 8.1 in that, firstly, no superfluous information is stored, and secondly, it involves three logical steps, with the possibility of examining the results of each step as the calculation proceeds. The steps are as follows:

- (i) The non-relativistic  $R$ -matrices  $\mathbf{R}_{nr}$  are calculated in  $LS$ -coupling.
- (ii) The reduced matrix elements RME (equation (69)) are evaluated.
- (iii) Equation (69) may now be applied to obtain  $R_{rel}(\Gamma_i S_i L_i J_i l_j J M; \Gamma'_i S'_i L'_i J'_i l'_j J' M)$ .

This could be done by using a computer program resembling the program JAJOM of Saraph (1972). JAJOM transforms the  $\mathbf{R}_{nr}$  to a 'pair-coupling' representation in which neither  $j$  nor  $J$  appear (see Appendix A). The visualized computer routine would need to transform  $\mathbf{R}_{nr}$  and RME to  $jJ$  coupling by means of (68).

We note a slight inconsistency in this procedure in that energies  $k_i^2$  used in the calculation of  $\mathbf{R}_{nr}$  are referred to the non-relativistic target energies rather than to the relativistic ones. This will not be a valid approximation in cases where  $\mathbf{R}$  is varying rapidly with  $k_i^2$ , when one should use the correct target energies. However, this difficulty may be overcome by use of an interpolation procedure in which a quantity slowly varying with energy is calculated; the  $R$ -matrices are deduced by an energy dependent transformation (see, for example, Burke & Mitchell 1974).

Once  $jJ$ -coupling  $R$ -matrices have been obtained, they may be used to deduce a wealth of information such as spin–flip cross-sections, total and differential cross-sections, electron-spin polarizations, and the polarization of line radiation emitted after electron impact excitation.

### 8.2.2. Calculation of the reduced matrix elements RME; formulation for the spin-orbit interaction

We outline the calculation of RME ( $\Gamma_i S_i L_i l_i SL; \Gamma_{i'} S_{i'} L_{i'} l_{i'} S' L'$ ) for the most important of the fine structure interactions, namely the spin-orbit interaction. We would expect that this would give most of the important physics in the  $R$ -matrices for the reasons that (i) mutual spin-orbit and spin-other-orbit interactions with undistorted closed shells behave like one-body spin-orbit interaction (Blume & Watson 1962; de-Shalit & Talmi 1963, ch. 22); (ii) spin-spin interaction with undistorted closed shells vanish (Elliot 1953). A suitably adjusted spin-orbit potential could therefore account for all fine structure interactions with the target closed shells.

We use a more general type of wavefunction than we used in §3 or §5. We impose the condition that the radial functions for the colliding electron are all orthogonal to those of the target, that is  $(P_\gamma | F_i) = 0$ . This implies no restriction on the functions  $\Psi$  for the  $(N+1)$  electron system provided that we add to  $\Psi$  a suitable linear combination of functions  $\Phi_j$  which have the form of bound state functions for the  $(N+1)$  electron problem. The functions  $\Phi_j$  are called bound channels and the number of such channels is denoted by NCHB.† The expression (18) is then replaced by:

$$\Psi = \sum_{i=1}^{\text{NCHF}} \Theta_i + \sum_{j=1}^{\text{NCHB}} \Phi_j c_j, \quad (130)$$

where we refer to the NCHF states  $\Theta_i = \Theta(\Gamma_i S_i L_i l_i SL)$  as free channels. The  $\Theta_i$  are given by (85). Eissner & Seaton (1972) give reasons for including a set of bound channels  $\Phi_j$ , and discuss the variational procedure which is used to obtain the coefficients  $c_j$ . Use of this formalism considerably simplifies the calculation of the quantities RME.

The matrix elements of an operator  $O$ , between functions of the form (130) are given by:

$$\langle \Psi | O | \Psi \rangle = \sum_{i,i'} \langle \Theta_i | O | \Theta_{i'} \rangle + \sum_{i,j'} \langle \Theta_i | O | \Phi_{j'} \rangle c_{j'} + \sum_{j,j'} c_j^* \langle \Phi_j | O | \Theta_{i'} \rangle + \sum_{j,j'} c_j^* \langle \Phi_j | O | \Phi_{j'} \rangle c_{j'}. \quad (131)$$

We will be interested in cases when the operator  $O$  represents a fine structure interaction. Then from (69) we see that

$$\left. \begin{aligned} \text{RME} &= \langle \Psi | O | \Psi \rangle, \\ O &= \mathbf{R}_k \cdot \mathbf{S}_k \quad (0 < k \leq 2). \end{aligned} \right\} \quad (132)$$

