

## TECHNIQUES FOR THE CALCULATION OF ATOMIC STRUCTURES AND RADIATIVE DATA INCLUDING RELATIVISTIC CORRECTIONS

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The theory incorporated in a general-purpose automatic atomic-structure program is formulated in detail. The computer program, which is called SUPERSTRUCTURE, will be published soon. SUPERSTRUCTURE can calculate term energies, intermediate-coupling energy levels, term-coupling coefficients, radiative data which includes permitted and forbidden transition probabilities, and cascade coefficients. The program uses multi-configuration type expansions. Relativistic corrections are made by means of the Breit–Pauli approximation. Special attention is paid to those features of the formulation which make it particularly suited to the computer. Such principal features are:

- (i) Wave functions are effectively expanded in Slater determinants.
- (ii) Expressions for the matrix elements of the relativistic operators are given in a concise form. These matrix elements are expressed in terms of coefficients  $c_{\lambda}(lm, l'm')$ , related to the corresponding coefficients of Condon and Shortley, and coefficients  $d_{\lambda}(lm, l'm')$ , which we introduce. Relativistic operators whose matrix elements have similar angular parts are grouped together to avoid superfluous calculation of angular coefficients.
- (iii) Radial functions can be either statistical-model functions or user-supplied functions. SUPERSTRUCTURE will calculate the statistical-model radial functions if they are required, and user-supplied functions will be processed to suite the internal requirements of the program.

Checking procedures used for testing the various parts of SUPERSTRUCTURE are discussed. We also give a critique of the techniques described, and, where appropriate, discuss them in relation to techniques used by other workers.

The wide range of atomic structure data which the program can calculate makes it highly suitable for astrophysical applications. The formulation developed here should be of wide application in various problems relating to atomic structure.

### 1. Introduction

The large quantities of numerical atomic data required in astrophysical applications have made it necessary to develop general-purpose automatic computer programs which can calculate energy levels, radiative transition probabilities and electron–ion collision data. In this context a general-purpose program means a program which is not specific to certain atoms, ions or iso-electronic sequences, but which can, in principle, be applied to all atomic systems. An “automatic” program means a self-contained program in the sense that all algebraic coefficients and wavefunctions are calculated within the program. The input required by such a program should be the minimum required to specify the atomic system and the level of approximation. Eissner [1] has given a brief descrip-

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tion of a program package which goes a long way to fulfilling the above requirements. The present paper relates to that part of the package dealing with atomic structure data, namely: term energies, intermediate-coupling energy levels, term-coupling coefficients and radiative data. This program will be referred to as "SUPERSTRUCTURE" and it will shortly be published in *Computer Physics Communications* under this name. In reference [1] SUPERSTRUCTURE has been quoted by the name ASAR.

A central feature of SUPERSTRUCTURE is the method used to generate eigenfunctions of the angular momentum operators  $L^2$ ,  $L_z$ ,  $S^2$  and  $S_z$ . It uses the Slater state expansion technique, which was described in detail by Condon and Shortley [2]. The particular suitability of this method for the computer was first pointed out by Godfredsen [3] in connection with the algebraic problems of configuration interaction. SUPERSTRUCTURE then uses these eigenfunctions in the calculation of the matrix elements of:

- (i) the non-relativistic many-electron hamiltonian [4],
- (ii) the relativistic operators of the Breit–Pauli hamiltonian [5, 6],
- (iii) the operators for electric dipole and quadrupole radiation [7].

The program allows the user to take into account configuration-mixing effects: in principle there is no restriction upon the types of configuration which may be included in the configuration expansion of the wavefunction.

When calculating astrophysical data, it is often particularly important to take account of relativistic effects: for example, transition probabilities can be strongly affected by breakdown in  $LS$ -coupling, which is caused mainly by spin–orbit interaction. SUPERSTRUCTURE calculates radiative data in both Russell–Saunders ( $LS$ )-coupling and intermediate coupling. Moreover, electron–ion collision cross-sections can also be considerably modified by departure from  $LS$ -coupling in the target ion [8]. SUPERSTRUCTURE also calculates term-coupling coefficients which enable Saraph's program JAJOM [9] to take into account intermediate-coupling effects when calculating fine structure collision strengths from  $LS$ -coupling reactance matrices.

Other important features of SUPERSTRUCTURE are:

- (a) Algebraic and analytic problems are dealt with in separate parallel branches of the program. This makes it particularly suitable for studying iso-electronic sequences: the algebra is calculated once and for all at the beginning, and the analytic branch is called to calculate radial wavefunctions, energies etc. for each new member of the sequence.
- (b) There is flexibility in the type of radial wavefunctions which may be used. Radial wavefunctions can either be (i) supplied by the user or (ii) computed within the program in a modified Thomas–Fermi potential [4].
- (c) The program can process the intermediate-coupling electric dipole transition probabilities to give cascade coefficients. These coefficients contain transition probability information in a compact form which is particularly suitable for a variety of astrophysical applications.

The plan of the paper is as follows: in section 2 the non-relativistic problem is considered, including a detailed description of the procedure used to generate the vector-coupling coefficients with which the eigenfunctions of  $L^2$ ,  $L_z$ ,  $S^2$  and  $S_z$  are constructed. Section 2 also includes a description of the way in which the variational procedure is applied within the program. In section 3, the matrix elements of the operators of the Breit–Pauli hamiltonian are expressed in a concise form, suitable for computation. After describing the method of calculation section 3 ends with a discussion of the accuracy of the Breit–Pauli approximation. The radiative problem is formulated in section 4. In section 5, the term-coupling coefficients are defined and discussed. Section 6 is a review of the checking procedures used for testing the various parts of SUPERSTRUCTURE. The paper is concluded with section 7 which consists of a critique of the techniques described in the sections which precede it. As well as containing some suggestions for further refinements of certain aspects of SUPERSTRUCTURE, section 7 contains a brief comparison of some of the techniques with those adopted by other workers.

It is hoped that this full description of the techniques incorporated in our multi-purpose atomic structure package will be of help to other workers who are developing similar packages. For this reason, the formulation of the theory sometimes extends beyond that actually incorporated in SUPERSTRUCTURE.

Throughout this paper, the works of Condon and Shortley [2], and Eissner and Nussbaumer [4] will be referred to as TAS and EN respectively.

## 2. The non-relativistic problem

### 2.1. The non-relativistic hamiltonian and its matrix elements

The non-relativistic bound-state problem of one electron in the field of a nucleus, that is hydrogenic systems, can be solved exactly. For systems with more than one electron it is not possible to obtain a solution in closed analytic form: approximate solutions are sought which satisfy the variational principle:

$$\delta \{ \langle t | H - E | t' \rangle \} = 0 \quad (1)$$

(see for example ref. [11]). In eq. (1)  $t$  and  $t'$  label the trial functions. In the non-relativistic problem  $H$  is given by:

$$H = H_{\text{nr}} = \sum_{i=1}^N h_i + \sum_{i>j} \frac{2}{r_{ij}}, \quad \text{where } h_i = -\nabla_i^2 - \frac{2Z}{r_i}. \quad (2)$$

In (2),  $N$  is the number of electrons, and  $Z$  is the electric charge of the nucleus as given by the number of protons. In eq. (2) and subsequently, the Bohr radius  $a_0 = \hbar^2/me^2 = 0.529 \times 10^{-8}$  cm is the unit of length, and the Rydberg  $\text{Ry} = e^2/2a_0 = 13.59$  eV is the unit of energy; angular momenta will be scaled in units of  $\hbar = 1.054 \times 10^{-27}$  erg·sec. In a system described by the hamiltonian (2), the total spin  $\mathbf{S}$  and the total orbital angular momentum  $\mathbf{L}$  are separately conserved. In practice, the rather formal matrix element on the left-hand side of (1) is evaluated between coordinate functions  $\langle X | t \rangle$ . If we assume that these functions are separable in the coordinates of each electron, it follows that each label  $t$  can be written more explicitly in terms of a configuration label and definite values of  $S$  and  $L$ , where a configuration is defined by a set of one-particle orbitals  $n_i l_i$ . We can represent a configuration thus:

$$C \equiv (n_1 l_1)^{q_1} (n_2 l_2)^{q_2} \cdots (n_m l_m)^{q_m}, \quad \text{where } \sum_{\gamma=1}^m q_\gamma = N. \quad (3)$$

Each configuration gives rise to a set of terms  $t$  where

$$t = C\beta SL, \quad (4)$$

in which  $\beta$  is a degeneracy parameter taking into account those cases when a configuration  $C$  gives rise to more than one term with the same  $SL$ .

In general, the wavefunctions determined from eq. (1), with  $H$  given by (2), will be linear combinations of wavefunctions designated by the labels  $t$  of eq. (4):

$$|\Gamma S L M_S M_L\rangle = \langle C\beta SL | \Gamma S L \rangle |C\beta S L M_S M_L\rangle. \quad (5)$$

On the right-hand side of eq. (5) there is an implied summation over  $C\beta$ . The expansion (5) is a consequence of the fact that  $H_{\text{nr}}$  is not diagonal with respect to configurations  $C$  nor with respect to any degenerate terms  $\beta$  within those configurations. We will refer to the representation  $t$  as the configuration representation. In this representation the angular coefficients  $A$  and  $B$  in the following expansion of the matrix elements of  $H_{\text{nr}}$  are purely algebraic:

$$\langle t M_S M_L | H_{\text{nr}} | t' M'_S M'_L \rangle = \delta(S, S') \delta(L, L') \delta(M_S, M'_S) \delta(M_L, M'_L) \left\{ \sum_{\nu} A_{tt'}^{(\nu)} I(a, c) + 2 \sum_{\nu} B_{tt'}^{(\nu)} R_{\lambda}(ab, cd) \right\}. \quad (6)$$

In (6),  $I$  and  $R_{\lambda}$  are the radial integrals

$$I(nl, n'l) = \int_0^\infty dr P_{nl}(r) \left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r} \right\} P_{n'l}(r), \quad (7)$$

and

$$R_\lambda(ab, cd) = \int_0^\infty dr P_b(r) P_d(r) y_\lambda(a, c; r) \quad \text{in which}$$

$$y_\lambda(a, c; r) = \frac{1}{r^{\lambda+1}} \int_0^r dr' P_a(r') r'^\lambda P_c(r') + r^\lambda \int_r^\infty dr' P_a(r') \frac{1}{r'^{\lambda+1}} P_c(r'). \quad (8)$$

In the expansion (6), the index  $\nu$  numbers each coefficient. It is assumed that in the first summation on the right-hand side of (6),  $a$  and  $c$  depend upon  $t, t'$  and  $\nu$  where  $a = n^a l^a, c = n^c l^c$ ; in the second summation it is assumed that  $a, b, c, d$  and  $\lambda$  depend upon  $t, t'$  and  $\nu$ .

The coefficients  $A^{(\nu)}$  and  $B^{(\nu)}$  are calculated from wave functions  $\langle X | t M_S M_L \rangle$ , which are effectively expanded in terms of Slater determinants. As discussed in section 2.2, we can work in terms of Slater states when calculating algebraic coefficients  $A^{(\nu)}$  and  $B^{(\nu)}$ : the states  $|t M_S M_L\rangle$  can be expanded in terms of Slater states thus:

$$|t\rangle = \langle u | t \rangle |u\rangle. \quad (9)$$

In (9) we have omitted  $M_S M_L$  from both sides of the equation: we assume that the value of  $M_S M_L$  is included within the Slater state label  $u$ , which is summed over in (9). A Slater state  $|u\rangle$  is defined by

$$|u\rangle = \prod_{q=1}^N |n_q l_q \mu_q m_q\rangle, \quad (10)$$

where  $n_q l_q \mu_q m_q$  represents the usual set of one-electron quantum numbers  $n l m_s m_l$  for the  $q$ th electronic state. In order to obtain consistent sets of coupling coefficients  $\langle u | t \rangle$  it is necessary, among other things, to list the sets of one-electron quantum numbers in some conventional order. Within SUPERSTRUCTURE we use the standard order specified in TAS (chapter 6), that is: (a) all the subsets are listed shell by shell, all the sets of a given shell being placed together, (b) within each shell, the sets are listed in decreasing order of  $m$ , the set with  $\mu = +\frac{1}{2}$  being placed before the set with  $\mu = -\frac{1}{2}$  when both sets have the same value of  $m$ . In eq. (9) the summation over the Slater states  $u$  must include all those states  $u$  satisfying

$$M_S = \sum_{q=1}^N \mu_q, \quad M_L = \sum_{q=1}^N m_q. \quad (11)$$

The matrix elements of  $H_{nr}$  are evaluated in the Slater state representation  $u$  and are then transformed into the configuration representation  $t$  using (9), that is

$$\langle t | H_{nr} | t' \rangle = \langle t | u \rangle \langle u | H_{nr} | u' \rangle \langle u' | t' \rangle. \quad (12)$$

The transformation coefficients  $\langle u | t \rangle$  appearing in (9) and (12) are normally referred to as vector-coupling coefficients: Eissner and Nussbaumer write them more explicitly in the form

$$C \begin{matrix} l_1 & l_2 & \dots, \dots, \dots & l_N & \beta & S & L \\ \mu_1 m_1 & \mu_2 m_2 & & \mu_N m_N & M_S & M_L \end{matrix},$$

where commas separate groups of equivalent electrons. The vector-coupling coefficients are obtained by means

of a procedure which is described in detail in section 2.2. Necessary precautions required to ensure phase consistency between the eigenvectors belonging to different  $M_S M_L$  of any given term  $SL$  are also discussed in that section. As coefficients relating the orthonormal basis sets  $|u\rangle$  and  $|tM_S M_L\rangle$  to each other within a given subspace  $\{M_S M_L\}$  the  $C$ 's must satisfy

$$\sum_{u\{M_S M_L\}} \mathbf{C}_{\mu_1 m_1 \mu_2 m_2 \dots \mu_N m_N}^{l_1 l_2 \dots l_N ; \beta S L} \mathbf{C}_{\mu_1 m_1 \mu_2 m_2 \dots \mu_N m_N}^{l_1 l_2 \dots l_N ; \beta' S' L'} = \delta(\beta, \beta') \delta(S, S') \delta(L, L'), \quad (13)$$

which reflects the identity

$$\langle t|u\rangle\langle u|t'\rangle = \delta(t, t'). \quad (14)$$

We now consider how  $\langle u|H_{\text{nr}}|u'\rangle$  is calculated. We note first that the matrix elements of  $H_{\text{nr}}$  are independent of  $M_S M_L$ . Secondly we note that the Slater determinants are constructed from one-electron wave functions which are separable in spherical polar coordinates:

$$\langle nl\mu m|\sigma r\rangle = \langle nl|r\rangle \langle lm|\hat{r}\rangle \langle \mu|\sigma\rangle,$$

where

(15)

$$\langle r|nl\rangle = R_{nl}(r) = (1/r)P_{nl}(r), \quad \langle \hat{r}|lm\rangle = Y_{lm}(\vartheta, \varphi), \quad \langle lm|\hat{r}\rangle = Y_{lm}^*(\vartheta, \varphi).$$

Choosing spherical harmonics  $Y_{lm}(\vartheta, \varphi)$  for orbital functions  $\langle \hat{r}|lm\rangle$  is consistent with the usual meaning of the component index  $m$  ( $\langle \hat{r}|1, 0\rangle = \sqrt{3/4\pi} \cos \vartheta$  and  $\langle \hat{r}|1, \pm 1\rangle = \mp \sqrt{3/8\pi} \sin \vartheta e^{\pm i\varphi}$  relates  $\vartheta$  and  $\varphi$  of the direction vector  $\hat{r}$  to the three vectors  $|1m\rangle$ );  $\langle \sigma|s = \frac{1}{2}, \mu\rangle$  is a spin function. Techniques for evaluating matrix elements between Slater states have been described in TAS (chapter 6). It will be assumed that the one-electron wave functions form an orthonormal set. The radial functions in (15) should therefore satisfy the condition

$$\int_0^\infty P_{nl}(r) P_{n'l'}(r) dr = \delta_{nn'}. \quad (16)$$

According to TAS, the matrix elements of one-electron operators in a Slater determinant representation can be expressed in terms of matrix elements between one-electron functions. The matrix elements of the one-electron operators of  $H_{\text{nr}}$  between one-electron wave functions satisfying (15) and (16) are

$$\langle a|-\nabla^2 - 2Z/r|c\rangle = \delta(\mu^a, \mu^c) \delta(m^a, m^c) \delta(l^a, l^c) I(a, c). \quad (17)$$

Similarly, the matrix elements of two-electron operators between  $N$ -electron Slater determinants can be expressed in terms of matrix elements between products of two-electron wavefunctions. Thus we also require

$$\langle ab|\frac{2}{r_{12}}|cd\rangle = \delta(m^a + m^b, m^c + m^d) \delta(\mu^a, \mu^c) \delta(\mu^b, \mu^d) \sum_{\lambda=0}^{\infty} (-1)^{m^a - m^d} c_\lambda(l^a m^a, l^c m^c) c_\lambda(l^b m^b, l^d m^d) R_\lambda(ab, cd),$$

where

(18)

$$c_\lambda(lm, l'm') = \frac{\sqrt{(2l+1)(2l'+1)}}{2\lambda+1} \mathbf{C}_{000}^{l l' \lambda} \mathbf{C}_{-m m' m'-m}^{l l' \lambda}$$

Eq. (A9), in Appendix A, indicates that the angular coefficients  $c_\lambda$  introduced in (18) originate from a spherical tensor operator  $C^{[\lambda]}$ , in fact from factorizing  $1/r_{ij}$ ; the coefficients  $C_{m m' \kappa}^{l l' \lambda}$  are Clebsch–Gordan coefficients.