The reduced matrix element RME will therefore comprise sums over three distinct types of reduced matrix elements, those between pairs of free channels, those between free and bound channels, and those between pairs of bound channels. We separately consider methods of calculating these types of matrix elements. Before doing so we define

$$\left. \begin{aligned} F^{(N+1)}(\text{so}) &= \sum_{j=1}^{N+1} \frac{1}{r_j} \frac{dV}{dr_j} \mathbf{l}_j \cdot \mathbf{s}_j, \\ F^{(N)}(\text{so}) &= \sum_{j=1}^N \frac{1}{r_j} \frac{dV}{dr_j} \mathbf{l}_j \cdot \mathbf{s}_j. \end{aligned} \right\} \quad (133)$$

(i) Matrix elements between free channels  $\Theta_i$

$$\begin{aligned} &\langle \Gamma_i S_i L_i l_i SL \| F^{(N+1)}(\text{so}) \| \Gamma_{i'} S_{i'} L_{i'} l_{i'} S' L' \rangle \\ &= \langle \Gamma_i S_i L_i l_i SL \| F^{(N)}(\text{so}) \| \Gamma_{i'} S_{i'} L_{i'} l_{i'} S' L' \rangle \\ &\quad + \left\langle \Gamma_i S_i L_i l_i SL \left\| \frac{1}{r_{N+1}} \frac{dV}{dr_{N+1}} \mathbf{l}_{N+1} \cdot \mathbf{s}_{N+1} \right\| \Gamma_{i'} S_{i'} L_{i'} l_{i'} S' L' \right\rangle. \end{aligned} \quad (134)$$

† We use here the FORTRAN notation introduced by Eissner & Seaton (1972).

Noting that  $F^N(\text{so})$  operates only upon  $(S_i, L_i)$  and that  $\mathbf{l}_{N+1} \cdot \mathbf{s}_{N+1}$  operates only upon  $(s, l)$ , we may use the relations

$$\langle j_1 j_2 J \| \mathbf{R}_k(1) \| j'_1 j'_2 J' \rangle = \delta(j_2, j'_2) [J']^{\frac{1}{2}} \begin{Bmatrix} J & J' & k \\ j'_1 & j_1 & j_2 \end{Bmatrix} (-1)^{k+j_1+j_2+J'} [j_1]^{\frac{1}{2}} \langle j_1 \| \mathbf{R}_k(1) \| j'_1 \rangle, \quad (135)$$

where  $\mathbf{R}_k(1)$  acts only on the first part of the composite system and

$$\langle j_1 j_2 J \| \mathbf{S}_k(2) \| j'_1 j'_2 J' \rangle = \delta(j_1, j'_1) [J']^{\frac{1}{2}} \begin{Bmatrix} J & J' & k \\ j'_2 & j_2 & j_1 \end{Bmatrix} (-1)^{k+j_1+j'_2+J} [j_2]^{\frac{1}{2}} \langle j_2 \| \mathbf{S}_k(2) \| j'_2 \rangle, \quad (136)$$

where  $\mathbf{S}_k(2)$  acts only on the second part of the system (Brink & Satchler 1968). It is necessary to apply these relations to the spin and orbital parts of the system separately. Using (135) we obtain

$$\begin{aligned} & \langle \Gamma_i S_i L_i s l S L \| F^N(\text{so}) \| \Gamma'_i S'_i L'_i s' l' S' L' \rangle \\ &= \delta(l_i, l'_i) (-1)^{S'+L'+S_i+L_i+\frac{1}{2}+l_i} [S', L', S_i, L_i]^{\frac{1}{2}} \begin{Bmatrix} S & S' & k \\ S_i & S_i & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & L' & k \\ L_i & L_i & l_i \end{Bmatrix} \\ & \times \langle \Gamma_i S_i L_i \| F^N(\text{so}) \| \Gamma'_i S'_i L'_i \rangle \int_0^\infty F_i F_{i'} dr. \end{aligned} \quad (137)$$

Using (136) we obtain

$$\begin{aligned} & \left\langle \Gamma_i S_i L_i s l S L \left\| \frac{1}{r_{N+1}} \frac{dV}{dr_{N+1}} \mathbf{l}_{N+1} \cdot \mathbf{s}_{N+1} \right\| \Gamma'_i S'_i L'_i s' l' S' L' \right\rangle \\ &= \delta(\Gamma_i S_i L_i; \Gamma'_i S'_i L'_i) (-1)^{S+L+S_i+L_i+\frac{1}{2}+l_i} 2^{\frac{1}{2}} [S', L', l_i]^{\frac{1}{2}} \\ & \times \begin{Bmatrix} S & S' & k \\ \frac{1}{2} & \frac{1}{2} & S_i \end{Bmatrix} \begin{Bmatrix} L & L' & k \\ l'_i & l_i & L_i \end{Bmatrix}^{\frac{1}{2}} \sqrt{[3l_i(l_i+1)]} \delta(l_i, l'_i) \int_0^\infty F_i \frac{1}{r} \frac{dV}{dr} F_{i'} dr, \end{aligned} \quad (138)$$

where we have also used

$$\langle l \| L \| l' \rangle = \{l(l+1)\}^{\frac{1}{2}} \delta(l, l') \quad \text{and} \quad \langle \frac{1}{2} \| S \| \frac{1}{2} \rangle = \frac{1}{2} \sqrt{3} \quad (139)$$

(Brink & Satchler 1968, appendix VI). Hence substituting (137) and (138) into (134) we obtain

$$\begin{aligned} & \langle \Gamma_i S_i L_i s l S L \| F^{(N+1)}(\text{so}) \| \Gamma'_i S'_i L'_i s' l' S' L' \rangle \\ &= \delta(l_i, l'_i) (-1)^{S'+L'+S_i+L_i+\frac{1}{2}+l_i} [S', L', S_i, L_i]^{\frac{1}{2}} \begin{Bmatrix} S & S' & k \\ S_i & S_i & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & L' & k \\ L'_i & L_i & l_i \end{Bmatrix} \\ & \times \langle \Gamma_i S_i L_i \| F^N(\text{so}) \| \Gamma'_i S'_i L'_i \rangle \int_0^\infty F_i F_{i'} dr + \delta(l_i, l'_i) \delta(\Gamma_i S_i L_i; \Gamma'_i S'_i L'_i) (-1)^{S+L+S_i+L_i+\frac{1}{2}+l_i} \\ & \times 2^{\frac{1}{2}} [S', L', l_i]^{\frac{1}{2}} \begin{Bmatrix} S & S' & k \\ \frac{1}{2} & \frac{1}{2} & S_i \end{Bmatrix} \begin{Bmatrix} L & L' & k \\ l'_i & l_i & L_i \end{Bmatrix}^{\frac{1}{2}} \sqrt{[3l_i(l_i+1)]} \int_0^\infty F_i \frac{1}{r} \frac{dV}{dr} F_{i'} dr. \end{aligned} \quad (140)$$

Hence matrix elements of the spin-orbit interaction between pairs of free channels take the form

$$\langle \Theta_i \| F^{(N+1)}(\text{so}) \| \Theta_{i'} \rangle = a_{ii'}(\text{so}) (F_i | F_{i'}) + b_{ii'}(\text{so}) \left( F_i \left| \frac{1}{r} \frac{dV}{dr} \right| F_{i'} \right), \quad (141)$$

where  $a_{ii'}(\text{so})$  depends upon spin-orbit interaction within the target, and  $b_{ii'}(\text{so})$  is a purely algebraic factor. A method of calculating  $\langle \Gamma_i S_i L_i \| F^N(\text{so}) \| \Gamma'_i S'_i L'_i \rangle$  and hence  $a_{ii'}(\text{so})$  will be discussed in the next section.

(ii) *Matrix elements between free channels and bound channels or between bound channels.* In these cases the algebra involved is somewhat different, since the bound channels are treated as a complete system (not as a composite system) when calculating vector coupling coefficients for the whole system. The vector coupling coefficients may be obtained by using either fractional parentage

techniques, or the Slater determinant expansion method. The latter method has been described by Condon & Shortley (1951) and was applied to the atomic structure problem by Eissner & Nussbaumer (1969). Jones (1970) applied the technique to the evaluation of the spin-orbit matrix elements between states of bound atomic systems. The Slater determinant method is particularly suited to the computer, and it is straightforward to maintain phase consistency. We will describe the calculation of the various reduced matrix elements with specific regard to the Slater determinant expansion method, but the basic ideas will apply to any coupling method.

It may be shown that

$$\langle \Theta_i \| F^{(N+1)}(\text{so}) \| \Phi_{j'} \rangle = e_{ij'}(\text{so}) \left( F_i \left| \frac{1}{r} \frac{dV}{dr} \right| P_\gamma \right), \quad (142)$$

where  $e_{ij'}(\text{so})$  is an algebraic coefficient, and it is understood that  $\gamma$  depends on  $i$  and  $j'$ . We now consider the calculation of the coefficients  $c_{ij}(\text{so})$ . To do this we first write down the expansions of the functions  $\chi_i$ ,  $\Phi_{j'}$  and  $\Theta_i$  in terms of Slater determinants. At this stage it is convenient to adopt a representation in which the target configurations are unmixed. One can then transform to a configuration-mixing representation by means of (110), i.e.

$$\chi_i(\Gamma_i S_i L_i M_{S_i} M_{L_i} | \mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{C_i \alpha_i} a^{S_i L_i}(\Gamma_i, C_i \alpha_i) \chi(C_i \alpha_i S_i L_i M_{S_i} M_{L_i} | \mathbf{x}_1, \dots, \mathbf{x}_N). \quad (143)$$