Eissner and Nussbaumer ([4], section 3) give full details of how the matrix elements  $\langle u|H_{\text{nr}}|u'\rangle$  are deduced from one-electron and two-electron matrix elements given in eq. (17) and (18) respectively. They also discuss how the transformation (12) is applied to yield  $\langle t|H_{\text{nr}}|t'\rangle$  and how the coefficients  $A^{(v)}$  and  $B^{(v)}$  are obtained.

## 2.2. The method for calculating vector-coupling coefficients

We consider in some detail the procedures employed in SUPERSTRUCTURE for the calculation of the vector-coupling coefficients of eq. (9), since considerable care is required to obtain sets of coefficients with consistent phases. Lack of phase consistency can lead to serious errors in the matrix elements of the fine-structure interactions and in the radiative matrix elements.

### 2.2.1. Slater states and Slater determinants

The program employs techniques in which all the angular operators act on Slater states  $|u\rangle$  rather than on the spatial and spin coordinates in the Slater determinants  $\langle x_1, \dots, x_N | \mathfrak{A} | u \rangle$ , where  $x_p = (r_p, \sigma_p)$  and  $\mathfrak{A}$  is the completely antisymmetric normalised permutation operator. Hence throughout the whole program we never deal explicitly with Slater determinants. A sufficiently large set of standard ordered Slater states is set up, and sufficient information to specify this set is retained in the algebraic branch of the program. The antisymmetrisation operation represented by  $\mathfrak{A}$  may be equally well carried out by permuting the sets  $(n_q l_q \mu_q m_q)$  or by permuting the particle vectors  $x_p$ . By considering the  $N!$  sets in  $\mathfrak{A} | u \rangle$  for each  $u$ , and incidentally promoting the sequential indices  $q$  in (10) to particle indices  $p$ , we can account for the effect of antisymmetrisation without explicitly using Slater determinants.

### 2.2.2. Procedure

The vector-coupling coefficients (VCC's) are obtained by finding linear combinations of Slater states which are simultaneous eigenvectors of  $S^2$  and  $L^2$ . This is accomplished by diagonalising the matrices of  $S^2$  and  $L^2$ , followed by application of stepping operators  $S_-$  and  $L_-$ . In practice, the program adopts the following procedure:

(i) The matrices of  $S^2$  and  $L^2$  are evaluated in the Slater state representation. Let  $J$  represent an angular momentum operator  $S$  or  $L$ . We express  $J$  in the orbital reference frame induced by our choice in (15), that is by its three spherical tensor components  $J_\kappa$ :

$$J^2 = J_+ J_- + J_0^2 - J_0, \quad J_\kappa = \sum_{p=1}^N j_\kappa(p), \quad \kappa = -1, 0, +1. \quad (19, 20)$$

Eq. (20) shows how  $J$  is composed of one-particle operators, and it introduces a useful notation for particle indices. In order to evaluate  $\langle u | j^2 | u' \rangle$ , the following relations will be required:

$$J_0 | u \rangle = M | u \rangle, \quad J_\pm \prod_{q=1}^N |\beta_q j_q m_q \rangle = \sum_{p=1}^N \sqrt{(j_p \mp m_p)(j_p \pm m_p + 1)} \prod_{q=1}^N |\beta_q j_q m_q \pm \delta_{pq} \rangle, \quad (21)$$

where  $\beta_q$  represents those one-particle quantum numbers that are not affected by  $J$ , and  $M$  is the sum over the  $m_q$ 's, which is  $M_S$  or  $M_L$ . Eqs. (19) and (21) bring out the reducibility pattern for  $S^2$  and  $L^2$ : state subspaces classified by  $\{M_S, M_L\}$  are invariant. Let us first consider one such set  $\{M_S, M_L\}$  of Slater states  $u$ .

(ii) The matrix  $\langle u | S^2 | u' \rangle$  is diagonalised. Let the real unitary matrix, which performs this diagonalisation, be  $T$ , that is

$$\sum_{u, u'} T_{u'i} \langle u | S^2 | u' \rangle T_{u'i'} = \delta_{ii'} S(S+1). \quad (22)$$

(iii) The matrix  $\langle u | L^2 | u' \rangle$  is set up and transformed thus:

$$\sum_{u, u'} T_{u'i} \langle u | L^2 | u' \rangle T_{u'i'} = U_{ii'}. \quad (23)$$

(iv) The matrix  $U_{ii'}$  is diagonalised:

$$\sum_{i,i'} V_{ii'} U_{ii'} V_{i't'} = \delta_{it'} L(L+1). \quad (24)$$

In eq. (23), the index  $t$  refers to the representation defined in (4).

(v) The VCC's are obtained from the columns of the product  $TV$ , that is

$$\sum_i T_{ui} V_{ii} = \langle u | t \rangle. \quad (25)$$

The subsequent steps in the procedure will depend upon the choice of an input parameter  $MOD^\dagger$  which governs the choice and range of  $M_S M_L$  for which VCC's are to be computed. The above diagonalisation procedure is adequate when a Slater state set belonging to only one  $\{M_S, M_L\}$  is required. For example, the set  $\{|M_S| = \text{minimum} - \text{i.e. } 0 \text{ or } \frac{1}{2}, M_L = 0\}$  suffices for computing term energies. However in the calculation of radiative data and matrix elements for fine structure interactions, VCC's for more than one  $M_S M_L$  of a given  $SL$  will be required. Use of the above diagonalisation procedure for more than one  $M_S M_L$  will in general lead to phase inconsistencies between the different sets of vector-coupling coefficients. Two separate cases arise:

(a) Non-degenerate terms  $SL$ . Systems of vectors belonging to  $\{M_S M_L\}$  and  $\{M'_S M'_L\}$  and the same  $SL$  are ambiguous by a factor  $\pm 1$ , corresponding to a reflection in the space of the  $SL$ 's.

(b) Configurations which give rise to  $\gamma$  degenerate terms  $SL$ . The ambiguity in a set of vectors belonging to a given  $M_S M_L$  will involve a rotation in the  $\gamma$ -dimensional subspace of  $SL$ .

Taking case (a) first, it is convenient to use the diagonalisation procedure for all required  $M_S M_L$ , since it automatically gives eigenvectors satisfying the orthogonality relation (13). Phase adjustments are made as they are required. In detail, the following sequence is used:

(1) The diagonalisation procedure [(i) to (v) above] is applied for the set of Slater states belonging to  $(M_S = S, M_L = L)$ , giving a set of coefficients  $\langle CSL M_S = S, M_L = L | u \rangle$ .

(2) The diagonalisation procedure is applied for the set of states belonging to  $(M_S = S - 1, M_L = L)$ , giving a set of coefficients  $\langle CSL M_S = S - 1, M_L = L | u \rangle$ .

(3) The first *non-vanishing* coefficient of a particular Slater state, say the  $p$ th state, is picked out from the set obtained in step (2). A partial application of  $S_-$  to the eigenvector  $|CSLM_S = S, M_L = L\rangle$  using the relation

$$S_- |CSLM_S M_L\rangle = \sum_u \langle u | CSLM_S M_L \rangle S_- |u\rangle = \sqrt{(S+M_S)(S-M_S+1)} |CSLM_S - 1 M_L\rangle, \quad (26)$$

together with the relation (21) for  $S_- |u\rangle$  yields the  $p$ th coefficient of the set  $u(M_S = S - 1, M_L = L)^*$ . The coefficient obtained in this way is compared with the corresponding coefficient obtained from step (2). If the sign differs, the whole of the latter vector is multiplied through by  $-1$ .

(4) Steps (1) to (3) may be repeated until coefficients for the required number of values of  $M_S$  are obtained.

(5) To obtain vectors with  $M_L < L$ ,  $L_-$  is applied to the eigenvector  $|CSLM_S = S, M_L + 1\rangle (M_L \neq L)$ .

In case (b) the procedure is very similar to that outlined in steps (1) to (5) above. However, in step (3), the whole eigenvector, rather than just one component is computed by the application of stepping operators (as in the example given in TAS ch. 8, section 5). The vectors obtained by the diagonalisation procedure for  $M_S < S$  and  $M_L < L$  are discarded. Of course application of the diagonalisation procedure for  $M_S = S, M_L = L$  is always sufficient to ensure orthogonality of vectors belonging to different  $SL$  [eq. (13)].

Steps (1) to (5) are a simplification of the procedure actually implemented in SUPERSTRUCTURE, since they concentrate on only one term  $SL$ . SUPERSTRUCTURE begins generating VCC's for the term with the highest values of  $S$  and  $L$  in the configurations being considered. As the step-down operators  $S_-$  and  $L_-$  are applied eigenvectors of terms with lower values of  $S$  and  $L$  appear successively. However the remaining terms (which have higher

<sup>†</sup> Here and in a number of subsequent examples the Fortran notation of the package is used.

\* Evaluation of VCC's by application of stepping operators is fully explained in chapter 8, section 5 of TAS.

values of  $S$  or  $L$  than the new term) have appeared before and so their eigenvectors are obtained either by phase adjustment of the eigenvectors resulting from the diagonalisation or entirely from the stepping procedure, depending on whether they are of type (a) or (b) respectively.

### 2.2.3. Critical discussion

We make three comments on the techniques employed:

- (i) The VCC's could all be derived by stepping operations  $S_{\pm}$  and  $L_{\pm}$  from the eigenvector  $|C\beta SL| M_S = \text{minimum}, M_L = 0\rangle$ . This would sometimes be faster, but even then only marginally. Use of this would have made the code considerably more complicated and in many cases it would increase the storage requirements. The procedure described above is very flexible in that it allows one to easily control the range of values of  $M_S M_L$  over which Slater states and VCC's are available. In SUPERSTRUCTURE this range is controlled by an input parameter MOD. For example MOD = 3 specifies that VCC's are to be calculated for  $M_S = S$  and  $M_L = L$ : this is adequate for calculation of non-relativistic term energies for a given type  $SL$ ; since the smallest possible set of Slater states and VCC's is used, both storage and computer time requirements are minimised. However this option would be difficult to implement economically if all coefficients were generated from the eigenfunction with  $M_S = \text{minimum}$  and  $M_L = 0$ .
- (ii) In our procedure, matrix diagonalisations are carried out, that is, eigenvalue problems are solved. In all cases the eigenvalues themselves are known, and thus all that is required is the solution of sets of linear simultaneous equations. However, with a matrix diagonalization routine available in the package for other purposes we adopted the approach described above; it is no thought that it leads to any significant inefficiency.
- (iii) It was remarked earlier that there is no need to carry out any matrix diagonalisations to generate VCC's for negative values of  $M_S$  or  $M_L$ . SUPERSTRUCTURE does however carry out matrix diagonalisations for all required values of  $M_S M_L$  and thus it may do some superfluous work. However, it is possible to reject Slater states and VCC's for all or most negative values of  $M_S$  and  $M_L$  in the majority of calculations, so that in practice very little timewasting occurs and an increase in the complexity of the code is avoided.

### 2.3. Radial wavefunctions

SUPERSTRUCTURE can use either (i) Thomas–Fermi statistical model radial functions calculated within the program, or (ii) radial functions provided as input in numerical form.

In case (i) the radial functions  $P_{nl}$  are solutions of the equation

$$\left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2V(\lambda_l, r) + \epsilon_{nl} \right\} P_{nl}(r) = 0, \quad (27)$$

subject to the boundary conditions

$$\lim_{r \rightarrow \infty} \{P_{nl}/r^{l+1}\} = A_{nl}, \quad \lim_{r \rightarrow \infty} \{P_{nl}(r)\} = B_{nl} \exp(-\sqrt{\epsilon}r), \quad (28)$$

where  $A_{nl}$  and  $B_{nl}$  are constants. In (27) the potential  $V(\lambda_l, r)$  is a scaled statistical model potential of Thomas–Fermi–Dirac type, described by Gombás [10]. This potential can be written in the form

$$V(\lambda_l, r) = \mathcal{L}(Z, N, r/\lambda_l)/r, \quad (29)$$

where

$$\lim_{r \rightarrow 0} \mathcal{L}(Z, N, r/\lambda_l) = Z, \quad \lim_{r \rightarrow \infty} \mathcal{L}(Z, N, r/\lambda_l) = Z - (N - 1). \quad (30)$$

The way in which the scaling parameter  $\lambda_l$  enters the potential is discussed in EN. Since the potential  $V$  in (27) is the same for all radial functions with the same  $l$ , it follows that the orthogonality condition (16) will be automatically satisfied. With wavefunctions which satisfy eq. (27) we can write the one-body integrals  $I$  of eq. (7) in the following form:

$$I(a, c) = \epsilon_a \delta(a, c) + 2 \int_0^{\infty} dr P_a(r) \{V(\lambda_l, r) - Z/r\} P_c(r). \quad (31)$$

In case (ii) the user must supply functions  $P_{nl}^{(0)}$  and functions  $Q_{nl}^{(0)}$  defined by

$$Q_{nl}^{(0)}(r) = \left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r} \right\} P_{nl}^{(0)}(r). \quad (32)$$

SUPERSTRUCTURE uses functions  $P$  and  $Q$  tabulated on a grid consisting of intervals containing a number of equal steps: the step length is doubled from one interval to the next as the radial variable increases. To accommodate radial functions tabulated on other grids, the program interpolates the supplied functions so that they suit the requirements of the program. A 6-point Lagrange interpolation formula is used:

$$f(x) = \sum_{t=t_1}^{t_1+5} L(x, t) f(x_t), \quad \text{where} \quad L(x, t) = \prod_{\substack{t=t_1 \\ (t \neq \tau)}}^{t_1+5} (x - x_\tau) / (x_t - x_\tau), \quad (33, 34)$$

The function  $f(x_t)$  is an input function  $P_{nl}^{(0)}$  or  $Q_{nl}^{(0)}$ . The points  $x_t$  are those at which the input functions are tabulated. The input functions do not need to be orthonormal: if they are not, a Schmidt procedure is used to produce orthonormal functions, so that (16) is satisfied:

$$P_{nl} = P_{nl}^{(0)} - \sum_{n' < n} c_{nl, n'l} P_{n'l}, \quad \text{where} \quad c_{nl, n'l} = \langle P_{nl}^{(0)} | P_{n'l} \rangle. \quad (35, 36)$$

In (35) and (36) the functions  $P_{n'l}$  are those which have already been orthogonalised, the sum over  $n'$  extending over the functions  $P_{n'l}$  which have already been processed. Starting with the first function read in by the program, which has  $n' = n_1$ , say, we set

$$P_{n_1 l} = P_{n_1 l}^{(0)}. \quad (37)$$

The recurrence relation (35) is then applied for each successive principal quantum number  $n$ , with  $n$  increasing. The same procedure is simultaneously applied to the input functions  $Q_{nl}$ , using the same coefficients  $c_{nl, n'l}$ . The functions  $P_{nl}^{(0)}$  are normalised in the usual way, and the corresponding  $Q_{nl}$  are multiplied by the same normalising factors.

Finally we note that in terms of the functions  $P_{nl}$  and  $Q_{nl}$ , the integrals  $I$  will be given by

$$I(a, c) = \int_0^{\infty} P_a(r) Q_c(r) dr. \quad (38)$$

#### 2.4. Energy eigenvalues and eigenfunctions: application of the variational principle

The variational principle (1) can be satisfied exactly for the off-diagonal matrix elements by straightforward matrix diagonalisation, which may be represented by the transformation

$$\langle \Gamma SL | H_{nr} | \Gamma' SL \rangle = \delta_{\Gamma \Gamma'} \langle \Gamma SL | t \rangle \langle t | H_{nr} | t' \rangle \langle t' | \Gamma' SL \rangle, \quad (39)$$

where the elements  $\langle \Gamma SL | t \rangle$  of the equivalence transformation are equal to the configuration-mixing coefficients of eq. (5); they are independent of  $M_S M_L$ . The vector space of the  $|C\beta SLM_S M_L\rangle$  is incomplete, since the configuration expansion is always truncated. With this property in mind we introduce an alternative notation for the coefficients of the real orthonormal configuration mixing matrix.

$$a^{SL}(\Gamma, C\beta) = \langle \Gamma SL | C\beta SL \rangle. \quad (40)$$

If scaled statistical model radial wave functions are employed, the wave functions  $P_{nl}$  depend upon the scaling parameters  $\lambda_l$ , which therefore can be treated as variational parameters. We write

$$E_i = E_i(\lambda_s, \lambda_p, \dots) = \langle \Gamma SL | H_{nr} | \Gamma SL \rangle, \quad (41)$$

where the maximum number NEXTRE of adjusting parameters is equal to the number of different orbital angular momenta in the set of orbitals involved. Eq. (1) can now be replaced by

$$\delta F = \delta \left\{ \sum_{i=1}^{\text{INCLUD}} g_i E_i(\lambda_s, \lambda_p, \dots) \right\} = 0, \quad (42)$$

where  $g_i$  is the statistical weight of the term  $i$  and INCLUD is the number of energies included in the minimisation procedure.