Free channel functions  $\Theta(C_i \alpha_i S_i L_i l S L M_S M_L)$  may be transformed to functions

$$\Theta(\Gamma_i S_i L_i l S L M_S M_L)$$

by the same transformation (143). The target function may be expanded thus:

$$\chi(C_i \alpha_i S_i L_i M_{S_i} M_{L_i} | \mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_u C_{\mu_1 m_1 \dots \mu_N m_N}^{l_1 \dots l_N; \alpha_i S_i L_i} \langle n_1 l_1 \mu_1 m_1 \dots n_N l_N \mu_N m_N | \mathbf{x}_1, \dots, \mathbf{x}_N \rangle, \quad (144)$$

where the summation extends over all Slater states  $u$  belonging to configuration  $C_i$  and having azimuthal quantum numbers  $(M_{S_i} M_{L_i})$ ,

$$C_{\mu_1 m_1 \dots \mu_N m_N}^{l_1 \dots l_N; \alpha_i S_i L_i} \langle n_1 l_1 \mu_1 m_1 \dots n_N l_N \mu_N m_N | \mathbf{x}_1 \dots \mathbf{x}_N \rangle$$

is a vector coupling coefficient and  $\langle n_1 l_1 \mu_1 m_1 \dots n_N l_N \mu_N m_N | \mathbf{x}_1 \dots \mathbf{x}_N \rangle$  is a Slater determinant. The bound channel functions can similarly be expanded in  $(N+1)$  electron Slater determinants

$$\begin{aligned} & \Phi_j(C_j(N+1) \beta S L M_S M_L) \\ &= \sum_\omega C_{\mu_1 m_1 \dots \mu_{N+1} m_{N+1}}^{l_1 \dots l_{N+1}; \beta S L} \langle n_1 l_1 \mu_1 m_1, \dots, n_{N+1} l_{N+1} \mu_{N+1} m_{N+1} | \mathbf{x}_1, \dots, \mathbf{x}_{N+1} \rangle, \end{aligned} \quad (145)$$

where  $C_j(N+1)$  is the configuration of the bound channel and  $\beta$  is a degeneracy parameter. The summation index runs over all Slater states  $\omega$  with the same  $M_S M_L$ . Finally we can combine (144) with (85) in order to obtain the expansion of the free channel functions

$$\begin{aligned} & \Theta_i(C_i \alpha_i S_i L_i l S L M_S M_L) \\ &= \sum_{\substack{M_{S_i} M_{L_i} \\ \mu m}} \sum_u [C_{M_{S_i} \mu}^{S_i \frac{1}{2} S} C_{M_{L_i} m}^{L_i l L} C_{\mu_1 m_1 \dots \mu_N m_N}^{l_1 \dots l_N; \alpha_i S_i L_i}] \\ & \times \left\{ (N+1)^{\frac{1}{2}} \sum_{p=1}^{N+1} (-1)^{p-N-1} \langle n_1 l_1 \mu_1 m_1, \dots, n_N l_N \mu_N m_N | x_p \rangle \Theta_i \langle l_i \mu m | x_p \rangle \right\}, \end{aligned} \quad (146)$$

where the quantity in square brackets on the right-hand side of (146) is an effective vector-coupling coefficient for the  $(N+1)$  electron Slater determinants, which are represented by the quantity enclosed by curly brackets in (146).



Consider first matrix elements

$$\langle \Theta_i(C_i \alpha_i S_i L_i l S L M_S M_L) | F^{(N+1)}(\text{so}) | \Phi_{j'}(C_{j'}(N+1) \beta S' L' M'_S M'_L) \rangle.$$

The functions  $\Theta$  and  $\Phi$  in this matrix element can now be expanded according to (145) and (146), so that the matrix element is expressed in terms of matrix elements between uncoupled antisymmetric states (that is, between Slater determinants). The matrix elements between Slater determinants may be easily evaluated by using methods described by Condon & Shortley (1951, ch. 6). For the one electron spin-orbit operator which we are considering here the matrix elements between  $N$  or  $(N+1)$ -electron Slater determinants reduce to sums over matrix elements between one-electron functions:

$$\begin{aligned} \left\langle nl\mu m \left| \frac{1}{r} \frac{dV}{dr} \mathbf{l} \cdot \mathbf{s} \right| n'l' \mu' m' \right\rangle &= \delta(l, l') \delta(m + \mu, m' + \mu') \\ &\times \{ \delta(\mu, \mu') \mu m + \frac{1}{2} \delta(\mu, \mu' \pm 1) \sqrt{[(l-m+\frac{1}{2})(l+m+\frac{1}{2})]} \} \\ &\times \left\langle nl \left| \frac{1}{r} \frac{dV}{dr} \right| n'l \right\rangle \end{aligned} \quad (147)$$

(Condon & Shortley, ch. 8). The expression (147) can also be written for free wavefunctions, in which case  $n$  (or  $n'$ ) will be replaced by the channel labels  $i$  (or  $i'$ ) specifying the radial function  $F_i$  uniquely. In the case of matrix-elements of the form  $\langle \Theta_i | O | \Phi_{j'} \rangle$  the two states involved will always differ in the quantum numbers of one pair of electrons, resulting in the single term which appears on the right-hand side of (142).

The reduced matrix elements may be obtained from the Wigner-Eckart theorem thus:

$$\begin{aligned} \langle C_i \alpha_i S_i L_i l_i S L \| F^{(N+1)}(\text{so}) \| C_{j'}(N+1) \beta S L \rangle \\ = \frac{\langle \Theta(C_i \alpha_i S_i L_i l_i S L M_S M_L) | F^{(N+1)}(\text{so}) | \Phi_{j'}(C_{j'}(N+1) \beta S' L' M'_S M'_L) \rangle}{C_{M'_S M_S - M'_S M_S}^{S' S} C_{M'_L M_L - M'_L M_L}^{L' L}}, \end{aligned} \quad (148)$$

provided that neither of the Clebsch-Gordan coefficients in the denominator of the right-hand side vanish. The numerator of (148) will consist of a product of an algebraic factor and a radial integral; the algebraic coefficient  $e_{ij'}(\text{so})$  may therefore be deduced from (148).

Very similar procedures may be used to calculate the reduced matrix elements:

$$\langle \Phi_j \| F^{(N+1)}(\text{so}) \| \Phi_{j'} \rangle \quad \text{and} \quad \langle \chi_i \| F^{(N)}(\text{so}) \| \chi_{i'} \rangle.$$

Knowing the elements  $\langle \chi_i \| F^{(N)}(\text{so}) \| \chi_{i'} \rangle$  we can calculate the coefficients  $a_{ii'}(\text{so})$ . Hence we finally obtain an expression for RME in terms of radial integrals involving the wavefunction of the colliding electron

$$\begin{aligned} \text{RME} &= \sum_{i, i'} \left\{ a_{ii'}(\text{so}) (F_i | F_{i'}) + b_{ii'}(\text{so}) \left( F_i \left| \frac{1}{r} \frac{dV}{dr} \right| F_{i'} \right) \right\} + \sum_{ij'} e_{ij'}(\text{so}) c_{j'} \left( F_i \left| \frac{1}{r} \frac{dV}{dr} \right| P_{j'} \right) \\ &+ \sum_{ij'} c_j^\dagger e_{ij'}(\text{so}) \left( P_{j'} \left| \frac{1}{r} \frac{dV}{dr} \right| F_{i'} \right) + \sum_{jj'} c_j^\dagger \langle \Phi_j \| F^{(N+1)}(\text{so}) \| \Phi_{j'} \rangle c_{j'}. \end{aligned} \quad (149)$$

The right-hand side of (149) is similar in form to the reduced radiative matrix elements obtained when applying a similar formalism to the calculation of non-relativistic photoionization cross-sections (see, for example, Luke 1973 and Jones 1974).



## 8.2.3. Discussion

We note that the coefficients  $a_{ii'}$ ,  $b_{ii'}$ ,  $e_{ij'}$  and the numbers  $\langle C_j \beta S L \| F^{(N+1)} \| C_j' \beta S' L' \rangle$  will be the same for any one-body spin-orbit type interaction involving the colliding electron. As remarked earlier, the spin-other-orbit and mutual spin-orbit interactions *with closed shells* behave like one-body spin-orbit interactions. Thus one could generalize the theory of Blume & Watson (1962) for the electron-atom scattering problem in the case of targets with closed shells. We put

$$\zeta_{ii'} = \int_0^\infty F_i \frac{1}{r} \frac{dV}{dr} F_{i'} dr, \quad (150)$$

where  $\zeta_{ii'}$  is a 'free-free spin-orbit parameter'. Application of the Blume & Watson theory would mean replacing  $\zeta_{ii'}$  by a corrected spin-orbit parameter  $\zeta_{ii'}^c$ . The parameter  $\zeta_{ii'}^c$  will be given by an expression similar to that for  $\zeta_n^{cd}$  which Blume & Watson give in their paper.

Two further points of some practical consequence should be mentioned.

(i) It would appear from condition (28) that the Breit-Pauli method would not be applicable to electron heavy-atom scattering. In particular the Breit-Pauli method would give a poor description of the properties of the inner electrons of the target (Grant 1970). However, it would be possible to use a hybrid method in which the relativistic core of the target is described by say Hartree-Fock-Dirac wavefunctions, and the valence electrons and the colliding electron are described within the framework of the Breit-Pauli approximation. This hybrid approach may be satisfactory for the following reasons:

(a) colliding and valence electrons will not 'see' a strong potential, since the core shields them from much of the nuclear field; hence condition (28) will hold for these electrons. Grant (1970) pointed out that although the outer electrons of heavy atoms move non-relativistically, the relativistic distortion of the charge distribution in inner shells affects the outer electrons in a non-trivial way. This objection is removed if one uses Dirac-type functions to describe the core. In practice one would construct a central core potential from the relativistic functions and include it in the operator  $h_i$  (equation (60)) (see Burke & Seaton (1971) for more details on the treatment of closed shells in the coupled equations).