SUPERSTRUCTURE allows some flexibility in the minimisation procedure. In discussing the possible ways of carrying out the procedure, we will use the following nomenclature:

(1) If an approximation to the physical term energies of a given configuration is required, that configuration will be called a “spectroscopic configuration”.

(2) Two types of configurations may be added in order to give a better description of the terms of interest. These are, firstly, configurations in the same complex\*, and secondly, so-called correlation configurations, which are additional configurations not belonging to the complex but whose effects are comparable to those of configurations belonging to the complex. The energies of terms arising from the correlation configurations will not be meaningful in a spectroscopic sense. In addition, terms belonging to spectroscopic and correlation configurations will be referred to as “spectroscopic terms” and “correlation terms” respectively. This nomenclature is consistent with that introduced by Weiss [13].

Returning to (42), it is usual to set the parameter INCLUD to a value such that all terms up to the highest term of interest are included in the summation. This choice leads to a common set of radial functions, particularly convenient for the calculation of relativistic corrections and radiative data. Terms arising from correlation configurations should not be included within the summation of (42). We also note that correlation terms which do not interact with any of the spectroscopic terms are redundant and may be suppressed. SUPERSTRUCTURE allows for this: a number KCUT, which can be specified in the input, signifies that configurations  $e_k$  having  $k > \text{K CUT}$  are to be treated as correlation configurations. Any correlation terms which are not matched by at least one spectroscopic term with the same values of  $S$  and  $L$  will then be suppressed. KCUT may also be used to suppress superfluous terms arising from configurations within the complex. The parameter INCLUD should not exceed the number of terms in the first KCUT configurations. For example, consider the terms arising from the three lowest configurations of a carbon-like ion:

$$e_1 = 1s^2 2s^2 2p^2, \quad e_2 = 1s^2 2s 2p^3, \quad e_3 = 1s^2 2p^4.$$

Suppose that a correlation configuration  $e_4 = 1s^2 2s 2p^2 3d$  is included, using a suitable 3d radial function. Only nine of the twenty-eight terms arising from  $e_4$  need be retained, namely the four  $^3P$  terms, the four  $^1D$  terms and the single  $^1S$  term, all of which couple with terms arising from  $e_1$  and  $e_3$ .

The following points of practical importance should be noted: (i) Layzer [14] has shown that it is essential to include all the configurations of the complex in order to correctly reproduce the first two terms of the  $Z$ -expansion of the non-relativistic energy. Thus, all the configurations of the complex should be included, as far as this is practicable. In the above example,  $e_1$  and  $e_3$  lie in the same complex and should thus both be included in the calculation. In some cases the number of configurations in the complex can be impracticably large.

\* A complex is defined by a set of principal quantum numbers and a definite parity [14].

Nussbaumer [15] has considered such a case. Using first-order perturbation theory for the configuration-mixing wavefunction as a basis for his discussion, Nussbaumer gives some criteria for selecting the most important configurations of the complex and illustrates their application with a detailed numerical example. (ii) When correlation configurations are included which contain orbitals with angular momenta  $l$  differing from those of any orbitals already present in the spectroscopic configurations, these orbitals should have a similar mean radius to those orbitals of the spectroscopic configurations for which they substitute ([16]; also ref. [17] gives numerical examples from multi-configuration Hartree–Fock calculations). In the C I sequence example given above, the 3d orbitals of configuration  $\mathcal{C}_4$  should have a similar mean radius to the 2s orbital [17, 18] to distinguish this correlation orbital from an ordinary excited-state orbital, we denote it by  $\overline{3d}$  or, more generally,  $\overline{nl}$ .

It is possible to run SUPERSTRUCTURE in a mode such that only terms with one value  $SL$  are considered. This approach, which is inherent in most selfconsistent-field programs, will result in a minor improvement in the term energies. However, this is achieved at the expense of having different sets of radial functions for different values  $SL$ . In applications such as calculation of radiative data or of collision processes involving more than one sort of  $SL$ , one would have to orthogonalize the sets first as described in section 2.3; otherwise one cannot solve the angular problems with mere algebraic means. Therefore in most applications it is better to assume a common set of radial functions right from the start, and to expand in terms of more configurations instead.

### 3. Relativistic corrections

#### 3.1. The Breit–Pauli hamiltonian

The Breit–Pauli hamiltonian  $H_{BP}$  can be written

$$H_{BP} = H_{nr} + H_{rc}, \quad (43)$$

where  $H_{nr}$  has been defined in (2) and  $H_{rc}$  is a sum of relativistic correction operators:

$$H_{rc} = \sum_{i=1}^N \{f_i(\text{mass}) + f_i(\text{d}) + f_i(\text{so})\} + \sum_{i>j} \{g_{ij}(\text{so} + \text{so}') + g_{ij}(\text{ss}') + g_{ij}(\text{css}') + g_{ij}(\text{d}) + g_{ij}(\text{oo}')\}. \quad (44)$$

In (44) the various operators are:

(i) The one-body terms

$$f_i(\text{mass}) = -\frac{1}{4}\alpha^2 \nabla_i^4, \quad f_i(\text{d}) = -\frac{1}{4}Z\alpha^2 \nabla_i^2 (1/r_i), \quad f_i(\text{so}) = (Z\alpha^2/r_i^3) l(i) \cdot s(i). \quad (45)$$

(ii) The two-body fine structure terms

$$g_{ij}(\text{so} + \text{so}') = -\alpha^2 \left\{ \left( \frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \right) \cdot (s(i) + 2s(j)) + \left( \frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_j \right) \cdot (s(j) + 2s(i)) \right\}, \quad (46)$$

$$g_{ij}(\text{ss}') = 2\alpha^2 \left\{ \frac{s(i) \cdot s(j)}{r_{ij}^3} - 3 \frac{(s(i) \cdot r_{ij})(s(j) \cdot r_{ij})}{r_{ij}^5} \right\}'.$$

(iii) The two-body non-fine structure terms

$$g_{ij}(\text{css}') = -\frac{16\pi}{3}\alpha^2 s(i) \cdot s(j) \delta^3(\mathbf{r}_{ij}), \quad g_{ij}(\text{d}) = \frac{1}{2}\alpha^2 \nabla_i^2 \left( \frac{1}{r_{ij}} \right), \quad g_{ij}(\text{oo}') = -\frac{\alpha^2}{r_{ij}} \left( \mathbf{p}_i \cdot \mathbf{p}_j + \frac{r_{ij} \cdot (r_{ij} \cdot \mathbf{p}_j) \mathbf{p}_i}{r_{ij}^3} \right). \quad (47)$$

In eqs. (45), (46) and (47), those operators already purely spherical have their particle index attached according to the notation in (20). Others have yet to be reduced before evaluating matrix elements in a Slater state representation: this will involve spherical vector operators  $C(q)$  when expanding the radius vector  $r_{ij} = r_j - r_i$  (see explicit expression in (105));  $p_q$  can be expressed in terms of  $l(q)$ ; factors  $1/r_{ij}$  involve products  $C^{[\lambda]}(i) \cdot C^{[\lambda]}(j)$  in a Legendre series, which is familiar from deriving (18).

A dot has been used to indicate scalar multiplication ( $\mathbf{a} \cdot \mathbf{b}$ ). When evaluating matrix elements of (47), the prime bracket in  $g_{ij}(ss')$  is to be replaced by zero for  $r_{ij} < \epsilon$  when used in an integral over position space, the limit of the integral being taken as  $\epsilon \rightarrow 0$ . With wavefunctions constructed from one-electron spin-orbitals (15) it is not necessary to perform this limiting process numerically.

The physical significance of the various operators in (45), (46) and (47) has been discussed elsewhere (e.g. [19]) and it will suffice here to name the interactions. In (45),  $f_i(\text{mass})$  is the mass-variation correction,  $f_i(\text{d})$  is the one-body Darwin term and  $f_i(\text{so})$  is the operator representing spin-orbit interaction of the  $i$ th electron in the field of the nucleus. In (46)  $g_{ij}(\text{so} + \text{so}')$  is made up of two contributions, namely spin-other-orbit interaction (terms in the first equation of (46) containing a factor 2) and mutual spin-orbit interaction. The former comes from the Breit interaction [19, 37], and the latter comes from reduction of the many-body generalisation of the Dirac equation from [37]. The interaction  $g_{ij}(ss')$  is the spin-spin interaction, and in (47)  $g_{ij}(css')$  is the spin-spin contact interaction,  $g_{ij}(\text{d})$  is the two-body Darwin term and  $g_{ij}(\text{oo}')$  is the orbit-orbit interaction.

We distinguish between fine structure and non-fine structure interactions. The interaction  $\sum_i f_i$  or  $\sum_{i>j} g_{ij}$  may all be written as scalar products

$$V^{[k;0]} = O^{[k]} \cdot S^{[k]}, \tag{48}$$

where

$$k = \begin{cases} 0 & \text{for non-fine structure interactions;} \\ 1 & \text{for spin-orbit, mutual spin-orbit and spin-other-orbit interactions;} \\ 2 & \text{for the spin-spin interaction.} \end{cases} \tag{48}$$

In (48)  $O^{[k]}$  is an orbital angular momentum operator and  $S^{[k]}$  is the spin angular momentum operator. In this paper we consider only those interactions which can be written as vector (i.e.  $k = 1$ ) or tensor forces of degree  $k = 2$  [20] to be fine structure interactions. In this we differ from some other workers: for example, Armstrong [21] considers the spin-spin contact interaction to be a fine structure interaction, although it is a scalar force ( $k = 0$ ) [20].

Since the non-fine structure interactions are scalars both in  $S$  and  $L$ , they will commute with  $S^2$ ,  $S_z$ ,  $L^2$  and  $L_z$ ; they can therefore be considered in the representation  $t$  [eq. (4)]. On the other hand, the fine structure interactions only commute with  $J^2$  and  $J_z$ , where  $J$  and  $J_z$  are the total angular momentum and its azimuthal component respectively. It follows that a convenient representation for  $H_{\text{BP}}$ , or more specifically, for the fine structure interactions is

$$UM = C\beta SLJM. \tag{49}$$

This representation can be obtained from the representation  $t$  of (4) by means of the additional coupling

$$|C\beta SLJM\rangle = \langle SLM_S M_L | JM\rangle |C\beta SLM_S M_L\rangle = \sum_{M_S M_L} \mathbf{C}_{M_S M_L M}^{S L J} |C\beta SLM_S M_L\rangle. \tag{50}$$

In the representation (50), the matrix elements of  $H_{\text{BP}}$  can be written

$$\langle UM|H_{\text{BP}}|U'M'\rangle = \delta(J, J') \delta(M, M') \quad (51)$$

$$\times \left\{ \sum_{\nu} A_{it}^{(\nu)} I^c(a, c) + 2 \sum_{\nu} B_{it}^{(\nu)} R_{\lambda}^c(ab, cd) + \sum_{\nu} C_{UU'}^{(\nu)} \zeta(a, c) + \sum_{\nu} D_{UU'}^{(\nu)} V^{\lambda}(ab, cd) + \sum_{\nu} E_{UU'}^{(\nu)} N^{\lambda}(ab, cd) \right\},$$

where the coefficients  $A_{it}^{(\nu)}$  and  $B_{it}^{(\nu)}$  are the same as those in eq. (6), and  $U = tJ$ . The angular coefficients  $C_{UU'}^{(\nu)}$ ,  $D_{UU'}^{(\nu)}$  and  $E_{UU'}^{(\nu)}$  are purely algebraic. As in (6), the summations over each  $\nu$  contain a finite number of terms, and the arguments of the radial quantities  $\zeta$ ,  $V$  and  $N$  will depend upon  $\nu$ ,  $U$  and  $U'$ . The quantity  $I^c(a, c)$  consists of the one-body integral  $I(a, c)$  of eq. (7) plus corrections taking into account the mass-variation and one-body Darwin terms, and orbit-orbit interaction between valence electron and the closed shells;  $R_{\lambda}^c(ab, cd)$  is made up of a Slater integral  $R_{\lambda}(ab, cd)$  plus corrections taking into account the effect of the two-body non-fine structure interactions (47);  $\zeta$  is a generalised spin-orbit parameter of the type introduced by Blume and Watson [23], and  $V^{\lambda}$  and  $N^{\lambda}$  are magnetic integrals. Definitions of  $\zeta$ ,  $V^{\lambda}$  and  $N^{\lambda}$  will be given in section 3.3.

In SUPERSTRUCTURE, the two-body non-fine structure interactions of  $H_{\text{BP}}$  are neglected. Thus in the present program, the code representing (51) contains: (i) integrals  $I^c(a, c)$  taking account of mass-variation and one-body Darwin corrections only; (ii) integrals  $R_{\lambda}$  rather than  $R_{\lambda}^c$ . Also the coefficients  $E_{UU'}$  in SUPERSTRUCTURE take account of the two-body *fine structure* interactions only\*. However in section 3.4 we give the two-body non-fine structure interactions full consideration, presenting complete expressions for  $I^c(a, c)$  and  $R_{\lambda}^c(ab, cd)$ , so that they may be introduced into SUPERSTRUCTURE at a later stage. In that section we also discuss the possible effects of omitting those interactions.

### 3.2. The one-body terms

The term  $f(\text{mass})$ , like the Darwin term  $f(d)$ , is a purely radial operator, thus contributing to  $I^c(a, c)$  in (51). Its matrix elements are derived in the conventional way [22]:

$$\langle \phi | f(\text{mass}) | \phi \rangle = -\frac{1}{4} \alpha^2 \langle \phi | \nabla^4 | \phi \rangle = -\frac{1}{4} \alpha^2 \langle \nabla^2 \phi | \nabla^2 \phi \rangle. \quad (52)$$

We note that

$$\nabla^2 \phi(r, \vartheta, \varphi) = \frac{1}{r} \left( \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right) P_{nl}(r) Y_{lm}(\vartheta, \varphi), \quad (53)$$

where  $\phi$  is a one-particle wavefunction of type (15). The right-hand side of (53) can be written in terms of the functions  $Q_{nl}$  thus:

$$\nabla^2 \phi = \left\{ -Q_{nl} - \frac{2Z}{r} P_{nl}(r) \right\} \frac{1}{r} Y_{lm}(\vartheta, \varphi). \quad (54)$$

Hence it follows that

$$\langle n^a l^a \mu^a m^a | f(\text{mass}) | n^c l^c \mu^c m^c \rangle =$$

$$-\frac{1}{4} \alpha^2 \delta(l^a, l^c) \delta(m^a, m^c) \delta(\mu^a, \mu^c) \int_0^{\infty} \left\{ Q_{n^a l^a}(r) + \frac{2Z}{r} P_{n^a l^a}(r) \right\} \left\{ Q_{n^c l^c}(r) + \frac{2Z}{r} P_{n^c l^c}(r) \right\} dr. \quad (55)$$

If the functions  $P_{nl}$  satisfy eq. (27) we can write:

\* In our formulation, the orbit-orbit interaction makes no contribution to the sum containing the  $V^{\lambda}$  integrals.

$$\langle n^a l^a \mu^a m^a | f(\text{mass}) | n^c l^c \mu^c m^c \rangle = -\frac{1}{4} \alpha^2 \delta(l^a, l^c) \delta(m^a, m^c) \delta(\mu^a, \mu^c) \int_0^\infty P_{n^a l^a}(r) (\epsilon_{n^a l^a} - 2V(r)) (\epsilon_{n^c l^c} - 2V(r)) P_{n^c l^c}(r) dr. \quad (56)$$

For the Darwin term it follows from the potential equation  $\nabla^2(1/r) = -4\pi\delta^3(r)$  and the relation  $\delta^3(r) = (1/4\pi r^2) \delta(r)$ ,

$$\quad (57)$$

that its matrix elements are

$$\langle n^a l^a \mu^a m^a | f(d) | n^c l^c \mu^c m^c \rangle = \delta(l^a, l^c) \delta(\mu^a, \mu^c) \delta(m^a, m^c) Z\alpha^2 R_{n^a l^a}(0) R_{n^c l^c}(0). \quad (58)$$

It follows from (28) that  $R_{n^a l^a}(0)$  and hence the matrix element (58) is nonvanishing for s-orbitals only.

Bringing eqs. (55) and (48) together we obtain

$$\langle n^a l^a \mu^a m^a | f(\text{mass}) + f(d) | n^c l^c \mu^c m^c \rangle = \delta(l^a, l^c) \delta(\mu^a, \mu^c) \delta(m^a, m^c) J(a, c), \quad (59)$$

where

$$J(a, c) = \frac{1}{4} \alpha^2 \left[ ZR_a(0) R_c(0) - \int_0^\infty dr \left\{ Q_{n^a l^a}(r) + \frac{2Z}{r} P_{n^a l^a}(r) \right\} \left\{ Q_{n^c l^c}(r) + \frac{2Z}{r} P_{n^c l^c}(r) \right\} \right]. \quad (60)$$

We note that the algebraic factor in (59) is the same as that in the expression (17) for the matrix elements of the non-relativistic one-body terms.