(b) One could solve the coupled equations for the colliding electrons in the central field of the core plus the (non-central) field of the valence electrons. One could then use all available techniques (including use of semi-empirical polarization potentials) to obtain accurate non-relativistic wavefunctions and  $R$ -matrices. These would then be used in the calculation of RME and  $\mathbf{R}_{\text{rel}}$ . By contrast, both formulations and computer programs for solving the Dirac coupled integro-differential equations (Carse & Walker 1973) are still at a fairly rudimentary stage of development. The methods suggested here can utilize the relatively highly developed theory and computer programs associated with the non-relativistic coupled equations (see, for example, Burke & Seaton 1971).

(ii) In some systems, the breakdown of  $LS$ -coupling may be important, and so calculations of RME and  $\mathbf{R}_{\text{rel}}$  (equation (68)) should take into account intermediate coupling. This may be done by applying the transformation (108) to  $\mathbf{R}_{\text{rel}}$  (transformation (108) can equally be applied to the  $\mathbf{R}_{\text{rel}}$  of (68) as to non-relativistic  $R$ -matrices).

In summary, in this section we have described how the reduced matrix element RME can be calculated for spin-orbit interaction. We have mentioned how the theory may be straightforwardly refined to take into account mutual spin-orbit and spin-other-orbit interactions

between the colliding electron and any closed shells of the target. We have not discussed how to take into account two-body fine structure interactions between the colliding electron and valence electrons. However, one would expect such interactions to be much less important than spin-orbit interaction (cf. interactions between valence electrons in the structure problem, Jones (1971*a*)). Finally, we have pointed out how one may also take into account intermediate coupling in the target.

## 9. CONCLUSION

We summarize the principal points developed in this paper:

(i) It is possible to apply the Breit–Pauli method to the electron-atom scattering problem. The Kohn variational principle has been specialized for the Breit–Pauli hamiltonian.

(ii) To order  $\alpha^2$ , fine structure interactions between the colliding electron and the target make no contributions to total collision strengths, provided that summation over fine structure levels of the target is carried out.

(iii) We have discussed how the non-fine structure interactions (that is, the Darwin, spin–spin contact and orbit–orbit interactions) can be introduced into the equations satisfied by the colliding electron wavefunction. The two-body Darwin and/or spin–spin contact terms can be introduced into the equations by simply adding correction integrals  $X_2$  onto the Slater integrals  $R_\lambda$  of the usual non-relativistic collision theory.

(iv) An asymptotic  $Z$ -expansion has been derived for collision strengths, which takes account of relativistic interactions between the colliding electron and the target. The validity of retaining the contributions of  $\alpha^4$  in this expansion has been discussed.

(v) The effect of breakdown of  $LS$ -coupling in the target upon the collision strengths has been discussed. An asymptotic  $Z$ -expansion for intermediate coupling collision strengths has been derived, and this has been contrasted with the expansion mentioned in (iv).

(vi) We have described a practical method for calculation of collision strengths, including both relativistic effects involving the colliding electron and those involving the target.

There are a number of areas in which further work is desirable. Firstly, in connexion with point (iii) it would be interesting to make calculations of total collision strengths for electron-hydrogen-like systems. As a first step, the two-body Darwin term could be included; the calculations could be carried out for the same nuclear charges  $Z$  and energies as Walker (1974). Direct comparison with Walker's work could possibly give further information about the accuracy and the range of validity of the Breit–Pauli method. Inclusion of spin–spin contact and orbit–orbit terms would make another interesting extension of this line of investigation. Secondly, development of computer programs to calculate  $R$ -matrices  $\mathbf{R}_{\text{rel}}$  as described in § 8 is of relevance to experimental studies of electron-atom collisions (Bedersen 1969, 1970; Kleinpoppen 1971). Once such  $R$ -matrices have been obtained, one can calculate differential cross-sections, spin–flip cross-sections and electron spin-polarizations. A third task remains, namely that of deriving expressions for calculation of these quantities (differential cross-sections, etc.) from  $J_i j$  coupling  $R$  or  $T$ -matrices. Moores & Norcross (1972) have given such expressions for the non-relativistic treatment of electron-sodium scattering. It should not be difficult to derive such expressions within the approximations discussed in the present paper.

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#### APPENDIX A. DERIVATION OF FORMULAE FOR TRANSFORMATION OF NON-RELATIVISTIC $R$ -MATRICES TO INTERMEDIATE COUPLING

We will derive here the algebraic transformation required to obtain  $J_i j$ -coupling  $R$ -matrices from  $LS$ -coupling  $R$ -matrices, and expressions for the 'term-coupling' coefficients, which introduce the effect of breakdown of target  $LS$ -coupling into the  $R$ -matrices.