The coefficients  $C_{JJ'}^{(v)}$  give the angular dependence of terms which behave like the spin-orbit interaction; they are constructed from the angular parts of the matrix elements of  $f_i(\text{so})$ :

$$\langle a | f_i(\text{so}) | c \rangle = \delta(l^a, l^c) \delta(\mu^a + m^a, \mu^c + m^c) \{ \delta(\mu^a, \mu^c) \mu^a m^a + \frac{1}{2} \delta(\mu^a, \mu^c \pm 1) \} \zeta, \quad (61)$$

$$\times \sqrt{(l^a - m^a - \mu^a + \frac{1}{2})(l^a + m^a + \mu^a + \frac{1}{2})} \zeta,$$

where  $\zeta_{\text{nu}}$  is the spin-orbit parameter obtained by taking into account the field of the nucleus only:

$$\zeta_{\text{nu}}(a, c) = \alpha^2 \int_0^\infty dr P_{n^a l^a}(r) P_{n^c l^c}(r) Z/r^3. \quad (62)$$

The coefficients  $C_{JJ'}^{(v)}$  are obtained from

$$\begin{aligned} \left\langle C\beta SLJM \left| \sum_{p=1}^N f_p(\text{so}) \right| C'\beta' S' L' J' M' \right\rangle &= \delta(J, J') \delta(M, M') \sum_{\substack{M_S M_L \\ M_{S'} M_{L'}}} \mathbf{C}_{M_S M_L}^{S L J} \mathbf{C}_{M_{S'} M_{L'}}^{S' L' J} \\ &\times \sum_{u, u'} \mathbf{C}_{\mu_1 m_1 \dots \mu_{N+1} m_{N+1}}^{l_1 \dots l_{N+1}; \beta S L} \mathbf{C}_{\mu'_1 m'_1 \dots \mu'_{N+1} m'_{N+1}}^{l'_1 \dots l'_{N+1}; \beta' S' L'} \left\langle u \left| \sum_{p=1}^N f_p(\text{so}) \right| u' \right\rangle. \end{aligned} \quad (63)$$

In (63)

$$\left\langle u \left| \sum_{p=1}^N f_p(\text{so}) \right| u' \right\rangle = (-1)^{q+q'} \langle n_q l_q \mu_q m_q | f(\text{so}) | n_{q'} l_{q'} \mu_{q'} m_{q'} \rangle \quad (64)$$

if the Slater states  $u$  and  $u'$  differ in one set of one-electron quantum numbers, namely the set  $q$  in  $u$  and the set

$q'$  in  $u'$ . Also

$$\left\langle u \left| \sum_{p=1}^N f_p(\text{so}) \right| u \right\rangle = \sum_q \langle n_q l_q \mu_q m_q | f(\text{so}) | n_q l_q \mu_q m_q \rangle \quad (65)$$

for diagonal matrix elements. In (64) and (65) the element  $\langle n l \mu m | f(\text{so}) | n' l' \mu' m' \rangle$  is obtained from (61). In the summations over  $u$  and  $u'$ , all coefficients of each spin-orbit parameter  $\zeta_{\text{nu}}(a, c)$  are added together to give the coefficients  $C_{UV}^{(v)}$ . The generalised spin-orbit parameter in (51) is discussed in section 3.3.

### 3.3. The two-body fine structure interactions

Blume and Watson [23] showed that mutual spin-orbit and spin-other-orbit interactions  $g_{ij}(\text{so} + \text{so}')$  between each valence electron and the closed shells behave like a one-body spin-orbit interaction. Thus these effects can be absorbed into the spin-orbit parameter to give a generalised spin-orbit parameter:

$$\zeta(n^a l^a, n^c l^c) = \zeta_{\text{nu}}(n^a l^a, n^c l^c) - \sum_{n^b l^b} 8(2l^b + 1)N^0(ab, cb) - \sum_{(1)}' - \sum_{(2)}' - \sum_{(3)}', \quad (66)$$

where

$$\sum_{(1)}' = -12 \sum_{n^b l^b} \sum_{\lambda=1}^{(a+l^b)} \left\{ \frac{l^a(l^a+1) + \lambda(\lambda+1) - l^b(l^b+1)}{2l^a(l^a+1)} \right\} \left[ \mathbf{C}_{0 \ 0 \ 0}^{l^a \ \lambda \ l^b} \right]^2 \{V^{\lambda-1}(ab, bc) - V^{\lambda-1}(ba, ab)\}, \quad (67)$$

$$\begin{aligned} \sum_{(2)}' &= -6 \sum_{n^b l^b} \sum_{\lambda=1}^{(a+l^b+1)} \frac{(\lambda+l^a+l^b+1)(\lambda-l^b+l^a+1)(\lambda-l^a+l^b+1)(l^a+l^b-\lambda+1)}{4l^a(l^a+1)(\lambda+1)} \\ &\times \left[ \mathbf{C}_{0 \ 0 \ 0}^{l^a \ \lambda-1 \ l^b} \right]^2 \{N^{\lambda-1}(ab, bc) + N^{\lambda-1}(ba, cb)\}, \end{aligned} \quad (68)$$

$$\begin{aligned} \sum_{(3)}' &= -6 \sum_{n^b l^b} \sum_{\lambda=1}^{(a+l^b)} \frac{l^a(l^a+1) + \lambda(\lambda+1) - l^b(l^b+1)}{2l^a(l^a+1)} \left[ \mathbf{C}_{0 \ 0 \ 0}^{l^a \ \lambda \ l^b} \right]^2 \\ &\times \{ [l^a(l^a+1) - l^b(l^b+1) - \lambda(\lambda+1)] [\lambda N^\lambda(ab, bc) - (\lambda+1)N^{\lambda-2}(ba, cb)] \\ &\quad - [l^b(l^b+1) - l^a(l^a+1) - \lambda(\lambda+1)] [\lambda N^\lambda(ba, cb) - (\lambda+1)N^{\lambda-2}(ab, bc)] \}. \end{aligned} \quad (69)$$

The integrals  $V^\lambda$  and  $N^\lambda$  are defined by

$$V^\lambda(ab, cd) = \frac{1}{4} \alpha^2 \int_0^\infty \int_0^\infty r_1^2 dr_1 r_2^2 dr_2 R_a(r_1) R_b(r_2) \frac{r_1^\lambda}{r_1^{\lambda+3}} r_2 \frac{\partial}{\partial r_1} R_c(r_1) R_d(r_2), \quad (70)$$

$$N^\lambda(ab, cd) = \frac{1}{4} \alpha^2 \int_0^\infty \int_0^\infty r_1^2 dr_1 r_2^2 dr_2 R_a(r_1) R_b(r_2) \frac{r_1^\lambda}{r_1^{\lambda+3}} \epsilon(r_1 - r_2) R_c(r_1) R_d(r_2). \quad (71)$$

where  $\epsilon$  is the Heaviside step function defined by

$$\epsilon(r_1 - r_2) = \begin{cases} 1, & r_1 \geq r_2; \\ 0, & r_1 < r_2. \end{cases} \quad (72)$$

In eqs. (67), (68) and (69) the summation over  $n^b l^b$  includes all the orbitals in the closed shells common to all configurations of the set chosen for the approximation. The prime on each  $\Sigma$  over  $b$  (that is  $n^b l^b$ ) indicates that only such contributions are included which arise when one electron is in the common core and the other is in the valence shell. Eqs. (67) to (69) are more general than the corresponding equations of Blume and Watson [23] in that they are valid for off-diagonal elements. The  $\Sigma'_{(i)}$  have been expressed in terms of Clebsch–Gordan coefficients instead of 3j-symbols; the 6j-symbols which appear in Blume and Watson’s original expressions have been eliminated with the help of the formulae given by Brink and Satchler ([12], table 4).

It remains to consider those fine structure interactions which do not behave like a one-body spin–orbit interaction. They have been discussed by Jones [6]; they consist of the mutual spin–orbit, spin–other-orbit and spin–spin interactions between valence electrons\*. We write (labelling particles by 1 and 2)

$$g_{12}(\text{so} + \text{so}') = 2V_{12}^{(1)} + V_{12}^{(2)} + V_{21}^{(2)} + V_{12}^{(3)} + V_{21}^{(3)}, \quad (73)$$

where the operators on the right-hand side of (73) are defined in Appendix A and they do *not* correspond to the operators  $V^{(1)}$ ,  $V^{(2)}$  and  $V^{(3)}$  defined by Blume and Watson [23]. The matrix elements of these operators are given by

$$\begin{aligned} \langle ab | V_{12}^{(1)} | cd \rangle = & \\ & K_1 \sum_{\lambda=0}^{\infty} (-1)^{\lambda - m^a - m^b} [(\lambda + 1)(\lambda + 2)(2\lambda + 3)]^{1/2} \\ & \times \begin{matrix} \lambda+1 & \lambda+1 & 1 \\ m^a - m^c & m^b - m^d & \kappa \end{matrix} c_{\lambda+1}(l^a m^a, l^c m^c) c_{\lambda+1}(l^b m^b, l^c m^c) V^{\lambda}(ab, cd), \end{aligned} \quad (74)$$

$$\begin{aligned} \langle ab | V_{12}^{(2)} | cd \rangle = & \sum_{\lambda=0}^{\infty} (-1)^{\lambda - m^a - m^b} \left\{ \left[ \frac{1}{4(\lambda + 1)} \right]^{1/2} [(\lambda + l^a + l^c + 2)(\lambda - l^c + l^a + 1)(\lambda - l^b + l^c + 1)(l^a - \lambda + l^c)]^{1/2} \right. \\ & \times \begin{matrix} \lambda+1 & \lambda & 1 \\ m^a - m^c & m^b - m^d & \kappa \end{matrix} d_{\lambda}(l^a m^a, l^c m^c) c_{\lambda}(l^b m^b, l^d m^d) K_1 \\ & - \left[ \frac{(\lambda + l^b + l^d + 2)(\lambda - l^b + l^d + 1)(\lambda + l^b - l^d + 1)(l^b - \lambda + l^d)(2\lambda + 5)}{4(2\lambda + 1)(\lambda + 2)} \right]^{1/2} \\ & \left. \times \begin{matrix} \lambda+2 & \lambda+1 & 1 \\ m^a - m^c & m^b - m^d & \kappa \end{matrix} d_{\lambda}(l^b m^b, l^d m^d) c_{\lambda+2}(l^a m^a, l^c m^c) K_2 \right\} N^{\lambda}(ab, cd), \end{aligned} \quad (75)$$

\* Spin–spin interactions between valence electrons and closed shells vanish provided the closed shells are unpolarised.

$$\begin{aligned}
\langle ab|V_{12}^{(3)}|cd\rangle &= \sum_{\lambda=0}^{\infty} (-1)^{\lambda-m^a-m^b} \left[ \frac{\lambda(2\lambda+1)}{4(\lambda+1)} \right]^{1/2} [l^a(l^a+1) - l^c(l^c+1) - \lambda(\lambda+1)] \\
&\times \mathbf{C}_{m^a-m^c, m^b-m^d}^{\lambda, \lambda, 1} c_{\lambda}(l^a m^a, l^c m^c) c_{\lambda}(l^b m^b, l^d m^d) K_1 \\
&- \left[ \frac{(2\lambda+5)(\lambda+3)}{4(\lambda+2)} \right] [l^b(l^b+1) - l^d(l^d+1) - (\lambda+2)(\lambda+3)] \\
&\times \mathbf{C}_{m^a-m^c, m^b-m^d}^{\lambda+2, \lambda+2, 1} c_{\lambda+2}(l^a m^a, l^c m^c) c_{\lambda+2}(l^b m^b, l^d m^d) K_2 N^{\lambda}(ab, cd), \tag{76}
\end{aligned}$$

where

$$\begin{aligned}
K_1 &= 2 \left[ \delta(\mu^b, \mu^d) \mathbf{C}_{\mu^c, \mu^a-\mu^c}^{\frac{1}{2}, 1, \frac{1}{2}} + 2\delta(\mu^a, \mu^c) \mathbf{C}_{\mu^d, \mu^b-\mu^d}^{\frac{1}{2}, 1, \frac{1}{2}} \right], \tag{77} \\
K_2 &= 2 \left[ \delta(\mu^a, \mu^c) \mathbf{C}_{\mu^d, \mu^b-\mu^d}^{\frac{1}{2}, 1, \frac{1}{2}} + 2\delta(\mu^b, \mu^d) \mathbf{C}_{\mu^c, \mu^a-\mu^c}^{\frac{1}{2}, 1, \frac{1}{2}} \right], \quad \kappa = m^a - m^c + m^b - m^d.
\end{aligned}$$

The coefficients  $c_{\lambda}$ , which occur in eqs. (74), (75) and (76), have been introduced in (18) and are defined in (A9); the coefficient  $d_{\lambda}$  in (75), which will be defined in (A12), is introduced here:

$$d_{\lambda}(lm, l'm') = \{(2l+1)(2l'+1)\}^{1/2} \mathbf{C}_{-m, m'}^{l, l', \lambda+1} \mathbf{C}_{0, 0}^{l, l', \lambda}. \tag{78}$$

Turning to the spin–spin interaction  $g_{ij}(ss')$ , the expression given by Jones [6] for the matrix elements of the spin–spin interaction can easily be rewritten in terms of the coefficients  $c_{\lambda}$ :

$$\begin{aligned}
\langle ab|g_{12}(ss')|cd\rangle &= \frac{3}{\sqrt{5}} \mathbf{C}_{\mu^a-\mu^c, \mu^b-\mu^d}^{1, 1, 2} \mathbf{C}_{\mu^c, \mu^a-\mu^c}^{\frac{1}{2}, 1, \frac{1}{2}} \mathbf{C}_{\mu^d, \mu^b-\mu^d}^{\frac{1}{2}, 1, \frac{1}{2}} \\
&\times \sum_{\lambda=0}^{\infty} (-1)^{\lambda-m^a-m^b} \mathbf{C}_{m^a-m^c, m^b-m^d}^{\lambda+2, \lambda, 1} c_{\lambda+2}(l^a m^a, l^c m^c) c_{\lambda}(l^b m^b, l^d m^d) \left[ \frac{(2\lambda+5)!}{(2\lambda)!} \right]^{1/2} N^{\lambda}(ab, cd). \tag{79}
\end{aligned}$$

The expressions on the right-hand side of (74), (75), (76) and (79) are all in the form of an algebraic coefficient multiplied by a radial integral. It follows that these expressions for the matrix elements are particularly suitable for the calculation of the coefficients  $D^{(\nu)}$  and  $E^{(\nu)}$ : these coefficients are calculated from the uncoupled two-electron matrix elements (74), (75), (76) and (79) using similar techniques to those employed in the calculation of  $B_{it}$  and  $C_{UV}$ .

### 3.4. The two-body non-fine-structure interactions

#### 3.4.1. The matrix elements

In this section we consider the matrix elements of the terms defined in the set of eqs. (47), that is the two-body Darwin, the spin–spin contact and the orbit–orbit terms.

The matrix elements of the two-body Darwin term follow straight forwardly from the expression given by Jones [24]:

$$\begin{aligned} & \langle n^a l^a \mu^a m^a, n^b l^b \mu^b m^b | g_{I_2}(d) | n^c l^c \mu^c m^c, n^d l^d \mu^d m^d \rangle = \\ & - \delta(\mu^a, \mu^c) \delta(\mu^b, \mu^d) \delta(m^a + m^b, m^c + m^d) \sum_{\lambda} (-1)^{m^a - m^d} c_{\lambda}(l^a m^a, l^c m^c) c_{\lambda}(l^b m^b, l^d m^d) (2\lambda + 1) X_2(abcd), \end{aligned} \quad (80)$$

where

$$X_2(abcd) = \alpha^2 \int_0^{\infty} dr (1/r^2) P_{n^a l^a}(r) P_{n^b l^b}(r) P_{n^c l^c}(r) P_{n^d l^d}(r). \quad (81)$$

The algebraic factor in (80) differs by a factor of  $(2\lambda + 1)$  from that involved in the Coulomb interaction [see eq. (18)]. Hence one may take into account the two-body Darwin term by adding to each Slater integral  $R_{\lambda}(ab, cd)$  the correction  $(2\lambda + 1) X_2(abcd)$ .

Turning to the spin-spin contact term, we note that De Shalit and Talmi [20] have shown that the matrix element of  $-\frac{16}{3} \pi \mathbf{s}(i) \cdot \mathbf{s}(j) \delta^3(\mathbf{r}_{ij})$  is equal to that of  $4\pi \delta^3(\mathbf{r}_{ij})$  provided that the wavefunction is antisymmetric with respect to interchange of the  $i$ th and  $j$ th electrons. Hence, since our wavefunctions are totally antisymmetric we may write

$$g_{ij}(css') = -2g_{ij}(d), \quad \text{that is } g_{ij}(css') + g_{ij}(d) = -g_{ij}(d) \quad \text{for all } i, j \quad (i \neq j). \quad (82)$$

It thus follows from (82) that we should add a correction  $2(2\lambda + 1) X_2(ab, cd)$  to each Slater integral  $R_{\lambda}(ab, cd)$  in order to take into account the spin-spin contact interaction. This was first pointed out by Feneuille [25].

Finally we consider the orbit-orbit interaction. Various workers [24, 26–29] have expressed the orbit-orbit interaction in terms of irreducible tensors, and from this, have derived various matrix elements. In Appendix B we give an expression for  $g_{I_2}(oo')$  in terms of spherical tensor operators; the derivation of its matrix elements is discussed there also. These matrix elements are given by

$$\begin{aligned} & \langle n^a l^a \mu^a m^a, n^b l^b \mu^b m^b | g_{I_2}(oo') | n^c l^c \mu^c m^c, n^d l^d \mu^d m^d \rangle = \\ & \delta(\mu^a, \mu^c) \delta(\mu^b, \mu^d) \delta(m^a + m^b, m^c + m^d) \sum_{\lambda} (1 - \delta(\lambda, 0)) (-1)^{m^a - m^d} c_{\lambda}(l^a m^a, l^c m^c) c_{\lambda}(l^b m^b, l^d m^d) Z_{\lambda}(ab, cd) \\ & - 2 \sum_{\lambda=0}^{\infty} (-1)^{m^a - m^d} d_{\lambda}(l^a m^a, l^c m^c) d_{\lambda}(l^b m^b, l^d m^d) \mathcal{N}^{\lambda}(ab, cd), \end{aligned} \quad (83)$$

where

$$\begin{aligned} Z_{\lambda}(ab, cd) = & -\lambda(\lambda + 1) [T^{\lambda+1}(ab, cd) - T^{\lambda-1}(ab, cd)] + [l^a(l^a + 1) - l^c(l^c + 1) - \lambda(\lambda + 1)] \\ & \times [U^{\lambda+1}(ab, cd) - U^{\lambda-1}(ab, ab)] + [l^b(l^b + 1) - l^d(l^d + 1) - \lambda(\lambda + 1)] [U^{\lambda+1}(ba, dc) - U^{\lambda-1}(ba, dc)] \\ & + \{ [l^a(l^a + 1) - l^c(l^c + 1) - \lambda(\lambda + 1)] [l^b(l^b + 1) - l^d(l^d + 1) - \lambda(\lambda + 1)] \}^{1/2} \\ & \times \left\{ \frac{-(\lambda + 3)}{(\lambda + 1)(2\lambda + 3)} [N^{\lambda}(ab, cd) + N^{\lambda}(ba, dc)] + \frac{\lambda - 2}{\lambda(2\lambda - 1)} [N^{\lambda-2}(ab, cd) - N^{\lambda-2}(ba, dc)] \right\}, \end{aligned} \quad (84)$$

and

$$\begin{aligned} \mathcal{N}^\lambda(ab, cd) &= \frac{1}{(\lambda+1)(\lambda+2)} \{(l^a+l^c+\lambda+2)(l^c-l^a+\lambda+1) \\ &\times (l^a-l^c+\lambda+1)(l^a+l^c-\lambda)(l^b+l^d+\lambda+2)(l^d-l^b+\lambda+1)(l^b-l^d+\lambda+1)(l^b+l^d-\lambda)\}^{1/2} \\ &\times \frac{1}{4}\alpha^2 \int_0^\infty \int_0^\infty P_a(r_1) P_b(r_2) \frac{r_1^\lambda}{r_1^{\lambda+3}} P_c(r_1) P_d(r_2) dr_1 dr_2. \end{aligned} \quad (85)$$

In (85), the integrals  $T^\lambda$  and  $U^\lambda$  were first defined by Beck [28]:

$$T^\lambda(ab, cd) = \frac{\alpha^2}{2\lambda+1} \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 P_{n^a l^a}(r_1) P_{n^b l^b}(r_2) \frac{r_1^\lambda}{r_1^{\lambda+1}} \frac{\partial}{\partial r_1} \left( \frac{P_{n^c l^c}(r_1)}{r_1} \right) \frac{\partial}{\partial r_2} \left( \frac{P_{n^d l^d}(r_2)}{r_2} \right), \quad (86)$$

$$\begin{aligned} U^\lambda(ab, cd) &= \frac{\alpha^2}{2(2\lambda+1)} \int_0^\infty dr_1 \int_0^\infty dr_2 P_{n^a l^a}(r_1) P_{n^b l^b}(r_2) \\ &\times \frac{1}{r_1} \frac{r_1^\lambda}{r_1^{\lambda+1}} [(\lambda-1)\epsilon(r_1-r_2) - (\lambda+2)\epsilon(r_2-r_1)] P_{n^c l^c}(r_1) \frac{\partial}{\partial r_2} \left( \frac{P_{n^d l^d}(r_2)}{r_2} \right). \end{aligned} \quad (87)$$

It is clear from (83) that the part of the orbit-orbit interaction involving  $Z_\lambda$  has the same angular dependence as that of the interelectron Coulomb interaction  $2/r_{ij}$ , and thus it may be absorbed into the Slater integrals as a shielding term. Hence, gathering together our results for the two-body Darwin, spin-spin contact and orbit-orbit terms we obtain the following expression for the relativistically corrected Slater integral:

$$R_\lambda^c(ab, cd) = R_\lambda(ab, cd) + (2\lambda+1) X_2(ab, cd) + (1 - \delta(\lambda, 0)) Z_\lambda(ab, cd). \quad (88)$$

In SUPERSTRUCTURE we do *not* take account of the two-body non-fine-structure terms and thus in that program we have

$$R_\lambda^c(ab, cd) = R_\lambda(ab, cd). \quad (89)$$

The second term in (83) can be considered in two separate parts:

(i) interactions between valence electrons. Since the integral  $\mathcal{N}^\lambda$  may be expressed in terms of the magnetic integrals  $N^\lambda$ , the algebraic factor may be absorbed into the factor  $E_{UU}^{(v)}$ .

(ii) interactions between valence electrons and closed shells. This behaves like a one-body interaction and expressions for it have been derived by Beck [28] and by Walker [29]: since the last term in (83) comes from the operator  $W_3$  (see Appendix B) it can be shown that

$$\sum_b' \langle ab | W_3 | bc \rangle = 0, \quad (90)$$

$$\sum_b' [\langle ab | W_3 | bc \rangle + \langle ba | W_3 | cb \rangle] = \delta(l^a, l^c) \delta(\mu^a, \mu^c) \delta(m^a, m^c) \xi(a, c), \quad (91)$$

where

$$\xi(a, c) = (1 - \delta(l^b, 0))(1 - \delta(l^c, 0)) \sum_{\lambda=1}^{l^a+l^b+1} \frac{1}{\lambda(\lambda+1)} \left[ \begin{matrix} C & l^a & \lambda-1 & l^b \\ & 0 & 0 & 0 \end{matrix} \right]^2$$

$$\times \left[ \frac{(l^a+l^b+\lambda+1)(l^a+\lambda-l^b)(l^b+\lambda-l^a)(l^b+l^a-\lambda+1)}{(2l^b+1)} \right] [N^{\lambda-1}(ab, bc) + N^{\lambda-1}(ba, cb)], \quad (92)$$

where the primes on the summations have the same meaning as in eqs. (66) to (69). Eqs. (89) and (90) agree with the corresponding expressions given by Beck ([28], eq. (A-20)). Comparing the right-hand sides of eqs. (91) and (17) it can be seen that the interaction  $W_3$  between a valence electron and closed shells has the same angular dependence as the non-relativistic one-body terms. Hence combining the results of eqs. (17), (59) and (90) we finally obtain an expression for the relativistically corrected one-body integral  $I^c(a, c)$

$$I^c(a, c) = I(a, c) + J(a, c) + \xi(a, c). \quad (93)$$

We could have absorbed the whole of the orbit-orbit interaction between valence electron and closed shells into a one-body term like  $\xi(a, c)$ . However, we do not do this because the matrix elements of  $W_1$ ,  $W_2$  and  $W_4$  can be absorbed as a correction to the Slater integrals  $R_\lambda$  [eq. (88)].

In SUPERSTRUCTURE, orbit-orbit interaction is omitted and thus in that program

$$I^c(a, c) = I(a, c) + J(a, c). \quad (94)$$

In (93) and (94),  $J(a, c)$  and  $\xi(a, c)$  are of order  $\alpha^2$  with respect to the non-relativistic term  $I(a, c)$ .

### 3.4.2. Discussion

Since the two-body non-fine structure interactions have been omitted from SUPERSTRUCTURE, it is necessary to discuss their effects and to consider cases when they may be important.

The two-body non-fine structure interactions will affect ionisation potentials, total energies and relative term separations. We would expect from the work of Walker [29] that the effect on ionisation potentials may be quite marked particularly for systems with medium to high  $Z$ . Jones [30] has recently discussed the application of SUPERSTRUCTURE to highly-ionised helium-like ions. He noted that SUPERSTRUCTURE tended to overestimate the relativistic correction to the  $1s^2 \ ^1S_0$  ionisation potentials in Ca XIX and Fe XXV, as compared with full Breit-Pauli calculations [31]. One might expect that inclusion of the two-body non-fine structure interactions would correct this tendency. However, relativistically-corrected *transition energies* from SUPERSTRUCTURE show much more satisfactory agreement with experiment [5] and with theoretical results which take into account the whole Breit-Pauli hamiltonian [30].

It is worth noting that the two-body non-fine structure interactions (47) may be considerably more sensitive to correlation effects than the one-body relativistic terms. Consider, for example the Darwin terms containing  $\delta^3(\mathbf{r}_{ij})$  and  $\delta^3(\mathbf{r}_i)$ . Cooper and Martin [32] and Bethe and Salpeter [19] have made estimates of the expectation values  $\langle \delta^3(\mathbf{r}_{ij}) \rangle$  and  $\langle \delta^3(\mathbf{r}_i) \rangle$  for simple two- and three-electron systems. The following two points emerge from their analyses:

(i) Generally, the contribution of spin-spin contact and two-body Darwin terms is quite small compared with the one-body relativistic corrections. This does not mean that these two-body terms are always unimportant, but it helps to explain why the results of Jones [5] mentioned above were so satisfactory even though he only included the one-body relativistic operators in his calculations.

(ii) The expectation values of  $\delta^3(\mathbf{r}_{ij})$  are much more sensitive to correlation effects than those of  $\delta^3(\mathbf{r}_i)$ . This is what one would expect physically. In general, it was found that single configuration Hartree-Fock functions overestimate  $\delta^3(\mathbf{r}_{ij})$  rather badly.

Ufford and Callen [33] have argued that orbit-orbit interaction may be highly sensitive to polarisation effects: however, no thorough numerical study of this has yet been made. Furthermore the relative importance of orbit-orbit

interaction and correlation effects has been studied: Rajnak and Wybourne [34] showed that electrostatic configuration interaction in  $l^n$  configurations can give rise to a term in the eigenenergy of the form  $L(L+1)\alpha$ , whereas Yanagawa [35] noted that orbit-orbit interaction can also give rise to a similar term\*. Wybourne [36] inferred from the observed sign and magnitude of the adjustable parameter  $\alpha$  that configuration interaction is dominant in  $d^n$  spectra.

In conclusion, it would appear that neglect of the two-body non-fine structure interactions is justified unless one is specifically interested in ionisation potentials. For systems of medium  $Z$ , ( $Z \sim 26$ ) these interactions do not appear to affect transition-energies significantly. If one does take account of these interactions in energy level calculations attention should be paid to the sensitivity of their matrix elements to correlation effects.

### 3.5. Calculation of energies and intermediate-coupling wavefunctions: accuracy of the Breit–Pauli approximation

The matrix  $\langle C\beta SLJM | H_{BP} | C'\beta'S'L'JM \rangle$  can be constructed with the help of the methods developed in sections 2 and 3. This matrix is then diagonalised:

$$\langle \Delta J | C\beta SLJ \rangle \langle C\beta SLJM | H_{BP} | C'\beta'S'L'JM \rangle \langle C'\beta'S'L'JM | \Delta'J \rangle = \delta_{\Delta\Delta'} \langle \Delta J | H_{BP} | \Delta'J \rangle. \quad (95)$$

The two summations  $|\rangle\langle|$  on the left-hand side of (95) run over  $C\beta SL$  and over  $C'\beta'S'L'$ . With the same arguments in mind that lead to (40) we introduce the alternate notation

$$b^J(\Delta, C\beta SL) = \langle \Delta J | C\beta SLJ \rangle. \quad (96)$$

In general, (95) corresponds to the first stage of application of the variational principle (1), in which the off-diagonal elements of the matrix  $H$  ( $= H_{BP}$  in this case) are reduced to zero by finding a suitable set of mixing coefficients  $\langle C\beta SL | \Delta J \rangle$ . In a single configuration approximation the diagonalisation (95) can be thought of as an application of degenerate perturbation theory, using as zero-order hamiltonian  $H_0 = \sum_i h_i$  [where  $h_i$  was defined in (2)]. With this choice of  $H_0$  there will be two perturbations, namely the inter-electron Coulomb interaction and  $H_{rc}$  (which comprises the relativistic correction terms of the Breit–Pauli hamiltonian): since these two perturbations have different  $Z$ -dependences, double perturbation theory must be used (for a fuller discussion see ref. [37]). Returning to the general multi-configuration case, it should be noted that we do not apply the variational principle (1) any further than the diagonalisation (95), since the radial functions used are non-relativistic and therefore take no account whatever of relativistic effects: it thus would be incorrect to vary the adjusting parameters  $\lambda_l$  to obtain a minimum in the intermediate-coupling energies.

According to Bethe and Salpeter ([19], section 38] the Breit–Pauli hamiltonian should only be treated in first order of perturbation theory. Ermolaev and Jones [38] have pointed out that this restriction does not necessarily apply to the fine structure interactions within a configuration, and they show that the diagonalisation (95) is approximately equivalent to a second order perturbation treatment of these interactions.

We complete this section with a few comments on the accuracy of the Breit–Pauli approximation:

(i) The Breit–Pauli approximation is valid subject to the condition

$$\alpha^2 Z_{\text{eff}}^3 \ll 1, \quad (97)$$

where  $Z_{\text{eff}}$  is the effective charge seen by any one electron in the system (that is, (97) should hold for each electron, but  $Z_{\text{eff}}$  will of course vary from one electron to another). The exact value of  $Z$  at which the Breit–Pauli method breaks down is not clearly defined: Ermolaev and Jones [31] have performed Breit–Pauli calculations in the helium sequence up to  $Z = 42$  and they suggest that the method is valid up to  $Z = 30$  and may be valid well beyond this value. However Grant [39] has demonstrated that the method breaks down for heavy atoms ( $Z \gtrsim 80$ ), as one would expect by examining the criterion (97) for the case of inner shell electrons of such systems.

\* This term comes from the operator  $W_3$ , which was the only part of the orbit–orbit interaction that Yanagawa [35] studied.

(ii) Ermolaev and Jones [37] have shown that provided the expectation values of  $H_{\text{BP}}$  are evaluated between exact non-relativistic functions, results will be obtained which agree with the corresponding relativistic  $Z$ -expansion (Doyle [40]) to order  $\alpha^2 Z^3$  Ry. For complex atoms it is impossible to obtain exact wavefunctions so the best variational wavefunctions available should be used. It is also appropriate to mention at this point the effect of poor non-relativistic wavefunctions and energies upon finestructure splittings. These manifest themselves in two ways:

(a) The Blume and Watson spin-orbit parameter of eq. (66) assume that the closed shells are undistorted. In practice the closed shells are polarised to some extent by the valence electrons, with the consequence that the spin-orbit parameter  $\zeta$  of (66) may differ considerably from the spin-orbit parameter deduced from experiment. One might expect that the discrepancy between calculated and "observed" spin-orbit parameters will increase as one proceeds to more highly-excited states since the polarisation potential produced by the closed core is a long range force. This indeed does appear to be the case: for example, the calculated spin-orbit parameter  $\zeta_{3d}$  ( $=\zeta(3d, 3d)$ ) for the sodium sequence is in far worse agreement with the experimental value than the corresponding  $\zeta_{3p}$  in the same sequence [50, 51].

(b) When spin-orbit interaction causes breakdown of  $LS$ -coupling, the fine structure splittings may be sensitive to non-relativistic term separations. For example, in the helium sequence, the fine structure splittings of the  $1s2p\ ^3P$  state can be considerably affected by the "singlet-triplet" interaction between  $1s2p\ ^3P_1$  and  $1s2p\ ^1P_1$  [38]. Since the diagonalisation (95) is approximately equivalent to second order perturbation theory, with *calculated* non-relativistic term separation  $\Delta E = E(^3P) - E(^1P)$ , errors in  $\Delta E$  may strongly affect the fine-structure splittings. We mention two further examples of this type of effect. Jones [6] noted that certain fine structure intervals in Fe VI are inverted, due mainly to second-order spin-orbit interaction. However, this inversion did not appear when rather crude calculated energies were used: Jones was able to partially produce these inversions when he semi-empirically adjusted the non-relativistic separations to approximate more closely to the observed separations between the centres of gravity of the terms. An example which clearly shows the inter-dependence of intermediate-coupling effects and configuration-mixing effects is given by Nussbaumer [15].

## 4. Radiative data

This section divides into two main parts. The first, more fundamental, part considers the calculation of transition probability data, whereas the second is concerned with the application of this data to the calculation of cascade coefficients.

### 4.1. Transition probabilities and $gf$ -values

The program can calculate radiative data for electric dipole and quadrupole transitions and also for magnetic dipole transitions.