The notation set out in § 3.3.1 will be used in the following discussion. Consider first the algebraic transformation:

$$|C_i \alpha_i S_i L_i J_i s l j; JM\rangle = \sum_{M_S M_L} \langle S_i L_i s l; SLM_S M_L | S_i L_i J_i s l j; JM \rangle |C_i \alpha_i S_i L_i s l; SLM_S M_L\rangle \quad (\text{A } 1)$$

This transformation may be written explicitly using the rule for the recoupling of the four angular momenta  $S, L, J_i, j$ . (Brink & Satchler 1968, ch. III, equation (3.24)).

$$|C_i \alpha_i S_i L_i J_i s l j; JM\rangle = [J_i, j]^{\frac{1}{2}} \sum_{SLM_S M_L} [S, L]^{\frac{1}{2}} \begin{Bmatrix} S_i & L_i & J_i \\ s & l & j \\ S & L & J \end{Bmatrix} C_{M_S M_L M}^{S_i L_i J_i} |C_i \alpha_i S_i L_i s l; SLM_S M_L\rangle. \quad (\text{A } 2)$$

In practice, the transformation which we require will not be purely algebraic as in (A 2), but will relate a configuration-mixed  $LS$ -coupled target and an intermediate coupling target also including configuration mixing. Thus in  $LS$ -coupling the eigenfunction of the  $(N+1)$ -electron system in a configuration mixing representation may be written

$$|\Gamma_i S_i L_i s l; SLM_S M_L\rangle = \sum_{C_i \alpha_i} \langle C_i \alpha_i S_i L_i | \Gamma_i S_i L_i \rangle |C_i \alpha_i S_i L_i s l; SLM_S M_L\rangle. \quad (\text{A } 3)$$

$$\text{Similarly } |\Delta_i S_i L_i s l j; JM\rangle = \sum_{C_i \alpha_i S_i L_i} \langle C_i \alpha_i S_i L_i J_i | \Delta_i J_i \rangle |C_i \alpha_i S_i L_i J_i l j; JM\rangle. \quad (\text{A } 4)$$

Since transformation (A 3) is unitary we may write:

$$|C_i \alpha_i S_i L_i s l; SLM_S M_L\rangle = \sum_{\Gamma_i} \langle \Gamma_i S_i L_i | C_i \alpha_i S_i L_i \rangle |\Gamma_i S_i L_i s l; SLM_S M_L\rangle \quad (\text{A } 5)$$

We now substitute (A 5) into the right-hand side of (A 2) and then apply the transformation (A 4) to both sides of (A 2), obtaining:

$$\begin{aligned} & |\Delta_i J_i s l j; JM\rangle \\ &= [J_i, j]^{\frac{1}{2}} \sum_{SLM_S M_L} [S, L]^{\frac{1}{2}} \begin{Bmatrix} S_i & L_i & J_i \\ s & l & j \\ S & L & J \end{Bmatrix} C_{M_S M_L M}^{S_i L_i J_i} \\ & \quad \times \sum_{\Gamma_i S_i L_i} [ \sum_{C_i \alpha_i} \langle C_i \alpha_i S_i L_i J_i | \Delta_i J_i \rangle \langle \Gamma_i S_i L_i | C_i \alpha_i S_i L_i \rangle ] |\Gamma_i S_i L_i s l; SLM_S M_L\rangle. \quad (\text{A } 6) \end{aligned}$$

Equation (A 6) gives the desired transformation between  $\Delta_i J_i j J$  and  $\Gamma_i S_i L_i l S L$  representations.

We now define:

$$\begin{aligned} f_{J_i}(\Delta_i, \Gamma_i S_i L_i) &= \sum_{C_i \alpha_i} \langle \Gamma_i S_i L_i | C_i \alpha_i S_i L_i \rangle \langle C_i \alpha_i S_i L_i | \Delta_i J_i \rangle \\ &= \sum_{C_i \alpha_i} a^{S_i L_i}(\Gamma_i, C_i \alpha_i) b^{J_i}(\Delta_i, C_i \alpha_i S_i L_i), \end{aligned} \quad (\text{A } 7)$$

where  $a^{S_i L_i}$  and  $b^{J_i}$  are defined in (110) and (111) respectively.

The  $R$ -matrix transformation may now be written down immediately by using (A 2) and (A 6) giving

$$\begin{aligned} R(\Delta_i J_i \frac{1}{2} l_j J; \Delta'_i J'_i \frac{1}{2} l'_j J) \\ = \sum_{\substack{S_i L_i \Gamma_i \\ S'_i L'_i \Gamma'_i}} f_{J_i}(\Delta_i, \Gamma_i S_i L_i) R(\Gamma_i S_i L_i J_i l_j J; \Gamma'_i S'_i L'_i J'_i l'_j J) f_{J'_i}(\Delta'_i, \Gamma'_i S'_i L'_i), \end{aligned} \quad (\text{A } 8)$$

where

$$\begin{aligned} R(\Gamma_i S_i L_i J_i l_j J; \Gamma'_i S'_i L'_i J'_i l'_j J) &= [j, j', J_i, J'_i]^{\frac{1}{2}} \sum_{SL} [S, L] \begin{Bmatrix} S_i & L_i & J_i \\ \frac{1}{2} & l & j \end{Bmatrix} \begin{Bmatrix} S'_i & L'_i & J'_i \\ \frac{1}{2} & l' & j' \end{Bmatrix} \\ &\quad \times R(\Gamma_i S_i L_i \frac{1}{2} l SL, \Gamma'_i S'_i L'_i \frac{1}{2} l' SL). \end{aligned} \quad (\text{A } 9)$$