#### 4.1.1. Electric multipole data

For electric multipole radiation of multipolarity  $2^k$  the transition probabilities  $\mathcal{A}^{[k]}$  for spontaneous emission can be expressed in terms of line strengths  $S^{[k]}$  in the following way:

$$\mathcal{A}_{i'i}^{[k]} = G^{[k]} \alpha^{2k+1} (E_i - E_{i'})^{2k+1} (1/g_i) S^{[k]}(i, i'), \quad (98)$$

where  $i$  and  $i'$  are the initial and final states respectively,  $g_i$  is the statistical weight of the initial state and  $G^{[k]}$  is a numerical factor. In the cases of electric dipole and quadrupole radiation  $G^{[k]}$  takes on the values

$$G^{[1]} = 1/3, \quad G^{[2]} = 1/160. \quad (99)$$

In eq. (98), if energies  $E$  are expressed in Rydbergs Ry and  $S^{[k]}$  is expressed in powers of Bohr radii  $a_0$ ,  $\mathcal{A}_{i'i}^{[k]}$

will be given in units inverse to the Rydberg time  $\tau_0 = 2a_0/(\alpha c) = \hbar/\text{Ry} = 4.839 \times 10^{-17}$  sec, where  $c$  is the speed of light. Thus  $\tau_0$  is the time taken for the electron in the ground state of hydrogen to traverse the diameter of its orbit;  $\frac{1}{2}\tau_0$  is often referred to as ‘‘atomic unit of time’’. Inserting modern values of  $\alpha$  and  $\tau_0$  (deduced from the atomic constants quoted by Kuhn [41]), we can transform  $\mathcal{A}$  back to a dimensioned expression  $A$ ; keeping  $E$  and  $S$  dimensionless as before, we obtain transition probabilities

$$A_{i'i}^{[1]} = 2.6774 \times 10^9 \text{ sec}^{-1} \times (E_i - E_{i'})^3 \frac{1}{g_i} S^{[1]}(i, i'), \quad (100)$$

$$A_{i'i}^{[2]} = 2.6733 \times 10^3 \text{ sec}^{-1} \times (E_i - E_{i'})^5 \frac{1}{g_i} S^{[2]}(i, i'). \quad (101)$$

Alternatively, especially in the context of absorption and dispersion, radiative transitions may be described by the oscillator strength  $f$  for absorption or emission; one can also use the  $(gf)$ -value:

$$(gf)_{i'i} = (gf)_{i'i} = g_i |f_{i'i}| = g_{i'} |f_{i'i'}|, \quad f_{i'i}^{[1]} = \frac{1}{g_{i'}} \frac{E_i - E_{i'}}{3} S^{[1]}(i, i'), \quad E_{i'} < E_i. \quad (102)$$

The atomic transition properties in both  $A$  and  $f$  are carried through the line strength  $S^{[k]}$ , which like  $(gf)$  is symmetric in the initial and final states  $i'$  and  $i$ . For radiation of a given multipolarity  $2^k$ ,  $S^{[k]}(i, i')$  can be constructed from matrix elements of the  $k$ 'th moment of the charge distribution; in our definition expressing  $A$  and  $f$  in terms of  $S$ , this quantity will be purely geometric, without factors  $\alpha$  (i.e. not involving  $e^2$  in the case of unreduced units):

$$S^{[k]}(i, i') = S^{[k]}(i', i) = \sum_{\kappa} |\langle i | P_{\kappa}^{[k]} | i' \rangle|^2, \quad \text{where} \quad P^{[k]} = b^{[k]} R^{[k]} = b^{[k]} \sum_{p=1}^N r_p^{[k]}. \quad (103, 104)$$

In (103) we have summed over the  $2k+1$  linearly independent tensorial space directions of multipole polarisation. We expand the one-particle vectors  $r_p$  in terms of spherical tensor operators  $C(p)$ :

$$(r_p)_{\kappa}^{[k]} = r_p^k C_{\kappa}^{[k]}(p), \quad (105)$$

using the notation of (20). The coefficient  $b^{[1]}$  has been given in TAS, and  $b^{[2]}$  has been given by Garstang [42]:

$$b^{[1]} = 1, \quad b^{[2]} = \sqrt{2/3}. \quad (106)$$

We now turn to particular coupling schemes. Considering first the  $LS$ -coupling representation  $t$  of eq. (4), we apply the Wigner–Eckart theorem [43] to the matrix element on the right of (103), obtaining

$$\langle t M_S M_L | R_{\kappa}^{[k]} | t' M'_S M'_L \rangle = \delta(M_S, M'_S) \frac{(-1)^{L'-M'_L}}{\sqrt{2k+1}} \mathbf{C}_{M_L M'_L \kappa}^{L L' k} \langle t || R^{[k]} || t' \rangle, \quad (107)$$

where

$$\langle t || R^{[k]} || t' \rangle = \langle C\beta SL || R^{[k]} || C'\beta' SL' \rangle = \sum_{\gamma, \gamma'} \langle C\beta SL || C^{[k]}(\gamma, \gamma') || C'\beta' SL' \rangle s_k(\gamma, \gamma'), \quad (108)$$

in which the multipole radial integrals  $s_k$  are defined by

$$s_k(\gamma, \gamma') = \int_0^{\infty} dr P_{\gamma}(r) r^k P_{\gamma'}(r) \quad (109)$$

in the length formulation. If we had chosen the velocity formulation in (103) instead, this would be equivalent to just replacing  $r$  by

$$\frac{2}{E' - E} \left[ \frac{d}{dr} + \frac{l'(l'+1) - l(l+1)}{2r} \right]$$

in (109) for the dipole case  $k = 1$ . On the right-hand side of (108)  $\gamma$  and  $\gamma'$  stand for orbitals  $nl$  and  $n'l'$  respectively, and there is an implied summation over repeated indices. The  $C_k(\gamma, \gamma')$  in (108) is related to the  $R^{[k]}$  of (104). The arguments  $\gamma$  and  $\gamma'$  imply that the matrix elements of  $C_k$  are taken between one-particle coordinate functions labelled by  $\gamma$  and  $\gamma'$ . However, as in the calculation of the structure angular coefficients  $A^{(v)}, B^{(v)}$  etc., the purely algebraic coefficients  $\langle t || C_k(\gamma, \gamma') || t' \rangle$  can be calculated without reference to coordinate functions. Using the Slater state expansion technique, the following expression is obtained for the matrix element on the left of (107):

$$\langle C\beta S L M_S M_L | R^{[k]} | C'\beta' S' L' M_S' M_L' \rangle = \sum_{u, u'} \mathbf{C}_{\mu_1 m_1 \dots \mu_N m_N; M_S M_L}^{l_1 \dots l_N; \beta S L} \mathbf{C}_{\mu'_1 m'_1 \dots \mu'_N m'_N; M_S' M_L'}^{l'_1 \dots l'_N; \beta' S' L'} \langle u | R^{[k]} | u' \rangle, \quad (110)$$

where

$$\langle u | R^{[k]} | u' \rangle = (-1)^{q+q'} \langle n_q l_q \mu_q m_q | r^{[k]} | n_{q'} l_{q'} \mu_{q'} m_{q'} \rangle, \quad (111)$$

in cases when the Slater states  $u$  and  $u'$  differ in one set of one-electron quantum numbers, namely the sets  $q$  and  $q'$ , and for diagonal elements:

$$\langle u | R^{[k]} | u \rangle = \sum_{q=1}^N \langle n_q l_q \mu_q m_q | r^{[k]} | n_q l_q \mu_q m_q \rangle. \quad (112)$$

Diagonal elements (112) only occur for  $k > 1$ : for dipole transitions ( $k = 1$ ) the initial and final states must differ in at least one set of one-electron quantum numbers. In eqs. (111) and (112) the one-electron matrix elements are given by

$$\langle n l \mu m | r_k^{[k]} | n' l' \mu' m' \rangle = \delta(\kappa, m - m') \delta(\mu, \mu') s_k(nl, n'l') (-1)^{k-m'} c_k(lm, l'm'). \quad (113)$$

The reduced radiative matrix elements  $\langle t || R^{[k]} || t' \rangle$  are obtained from  $\langle t M_S M_L | R^{[k]} | t' M_S' M_L' \rangle$  by inverting eq. (107);<sup>‡</sup> the expansion coefficients  $\langle t || C^{[k]}(\gamma, \gamma') || t' \rangle$  are obtained by collecting together the coefficients of each radial integral  $s_k(\gamma, \gamma')$  occurring in the summation on the right of (108).

In the case of configuration mixing in  $LS$ -coupling, the states  $i = \Gamma S L$  and  $i' = \Gamma' S' L'$  are expanded according to (5):

$$S^{[k]}(i, i') = \sum_{\substack{M_S, M_S' \\ M_L, M_L' \\ \kappa}} | \langle i | t \rangle \langle t M_S M_L | R_{\kappa}^{[k]} | t' M_S' M_L' \rangle \langle t' | i' \rangle |^2, \quad (114)$$

where the quantities  $\langle i | t \rangle$  are the configuration mixing coefficients which were discussed in section 2.4. Substituting (105) into (112), and noting that the coefficients  $\langle i | t \rangle$  are independent of  $M_S M_L$  it follows that the summations on the right-hand side of (112) can be performed giving

$$S^{[k]}(\Gamma S L, \Gamma' S' L') = (2S+1) \delta(S, S') \langle \Gamma S L | C\beta S L \rangle \langle C\beta S L || P^{[k]} || C'\beta' S' L' \rangle \langle C'\beta' S' L' | \Gamma' S' L' \rangle^2. \quad (115)$$

In order to transform the line strengths into a suitable representation for intermediate-coupling calculations, the following relation is used:

$$\langle C\beta S L || R^{[k]} || C'\beta' S' L' J' \rangle = (-1)^{S+L'+J+k} [(2J+1)(2J'+1)]^{1/2} \delta(C\beta, C'\beta') \delta(S, S') \left\{ \begin{matrix} L & J & S \\ J' & L' & k \end{matrix} \right\} \langle C\beta S L || R^{[k]} || C\beta S L' \rangle. \quad (116)$$

<sup>‡</sup> In the program, both computation time and the size of the file of algebraic coefficients  $\langle t || C^{[k]}(\gamma, \gamma') || t' \rangle$  is reduced by exploiting in eq. (108) the relation  $\langle \alpha' L' || C^{[k]} || \alpha L \rangle = (-1)^{L-L'} \langle \alpha L || C^{[k]} || \alpha' L' \rangle$ .

Eq. (116) was obtained from eq. (44b) of ref. [43]. The reduced matrix element of (116) is now substituted into the intermediate-coupling analogue of (113) giving

$$S_m^{[k]}(\Delta J, \Delta'J') = \langle \Delta J | C\beta SLJ \rangle \langle C\beta SLJ || P^{[k]} || C'\beta'S'L'J' \rangle \langle C'\beta'S'L'J' | \Delta'J' \rangle^2. \quad (117)$$

#### 4.1.2. Magnetic dipole transition probabilities

We define the magnetic dipole line strength by

$$S_m(i, i') = \langle i | P | i' \rangle^2, \quad \text{where } P_m = - \sum_{p=1}^N (I(p) + 2s(p)). \quad (118, 119)$$

The magnetic dipole transition probability is defined thus:

$$\mathcal{A}_{i'i}^m = \frac{\alpha^2}{12} (E_i - E_{i'})^3 \frac{1}{g_i} S_m(i, i'), \quad (120)$$

in the same units as eq. (98). Inserting values of  $\alpha$  and  $\tau$  as in section 4.1.1 we obtain

$$A_{i'i}^m = 3.5644 \times 10^4 \text{ sec}^{-1} (E_i - E_{i'})^3 \frac{1}{g_i} S_m(i, i'). \quad (121)$$

Shortley [44] has given closed expressions for  $S_m(i, i')$  using a representation  $C\beta SLJM$ , in which intermediate coupling between different terms  $SL$  was neglected. This  $LS$ -coupling line strength can be divided into three cases:

$$S_m^{LS}(C\beta SLJ, C'\beta'S'L'J) = \delta(C\beta SL, C'\beta'S'L') J(J+1)(2J+1) \left[ 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right]^2, \quad \text{for } J' = J; \quad (122)$$

eq. (122) does not apply for  $J = 0$ , when  $S_m^{LS}(J = 0 \rightarrow J' = 0)$  vanishes.

$$S_m^{LS}(C\beta SLJ, C'\beta'S'L'J+1) = \delta(C\beta SL, C'\beta'S'L') \frac{(J-S+L+1)(J+S-L+1)(J+S+L+2)(S+L-J)}{4(J+1)},$$

$$\text{for } J' = J+1. \quad (123)$$

The third case, namely  $J' = J - 1$ , is easily obtained from (123), with the help of the symmetry of the line strength. The intermediate coupling line strength  $S_m^{IC}(\Delta J, \Delta'J')$  may be obtained with the help of the transformation on the left-hand side of (95). We finally obtain

$$\begin{aligned} S_m^{IC}(\Delta J, \Delta'J') &= \sum_{C\beta SL} \langle \Delta J | C\beta SLJ \rangle \langle C\beta SLJ' | \Delta'J' \rangle^2 S_m^{LS}(C\beta SLJ, C\beta SLJ') \\ &= \sum_{C\beta SL} \langle \Delta J | C\beta SLJM \rangle [S_m^{LS}(C\beta SLJ, C\beta SLJ')]^{1/2} \langle C\beta SLJ' | \Delta'J' \rangle^2, \end{aligned} \quad (124)$$

which corresponds to a transformation of the positive square root of the line strengths  $S_m^{LS}$ .

#### 4.1.3. Selection rules in intermediate coupling

The intermediate-coupling selection rules for radiation are somewhat different from the corresponding  $LS$ -coupling selection rules. Knowledge of these rules will help users of SUPERSTRUCTURE or similar programs to interpret their results. We note that the selection rules will depend upon (a) the type of transition (electric dipole etc.), (b) the type of fine structure terms which are included in the hamiltonian when calculating the intermediate coupling wavefunctions. The selection rules for radiative transitions in  $LS$ -coupling are well known (TAS, chapter 9).

With regard to point (b), we note that the spin–spin interaction can couple terms  $SL$  and  $S'L'$  according to

$$|L - L'| \leq 2 \quad \text{and} \quad |S - S'| \leq 1 \quad (125)$$

([6], section 4), whereas the spin–orbit, mutual spin–orbit and spin–other-orbit interactions couple terms satisfying

$$|L - L'| \leq 1 \quad \text{and} \quad |S - S'| \leq 1. \quad (126)$$

The Coulomb interaction and the non-fine structure interactions of the Breit–Pauli hamiltonian can only couple terms with the same  $SL$ .

In the remainder of this sub-section we assume that the hamiltonian used in the atomic structure calculation contains all the fine structure interactions so that the coupling rules represented by the inequalities (125) apply [these rules also cover all cases included in the inequalities (126)]. In addition it should be noted that the parity selection rules are always the same as in the  $SL$ -coupling case, and we therefore make no further mention of parity selection rules. In all cases, transitions  $J = 0$  to  $J' = 0$  are not allowed.

*Electric-dipole transitions.* In  $LS$ -coupling the selection rules are

$$S = S', \quad |L - L'| \leq 1 \quad \text{and} \quad |J - J'| \leq 1. \quad (127)$$

The rules (125) apply when working out the mixing coefficients  $\langle C\beta SLJ | \Delta J \rangle$ , that is, if  $SL$  is the term making the dominant contribution to an eigenvector  $|\Delta J\rangle$ , the other components  $S'L'$  of the eigenvector are restricted by (125). In practice, the fine structure interactions are only likely to couple appreciably those terms which belong to the same configuration. Applying (125) and (127) to (117) we obtain the *intermediate-coupling selection rules*

$$|S - S'| \leq 4, \quad |L - L'| \leq 5 \quad \text{and} \quad |J - J'| \leq 1. \quad (128)$$

*Electric-quadrupole transitions.* In  $LS$ -coupling the selection rules are

$$|S - S'| = 0, \quad |L - L'| \leq 2 \quad \text{and} \quad |J - J'| \leq 2, \quad (129)$$

whereas in our intermediate-coupling case we have

$$|L - L'| \leq 7, \quad |S - S'| \leq 4 \quad \text{and} \quad |J - J'| \leq 2. \quad (130)$$

*Magnetic dipole transitions.* In the absence of intermediate coupling, the selection rules for magnetic dipole radiation are given by the Kronecker delta on the right-hand sides of eqs. (122) and (123). It follows from (124) that in intermediate coupling the selection rules are

$$|L - L'| \leq 4, \quad |S - S'| \leq 4 \quad \text{and} \quad |J - J'| \leq 1. \quad (131)$$

#### 4.1.4. Accuracy of radiative data

We mention here two sources of error in the intermediate-coupling radiative data:

(i) the transition probabilities  $A^{[k]}$  and  $A^m$  can be affected by errors in the calculated energy differences  $E_i - E_j$ . They can be corrected with the help of the observed wavelengths in the usual way.