Transformation (A 8) corresponds to the transformation (11) of Saraph (1972). It should be noted that Saraph's equation (11) erroneously omits the summation indices  $\Gamma_i$  and  $\Gamma'_i$ , but this does not affect the operation of the computer program (H. E. Saraph 1973, private communication). It should also be noted that for reasons of technical convenience, Saraph transforms to 'pair coupling' where:

$$S_i + L_i = J_i; \quad J_i + l = K \quad \text{and} \quad K + s = J.$$

The reader is referred to Saraph's paper for further details. However, whether the  $J_i j$  coupling scheme or the pair coupling scheme is used, the same term coupling coefficients  $f_{J_i}$  defined by (A 7) will be valid.

#### APPENDIX B. THE ORBIT-ORBIT INTERACTION

The matrix elements of the orbit-orbit interaction in an uncoupled representation are given by the expression (93) of § 5.2.2. In this expression the quantity  $Z_\lambda$  is defined by:

$$\begin{aligned} Z_\lambda(P_\gamma F_i, P_{\gamma'} F'_i) &= -\lambda(\lambda+1) [T^{\lambda+1}(\gamma i, \gamma' i') - T^{\lambda-1}(\gamma i, \gamma' i')] \\ &\quad + [l_\gamma(l_\gamma+1) - l_{\gamma'}(l_{\gamma'}+1) - \lambda(\lambda+1)] [U^{\lambda+1}(\gamma i, \gamma' i') - U^{\lambda-1}(\gamma i, \gamma' i')] \\ &\quad + [l_i(l_i+1) - l_{i'}(l_{i'}+1) - \lambda(\lambda+1)] [U^{\lambda+1}(i\gamma, i'\gamma') - U^{\lambda-1}(i\gamma, i'\gamma')] \\ &\quad + \{ [l_\gamma(l_\gamma+1) - l_{\gamma'}(l_{\gamma'}+1) - \lambda(\lambda+1)] [l_i(l_i+1) - l_{i'}(l_{i'}+1) - \lambda(\lambda+1)] \}^{\frac{1}{2}} \\ &\quad \times \left\{ \frac{-(\lambda+3)}{(\lambda+1)(2\lambda+3)} [N^\lambda(\gamma i, \gamma' i') + N^\lambda(i\gamma, i'\gamma')] \right. \\ &\quad \left. + \frac{(\lambda-2)}{\lambda(2\lambda-1)} [N^{\lambda-2}(\gamma i, \gamma' i') + N^{\lambda-2}(i\gamma, i'\gamma')] \right\}. \end{aligned} \quad (\text{B } 1)$$

In (B 1) the integrals  $T^\lambda$ ,  $U^\lambda$  and  $N^\lambda$  correspond to those defined by Beck (1969):

$$T^\lambda(\gamma i, \gamma' i') = \frac{\alpha^2}{2\lambda+1} \int_0^\infty \int_0^\infty r_1 dr_1 r_2 dr_2 P_\gamma(r_1) F_i(r_2) \frac{r_1^\lambda}{r_1^{\lambda+1}} \frac{\partial}{\partial r_1} \left( \frac{P_{\gamma'}(r_1)}{r_1} \right) \frac{\partial}{\partial r_2} \left( \frac{F_{i'}(r_2)}{r_2} \right), \quad (\text{B } 2)$$

$$U^\lambda(\gamma i, \gamma' i') = \frac{\alpha^2}{2(2\lambda+1)} \int_0^\infty \int_0^\infty dr_1 dr_2 P_\gamma(r_1) F_i(r_2) \frac{1}{r_1 r_2^{\lambda+1}} \left[ (\lambda-1) \epsilon(r_1-r_2) - (\lambda+2) \epsilon(r_2-r_1) \right] P_{\gamma'}(r_1) r_2 \frac{\partial}{\partial r_2} \left( \frac{F_{i'}(r_2)}{r_2} \right), \quad (\text{B } 3)$$

$$\text{where} \quad \epsilon(r_1-r_2) = \begin{cases} 1 & \text{if } r_1-r_2 \geq 0, \\ 0 & \text{if } r_1-r_2 < 0. \end{cases} \quad (\text{B } 4)$$

$$\text{Finally} \quad N^\lambda(\gamma i, \gamma' i') = \frac{1}{4} \alpha^2 \int_0^\infty \int_0^\infty dr_1 dr_2 P_\gamma(r_1) F_i(r_2) \frac{r_2^\lambda}{r_1^{\lambda+1}} \epsilon(r_1-r_2) P_{\gamma'}(r_1) F_{i'}(r_2). \quad (\text{B } 5)$$

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