(ii) intercombination line strengths may be unreliable if non-relativistic term separations between terms coupled by fine structure interactions are poor, where the line strength amplitude  $\langle C\beta SLJ || R^{[k]} || C'\beta' S'L'J' \rangle$  connecting those terms dominates the intermediate-coupling line strength amplitude. Poor non-relativistic term separations lead to poor mixing coefficients  $\langle C\beta SLJ | \Delta J \rangle$  in (117) or (124) thus yielding unreliable line strengths. For example, the transition probability for  $3s3p \ ^1P \rightarrow 3s3p \ ^3P$  in Mg I produced by SUPERSTRUCTURE contains an error of 30% when the non-relativistic energy separation of these two terms is in error by 15% [67]. This state of affairs is similar to that prevailing in the calculation of fine structure splittings, as discussed in section 3.5. We note that these line strengths may also be affected by poor spin–orbit parameters.

#### 4.2. Cascade coefficients

In many astrophysical plasmas, the population distribution of a given ion between the various states of its ground configuration can be strongly influenced by the effects of collisional excitation to a higher configuration followed by radiative de-excitation via cascade to the levels of the ground configuration. Pecker and Thomas [45] have studied such effects theoretically in the solar corona. For such analyses, one requires (a) the forbidden transition probabilities between the levels of the ground configuration, (b) radiative data connecting the excited configurations to one another and to the ground configuration, and (c) various collision data, outside the scope of the present paper. Data of types (a) and (b) can be obtained from the program. However, it is inconvenient to manipulate the vast amount of radiative data which can be involved when accounting for cascade effects. One can allow for cascade effects by using cascade coefficients, which incorporate all relevant information in a compact form. In the remaining part of this section we define the cascade coefficients and set up the system of linear equations which they satisfy.

Consider an atomic system in which we restrict ourselves to studying the first  $N_t$  levels. We suppose that the ground configuration has  $N_g$  levels. We denote a cascade coefficient by  $C_{j,i}$  where  $i > N_g$  and  $j \leq N_g$ .  $C_{j,i}$  is the probability that an excitation to the level  $i$  gives a cascade to the level  $j$  of the ground configuration. We may obtain a general expression for the cascade coefficients in terms of normalised transition probabilities:

$$P_{k,i} \equiv A_{k,i}/A_i, \quad \text{where } A_i = \sum_{k < i} A_{k,i}, \quad (132, 133)$$

$A_{k,i}$  being the probability for a transition from  $i$  down to  $k$ . It follows that

$$C_{k,N_g+1} = P_{k,N_g+1}, \quad C_{k,N_g+2} = P_{k,N_g+2} + P_{N_g+1,N_g+2} C_{k,N_g+1} \quad (134)$$

where  $k \leq N_g$ . In general

$$C_{k,i} = P_{k,i} + \sum_{j=N_g+1}^{i-1} P_{j,i} C_{k,j}, \quad N_t \geq i > N_g, \quad k \leq N_g. \quad (135)$$

In practice, since  $C_{j,i}$  is undefined when  $i \leq N_g$  or when  $j > N_g$ ,  $C_{j,i}$  can be stored as a matrix of size  $(N_t - N_g)N_g$ .

#### 5. Term-coupling coefficients

Term-coupling coefficients are required by Saraph's program JAJOM [9], which processes  $LS$ -coupling reactance matrices  $R$  to produce intermediate-coupling  $R$ -matrices. In order to see where the term-coupling coefficients come into the procedure we write down the necessary transformations. We use the following notation: upper case letters with a subscript  $i$  refer to the target ion; lower case letters are used for quantum numbers of the colliding electron; upper case letters without any suffixes are used for the angular momenta of the whole system (target + electron). With Saraph we denote the  $LS$ -coupling  $R$ -matrices by  $R^{SLP}(\Gamma_i S_i L_i l s; \Gamma'_i S'_i L'_i l' s')$  and the intermediate-coupling  $R$ -matrices by  $R^{JP}(\Delta_i J_i l K; \Delta'_i J'_i l' K')$ , where  $p$  is the parity of the whole system, and good quantum numbers for the system appear as superscripts to the appropriate  $R$ -matrix elements. The above matrices  $R^{JP}$  are obtained from the  $R^{SLP}$  by two successive transformations. Firstly, a purely algebraic transformation to pair coupling is carried out:

$$S_i + L_i = J_i, \quad J_i + l = K \quad \text{and} \quad K + s = J, \quad (136)$$

$$R^{JP}(\Gamma_i S_i L_i J_i l K; \Gamma'_i S'_i L'_i J'_i l' K') = \sum_{SL} X(SLJ, S_i L_i J_i, l K) R^{SLP}(\Gamma_i S_i L_i l s; \Gamma'_i S'_i L'_i l' s') X(SLJ, S'_i L'_i J'_i, l' K'), \quad (137)$$

where the recoupling coefficients  $X$  involve products of Racah coefficients:

$$X(SLJ, S_i L_i J_i, lK) = \{(2S+1)(2L+1)(2K+1)(2J_i+1)\}^{1/2} W(LLS_i L_i; L_i K) W(LJS_i s; SK). \quad (138)$$

Secondly the  $R^{Jp}$  matrix on the left-hand side of (137) is transformed to allow for term coupling (i.e. departures from  $LS$ -coupling) in the target:

$$R^{Jp}(\Delta_i J_i lK; \Delta'_i J'_i l'K') = \sum_{\substack{\Gamma_i S_i L_i \\ \Gamma'_i S'_i L'_i}} f_{J_i}(\Delta_i, \Gamma_i S_i L_i) R^{Jp}(\Gamma_i S_i L_i J_i lK; \Gamma'_i S'_i L'_i J'_i l'K') f_{J_i}(\Delta'_i, \Gamma'_i S'_i L'_i), \quad (139)$$

where the  $f_{J_i}$  are term-coupling coefficients defined by

$$f_{J_i}(\Delta_i, \Gamma_i S_i L_i) = \sum_{C_i \beta_i} a^{S_i L_i}(\Gamma_i, C_i \beta_i) b^{J_i}(\Delta_i, C_i \beta_i S_i L_i). \quad (140)$$

The eigenfunction labels  $\Gamma_i$  and  $\Delta_i$  implicitly contain a definite target parity  $p_i$ , since any one eigenfunction can only be constructed from states  $|t\rangle$  or  $|U\rangle$  having one definite parity. Hence the coefficients  $f_{J_i}$  refer to a definite target parity  $p_i$ ; in general there will be two sets of  $f_{J_i}$  for each  $J_i$ , corresponding to the two possible target parities.

Eqs. (139) and (140) have been derived by Jones [8], who uses  $J_i j$  coupling introduced by Saraph et al. [46] rather than the pair coupling of (136): this does not affect the form of (139) and (140). It should be noted that (139) differs from eq. (11) of Saraph [9], in that the summations over  $\Gamma_i$  and  $\Gamma'_i$  are incorrectly omitted in the latter equation. However the full summations of (139) are carried out within JAJOM and therefore this criticism does not apply to JAJOM itself [68].

In eq. (139) it is assumed that the same vector coupling techniques are used to calculate the  $f_{J_i}$  coefficients as are used to calculate the matrices  $R^{Jp}$  [8]. Thus, in the calculation of the  $f_{J_i}$  and the  $R^{Jp}$ , the same linear combinations  $|C_i \beta_i S_i L_i\rangle$  of Slater states must be used throughout. Use of the present program avoids phase inconsistencies that might develop within the calculation of the  $f_{J_i}$ , since the representations  $\Gamma_i$  and  $\Delta_i$  are calculated from the same basis set  $|C_i \beta_i S_i L_i\rangle$ .  $R$ -matrices calculated in a representation consistent with these  $f_{J_i}$  may be obtained from the distorted wave program of Eissner [1] or the coupled equations program IMPACT [47]. The latter program sets up and solves the coupled equations using algebraic coefficients calculated by one of Eissner's programs [1, 48]. As discussed in section 2.2, SUPERSTRUCTURE allows some flexibility in the way Slater states and VCC's are set up, and this can affect the phase of the  $f_{J_i}$ . There is a safeguard incorporated in the program which prevents a choice being made which could produce phases inconsistent with the distorted wave or collision algebra programs of Eissner [1].

Finally, we note that term-coupling coefficients connecting terms of different multiplicity may be sensitive to the accuracy of the non-relativistic term separations and to the accuracy of the off-diagonal element of the finestructure interactions which couple the terms. The errors in intercombination collision strengths produced by such errors in term-coupling coefficients resemble those produced in the corresponding line strengths from the same sources (see sections 3.5 and 4.1.4). A detailed numerical example is given by Jones ([30], section 5).

## 6. Program checking

A multi-purpose program which can carry out the wide range of atomic data calculations discussed in sections 2 to 5 obviously requires quite extensive checking in all its aspects. In the following three subsections we outline the various checks which have been used.

### 6.1. The non-relativistic structure problem

Four kinds of checks were carried out:

- (i) The program was checked for consistency by varying  $M_S M_L$ .
- (ii) On modifying appropriate input parameters the program will replace the potential (29) by a Coulomb potential (scaled or unscaled). Using this facility, results of Layzer [14] and of Godfredsen [3], who employed hydrogenic wave functions to carry out calculations for a number of iso-electronic sequences, were reproduced.
- (iii) Coefficients  $B_{II'}^{(p)}$  were checked in cases which have been tabulated in Chapter 7 of TAS.
- (iv) Calculated term energies using statistical model radial functions have been compared with various Hartree–Fock selfconsistent field calculations, e.g. by Eissner and Jones [7], who carried out such a comparison for O III and Si IX; they also compared term mixing coefficients with corresponding Hartree–Fock values.

## 6.2. The relativistic corrections

The coefficients  $C_{UU'}^{(p)}$ ,  $D_{UU'}^{(p)}$  and  $E_{UU'}^{(p)}$  were checked in the following ways:

- (i) The coefficients were calculated with different choices of  $M$ , the azimuthal component of  $J$ .
- (ii) The coefficients  $C_{UU'}^{(p)}$  were checked against those tabulated in Chapter 11 of TAS, and against some of the coefficients tabulated by Condon and Odabasi [49].
- (iii) The coefficients  $D_{UU'}^{(p)}$  and  $E_{UU'}^{(p)}$  were checked against the results of a number of previous calculations, mainly for  $p^n$ ,  $sp$  and  $d^n$  configurations. The sources of the results which were used for comparison have been listed fully by Jones [6]. In the case of *off-diagonal* elements, the coefficients  $D$  and  $E$  tabulated by some other workers are incomplete for the reasons discussed in [6]. We made spot checks of certain off-diagonal elements by comparing them with our own hand calculations.

It is worth remarking that in the case of degenerate terms  $SL$  the coefficients  $B$ ,  $C$ ,  $D$  and  $E$  need not agree with results calculated by other workers, due to the arbitrariness of the frame of reference of the vector-coupling coefficients (see section 2.2).

A further general check may be made on the diagonal elements of fine structure interaction by using the following sum rule:

$$\sum_J (2J+1) \langle C\beta SLJM | O^{[k]} \cdot S^{[k]} | C\beta SLJM \rangle = 0 \quad \text{if } k > 0. \quad (141)$$

De Shalit and Talmi ([20], p. 215) have derived the  $jj$ -coupling analogue of (141) and it is a simple matter to apply their arguments in  $LS$ -coupling. It follows from (141) that the weighted sum of the coefficients  $C_{UU'}^{(p)}$  of a given spin–orbit parameter will vanish when the sum is taken over all the fine structure components of a given term<sup>‡</sup>. A similar check may be applied to the coefficients  $D$  and  $E$  of the  $V^\lambda$  and  $N^\lambda$  integrals, considering each  $\lambda$  separately.

Checks on the one-body relativistic corrections were made by carrying out calculations for hydrogenic systems, comparing the energies obtained with the usual Pauli formulae for the energies of  $ns$ ,  $np$  and  $nd$  ( $n \leq 3$ ) states.

It was more difficult to carry out checks on the Blume and Watson spin–orbit parameters, since other calculations of these parameters use different wavefunctions. Two types of checks were made:

(a) We make use of an input facility of practical importance, which allows to specify a set  $C_0$  as closed shells common to all configurations considered; this set  $C_0$  of electrons is treated separately in the code, making full use of closed-shell properties. As an example we consider the configuration  $C = 1s^2 2s^2 2p$ . The check consists of comparing the results from different choices of  $C_0$ , say either  $C_0 = 1s^2 2s^2$  or  $C_0 = 1s^2$ ; in the latter case, where we have  $C = C_0 2s^2 2p$ , the program processes the two  $2s$  electrons on the same basis as others (in this instance  $2p$ ) that do not happen to form a closed shell. However, the resulting fine structure splitting must not depend upon the specification of  $C_0$ .

(b) Comparisons were made with the single-configuration Hartree–Fock spin–orbit parameters calculated by Froese [50]. One would expect results from single-configuration Hartree–Fock and statistical model functions to be similar for positive ions (see ref. [7]), and the agreement between the two sets of theoretical spin–orbit

<sup>‡</sup> However, the sum rule does not necessarily hold when  $C\beta$  is replaced by  $\Gamma$ , i.e. when off-diagonal elements are taken into account.

parameters is very satisfactory \* (Jones [51]), although in the case of the  $1s^2 2s^2 2p^6 3p$  configuration of the sodium sequence, the spin-orbit parameters  $\zeta(3p, 3p)$  from SUPERSTRUCTURE agree slightly better with experiment than those from Froese's work; there is no apparent physical reason for this.

### 6.3. Non-relativistic radiative data

Checks of radiative data were made in the following cases:

(i) Oscillator strengths  $f$  for transitions between states  $n \leq 3$  in hydrogen were compared with the values tabulated by Glennon et al. [52].<sup>‡</sup>

(ii) For O III,  $f$ -values for the transitions between the ground configuration and first excited, odd parity configuration have been compared with the values given by Smith and Wiese [53]. The results obtained in a five configuration approximation are in excellent agreement [54].

(iii) In the beryllium iso-electronic sequence,  $f$ -values for various transitions were calculated in various levels of configuration mixing. These results were compared with corresponding results calculated by Burke et al. [55].

(iv) Algebraic part  $\langle C\beta SL \| C^{[2]}(\gamma, \gamma') \| C'\beta' S'L' \rangle$  of line strength amplitudes were checked against values given by Garstang [42, 56, 57] for electric quadrupole transitions in certain configurations of the type  $d^n$  and  $d^n s'$ .

### 6.4. Intermediate-coupling radiative data

Intermediate-coupling radiative data was checked in the following ways:

(i) Hydrogen as in 6.3, but we made comparison with the fine structure transition probabilities given by Glennon et al. [52].

(ii)  $gf$ -values for permitted transitions and transition probabilities for forbidden transitions were compared with results of Garstang [58] in the cases of Fe XIV and Si X [7, 24]. Transition probabilities for forbidden transitions in the ground configurations of O II and O III were calculated and compared with the values compiled by Glennon et al. [52] respectively. In all these cases overall agreement was excellent.

(iii) One of us (HN) developed an independent version of the program for calculating radiative data: this version uses the same subroutines for dealing with the non-relativistic structure problem and the algebra of the spin-orbit interaction. Results from the two programs were compared in the following two cases:

- (a) a six-configuration approximation for Fe XVII;
- (b) a three-configuration approximation for Fe XIII.

(iv) Mason [59] has carried out calculations of intermediate-coupling collision strengths for Fe X, Fe XI, Fe XIV, Ca XII, Ca XIII and Ca XV. These calculations can be used as a consistency check on the radiative data, since one would expect the collision strengths to be roughly proportional to the corresponding  $gf$ -values [60]. This type of proportionality is indeed observed, which indicates phase consistency between data from SUPERSTRUCTURE and Mason's collision strength data<sup>☆</sup>.

\* The spin-orbit parameters quoted in ref. [5] for the sodium sequence are wrong, because there was an error in the program at the time: corrected results appear in ref. [51].

‡ (Footnote added in proof.) Also boron sequence transitions, using hydrogenic wave functions and representing each term by the full complex, were checked against calculations of Weiss [69].

☆ However, the two sets of calculations are not completely independent, since Mason's collision strengths incorporate term-coupling coefficients from SUPERSTRUCTURE. Elsewhere in Mason's calculations the algebraic manipulations are completely independent of SUPERSTRUCTURE.

## 7. Critical discussion

In this section we discuss the advantages and disadvantages of the formulation developed in the earlier sections. We consider first some of the advantages:

(i) The Slater state expansion method makes no reference to parentages of terms: consequently the data which SUPERSTRUCTURE requires in order to enable it to calculate all necessary algebra consists merely of a list of configurations. On the other hand, currently available programs based upon fractional parentage techniques require information about the genealogy of each term, as for example in the program of Hibbert [61]. This implied option in programs such as that of Hibbert [61] means that one can drop terms of certain parentage, but further down the genealogical tree it becomes increasingly difficult to assess the consequences of doing this; there is also a risk of errors due to accidental omission of important parent terms. Thus it is considerably more convenient to specify the configuration only. A less serious point is that currently available routines for calculation of fractional parentage coefficients are restricted to configurations with specific types of electrons (e.g. the routines of Allison [62] calculate fractional parentage coefficients for equivalent p-shell and d-shell electrons). The Slater state coupling routines which incorporate methods of section 2.2 are in principle applicable to all configurations.\*

(ii) The program is not restricted to using only the internally-generated statistical model wavefunctions, but may alternatively employ user-supplied wavefunctions. These supplied functions may, for example, be multiconfiguration Hartree–Fock functions obtained from the program of Froese-Fischer [63], or frozen cores functions obtained from the program IMPACT of Seaton and Wilson [47].

(iii) Configuration mixing effects involving bound configurations can be taken into account in a very general way.

(iv) The algebraic coefficients of the two-electron operators of the Breit–Pauli hamiltonian have been expressed in terms of coefficients  $c_\lambda(lm, l'm')$  and  $d_\lambda(lm, l'm')$ . This makes it possible to set up tables of  $c_\lambda$  and  $d_\lambda$  coefficients before calculating the algebra, so that recalculation of them is avoided. This results in considerable saving of computer time.

(v) The wide range of atomic structure data considered makes SUPERSTRUCTURE highly suited for astrophysical applications.

Criticisms of the techniques employed are:

(i) Froese-Fischer [64] has pointed out that the number of Slater determinants may become quite large: this could lead to inaccuracies in the evaluation of matrix elements due to cancellation. In practice, we find that, using double precision on an IBM 360/65, coefficients  $A$ ,  $B$  and  $C$  have errors of less than one part in  $10^7$ , even in cases involving large numbers of Slater states. This small error is due to: (a) inaccuracies in the vector-coupling coefficients  $\langle u|t \rangle$  resulting from numerical errors inherent in the Jacobi procedure [65] used in the diagonalisation of the  $S^2$  and  $L^2$  matrices. (b) Cancellation errors in the transformation from the Slater state representation to that of  $SLM_S M_L$  or of  $JM$ . We have not investigated the relative importance of (a) and (b), since the overall error is insignificant for practical purposes. The errors in the coefficients  $D$  and  $E$  are larger, but they are still less than one part in  $10^5$ : this larger error is probably the result of the greater complexity of the corresponding matrix elements [see eqs. (74) to (77)].

(ii) It has been pointed out that statistical model functions could be poor for neutral or near-neutral atomic systems. However, when configuration mixing is allowed for, statistical model functions provide a better representation than is generally recognized. Statistical model wave functions have been used for targets in electron-atom collision calculations, e.g. for  $e^- + O^{2+}$  by Eissner and Seaton [54], and for  $e^- + O$  by Saraph [66]. The same set of O III target functions yields excellent radiative data, as mentioned in section 6.2. Saraph's functions reproduce

\* Though is not always true in practice: in nuclear physics, where orbitals with high angular momenta such as f or g occur with relatively small numbers of nucleons, the Slater state coupling procedure rapidly becomes impracticable owing to the large number of Slater states, resulting in excessive demands on CPU and storage resources. Therefore fractional parentage techniques are commonly used in nuclear structure problems.

the observed target energies of neutral O I just as satisfactorily as far more elaborate selfconsistent-field calculations

(iii) In cases such as  $d^6$ , the computer time used in the calculation of the algebra of the interactions  $g_{ij}(\text{so} + \text{so}')$  and  $g_{ij}(\text{ss}')$  becomes large, despite the use of the technique (iv) described above. Further reductions in computer time can be achieved by making more use of the Wigner–Eckart theorem. The use of transformation (50) to obtain eigenfunctions of  $J^2$  and  $J_z$  is then avoided by working in terms of eigenstates  $|SLM_S M_L\rangle$ . Assuming that the interaction is of the form  $V^{[k;0]}$  as in eq. (48), we have [12, 43]

$$\langle C\beta SLJ \| S^{[k]} \cdot O^{[k]} \| C'\beta' S' L' J \rangle = (-1)^{S'+L+J} [(2S+1)(2L+1)]^{1/2} \left\{ \begin{matrix} S & S' & k \\ L' & L & J \end{matrix} \right\} \langle C\beta SL \| S^{[k]} \cdot O^{[k]} \| C'\beta' S' L' \rangle. \quad (142)$$

Hence it is only necessary to work out the single matrix element  $\langle C\beta SLM_S M_L \| S^{[k]} \cdot O^{[k]} \| C'\beta' S' L' M'_S M'_L \rangle$ : the reduced matrix element on the right-hand side of (142) is easily deduced from this using

$$\langle C\beta SL \| S^{[k]} \cdot O^{[k]} \| C'\beta' S' L' \rangle = \frac{\langle C\beta SLM_S M_L \| S^{[k]} \cdot O^{[k]} \| C'\beta' S' L' M'_S M'_L \rangle}{\begin{matrix} C & S' & k & S & C & L' & k & L \\ & M'_S & M'_S - M_S & M_S & & M'_L & M'_L - M_L & M_L \end{matrix}}, \quad (143)$$

where we have made a double application of the Wigner–Eckart theorem [12]. Clearly, in order to apply (143),  $M_S M_L$  and  $M'_S M'_L$  must be chosen so that the Clebsch–Gordan coefficients in the denominator do not vanish. When calculating the fine-structure algebra, it can be shown that the above modification will result in a reduction of the computer time requirements by a factor whose maximum value will be roughly equal to the mean square of the multiplicities of all the terms arising from the configuration.

(iv) SUPERSTRUCTURE omits the non-fine structure interactions discussed in section 3.4. As mentioned there, this will affect the accuracy of total energies and ionisation potentials. Using the theory developed in section 3.4 it would be straightforward to introduce these interactions into SUPERSTRUCTURE. However, the effect of these terms upon intermediate coupling radiative data and term-coupling coefficients will be negligible.

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## Appendix A

### Expressions for the mutual spin–orbit and spin–other-orbit interactions in terms of spherical tensor operators

Such expressions have been given by Blume and Watson [23], who write (labelling particles by 1 and 2):

$$-\alpha^2 \left( \frac{r_{12}}{r_{12}^3} \times p_1 \right) \cdot (s_1 + 2s_2) = V_1 + V_2 + V_3, \quad (A1)$$

where  $V_1$ ,  $V_2$  and  $V_3$  are made up of products of spherical tensor operators, and have been defined in [23]. However, except in the case of  $V_1$ , their matrix elements between products of one-electron functions yield expressions containing more than one type of integral. For example, the matrix element of  $V_3$  consists of a sum over terms containing integrals  $N^\lambda(ab, cd)$  and  $N^{\lambda-2}(ba, dc)$ . In order to obtain expansions of type (51), in which the algebraic coefficients of specific integrals are required, we recast Blume and Watson's expression in the following form (utilizing the notation of eq. (20) with regard to particle labels

$$g_{I2}(\text{so} + \text{so}') = 2V_{I2}^{(1)} + V_{I2}^{(2)} + V_{2I}^{(2)} + V_{I2}^{(3)} + V_{2I}^{(3)}, \quad (\text{A2})$$

where

$$V_{I2}^{(1)} = \alpha^2 \sum_{\lambda > 0} (-1)^\lambda \left\{ \frac{1}{3} \lambda (\lambda + 1) (2\lambda + 1) \right\}^{1/2} \{C^{[\lambda]}(I) C^{[\lambda]}(2)\}^{[11]} \cdot (s(I) + 2s(2)) \frac{r_2^{\lambda-1}}{r_1^{\lambda+2}} r_2 \frac{\partial}{\partial r_1}, \quad (\text{A3})$$

$$V_{I2}^{(2)} = \alpha^2 \sum_{\lambda} (-1)^\lambda \left\{ \frac{1}{3} (2\lambda + 1) \right\}^{1/2} \left[ (2\lambda - 1) \{T^{[\lambda-1; \lambda]}(I) C^{[\lambda-1]}(2)\}^{[11]} \cdot (s(I) + 2s(2)) \right. \\ \left. - \left( \frac{(2\lambda - 1)(2\lambda + 3)}{\lambda + 1} \right)^{1/2} \{T^{[\lambda-1; \lambda]}(2) C^{[\lambda+1]}(I)\}^{[11]} \cdot (s(2) + 2s(I)) \right] \frac{r_2^{\lambda-1}}{r_1^{\lambda+2}} \epsilon(r_1 - r_2), \quad (\text{A4})$$

and

$$V_{I2}^{(3)} = \alpha^2 \sum_{\lambda} (-1)^\lambda \left\{ \frac{1}{3} (2\lambda + 1) \right\}^{1/2} \lambda \{T^{[\lambda; \lambda]}(I) C^{[\lambda]}(2)\}^{[11]} \cdot (s(I) + 2s(2)) \\ - (\lambda + 1) \{T^{[\lambda; \lambda]}(2) C^{[\lambda]}(I)\}^{[11]} \cdot (s(2) + 2s(I)) \frac{r_2^\lambda}{r_1^{\lambda+3}} \epsilon(r_1 - r_2). \quad (\text{A5})$$

In eqs. (A3), (A4) and (A5) terms of the type  $\{A^{[k_1]} B^{[k_2]}\}^{[k]}$  denote a product spherical tensor of degree  $k$  formed from tensors  $A^{[k_1]}$  and  $B^{[k_2]}$ , which are of degree  $k_1$  and  $k_2$  respectively, that is

$$\{A^{[k_1]} B^{[k_2]}\}_q^{[k]} = \sum_{q_1 q_2} \mathbf{C}_{q_1 q_2 q}^{k_1 k_2 k} A_{q_1}^{[k_1]} B_{q_2}^{[k_2]}, \quad (\text{A6})$$

where the subscript  $q$  on the left denotes the  $q$ th component of the product tensor. A particular example among these product tensors is  $T^{[\lambda'; \lambda]}$ , which has been used in (A4) and (A5); it is defined as

$$T^{[\lambda'; \lambda]}(I) = \{C^{[\lambda']}(I) I(I)\}^{[\lambda]}. \quad (\text{A7})$$

Its spherical components are

$$T_{q' \kappa}^{[\lambda'; \lambda]}(I) = \sum_{q''} \mathbf{C}_{q'' \kappa q}^{\lambda' 1 \lambda} C_{q''}^{[\lambda']}(I) I_{\kappa}(I). \quad (\text{A8})$$

The function  $\epsilon(x)$  has been defined in eq. (72). It should be noted that the tensors  $T^{[\lambda'; \lambda]}$  defined in (A7) differ from  $T_{\lambda}^{(\lambda')}$  introduced by Blume and Watson [23] by a factor of  $[4\pi/(2\lambda' + 1)]^{1/2}$ . Throughout this paper we have preferred definitions like that of  $T^{[a; b]}$ , because they are closer to the origin of these tensors as well as more convenient when applying the tensors strictly as spherical operators in a Slater state space.

The operator  $V_{I2}^{(1)}$  is symmetric in particles  $I$  and  $2$ ; it is equal to the operator  $V_1$  of Blume and Watson. The operators  $V_{ij}^{(2)}$  and  $V_{ij}^{(3)}$  can easily be obtained by rearrangement of the terms within Blume and Watson's operators  $V_2$  and  $V_3$ .

The matrix elements of the operators defined by (A3), (A4) and (A5) can be obtained in a similar way to that described by Jones [6]; this reference employs  $T_{b\beta}^{(a)}$  as introduced by Blume and Watson [23] rather than  $T_{\beta}^{[a;b]}$ . In order to obtain matrix elements in terms of the coefficients  $c_{\lambda}$  and  $d_{\lambda}$  it is convenient to use the following relations:

$$\langle l_1 m_1 | C_{\kappa}^{[\lambda]} | l_2 m_2 \rangle = \delta(\kappa, m_1 - m_2) (-1)^{\lambda - m_2} c_{\lambda}(l_1 m_1, l_2 m_2), \tag{A9}$$

$$c_{\lambda}(l_1 m_1, l_2 m_2) = \frac{\sqrt{(2l_1 + 1)(2l_2 + 1)}}{2\lambda + 1} \begin{C} l_1 & l_2 & \lambda \\ 0 & 0 & 0 \end{C} \begin{C} l_1 & l_2 & \lambda \\ -m_1 & m_2 & m_2 - m_1 \end{C},$$

and

$$\langle l_1 m_1 | T^{[\lambda'; \lambda]_{\kappa}} | l_2 m_2 \rangle = (-1)^{\lambda' - m_2} \left[ \frac{l_2(l_2 + 1)(2l_1 + 1)}{2\lambda' + 1} \right]^{1/2} (2l_2 + 1) \times \delta(\kappa, m_1 - m_2) \begin{C} l_1 & l_2 & \lambda \\ 0 & 0 & 0 \end{C} \begin{C} l_1 & l_2 & \lambda \\ -m_1 & m_2 & m_2 - m_2 \end{C} \begin{B} l_1 & l_2 & \lambda \\ 1 & \lambda & l_2 \end{B} \tag{A10}$$

rather than (A2) and (A5) of Jones [6]. Our definition (A7) shows that, in general, three distinct irreducible tensors arise for a given  $\lambda'$ ; thus we may distinguish three cases of (A10), defining an additional coefficient  $d_{\lambda}$ :

(i)  $\lambda' = \lambda$ ,

$$\langle l_1 m_1 | T^{[\lambda; \lambda]_{\kappa}} | l_2 m_2 \rangle = (-1)^{\lambda - m_2} [l_2(l_2 + 1)(2l_2 + 1)(2\lambda + 1)]^{1/2} \delta(\kappa, m_1 - m_2) c_{\lambda}(l_1 m_1, l_2 m_2) \begin{B} l_1 & l_2 & \lambda \\ 1 & \lambda & l_2 \end{B}. \tag{A11}$$

(ii)  $\lambda' = \lambda - 1$ ,

$$\langle l_1 m_1 | T^{[\lambda - 1; \lambda]_{\kappa}} | l_2 m_2 \rangle = -\delta(\kappa, m_1 - m_2) (-1)^{\lambda - m_2} \left[ \frac{l_2(l_2 + 1)(2l_2 + 1)}{2\lambda - 1} \right]^{1/2} d_{\lambda - 1}(l_1 m_1, l_2 m_2) \begin{B} l_1 & l_2 & \lambda \\ 1 & \lambda - 1 & l_2 \end{B}, \tag{A12}$$

$$d_{\lambda}(l_1 m_1, l_2 m_2) = \sqrt{(2l_1 + 1)(2l_2 + 1)} \begin{C} l_1 & l_2 & \lambda \\ 0 & 0 & 0 \end{C} \begin{C} l_1 & l_2 & \lambda + 1 \\ -m_1 & m_2 & m_2 - m_1 \end{C}.$$

The third possible case, namely  $\lambda' = \lambda + 1$  is not needed because in (A4) we have eliminated  $T^{[\lambda + 1; \lambda]}$  from (A4) by using the fact that

$$\frac{\langle l_1 m_1 | T^{[\lambda + 1; \lambda]_{\kappa}} | l_2 m_2 \rangle}{\langle l_1 m_1 | T^{[\lambda - 1; \lambda]_{\kappa}} | l_2 m_2 \rangle} = \left[ \frac{\lambda(2\lambda - 1)}{(\lambda + 1)(2\lambda + 3)} \right]^{1/2} \tag{A13}$$

(c.f. ref. [23], eq. (A17)). If we did not use (A13), it would be necessary to introduce another coefficient in addition to the  $d_{\lambda}$  of eq. (78). As noted by Jones ([6], Appendix 1), the  $6j$ -symbols in (A11) and (A12) can be expressed in closed form thus:

$$\begin{B} l_1 & l_2 & \lambda \\ 1 & \lambda & l_2 \end{B} = (-1)^{\lambda + l_2 - l_1} \frac{l_1(l_1 + 1) - \lambda(\lambda + 1) - l_2(l_2 + 1)}{[4l_1(l_2 + 1)(2l_2 + 1)\lambda(\lambda + 1)(2\lambda + 1)]^{1/2}} \tag{A14}$$

and

$$\left\{ \begin{matrix} l_1 & l_2 & \lambda \\ 1 & \lambda-1 & l_2 \end{matrix} \right\} = (-1)^{\lambda+l_2-l_1} \left[ \frac{(l_2 - \lambda + l_1 + 1)(l_1 + l_2 + \lambda + 1)(\lambda - l_2 + l_1)(\lambda - l_1 + l_2)}{4(2\lambda + 1)\lambda(2\lambda - 1)l_2(l_2 + 1)(2l_2 + 1)} \right]^{1/2}. \quad (\text{A15})$$

## Appendix B

### Expressions for the orbit-orbit interaction in terms of spherical tensor operators

It can be shown [24], that the orbit-orbit interaction can be written

$$g_{I2}(oo') = W_1 + W_2 + W_3 + W_4, \quad (\text{B1})$$

where

$$W_1 = -\alpha^2 \sum_{\lambda > 0} C^{[\lambda]}(I) \cdot C^{[\lambda]}(2) \lambda(\lambda + 1) \left[ \frac{1}{2\lambda + 3} \frac{r_{<}^{\lambda+1}}{r_{>}^{\lambda+2}} - \frac{1}{2\lambda - 1} \frac{r_{<}^{\lambda-1}}{r_{>}^{\lambda}} \right] \frac{\partial}{\partial r_1} \frac{\partial}{\partial r_2}, \quad (\text{B2})$$

$$W_2 = -2\alpha^2 \sum_{\lambda > 0} C^{[\lambda]}(I) \cdot T^{[\lambda;\lambda]}(2) \sqrt{\lambda(\lambda + 1)} \left[ \frac{M^{\lambda+1}(r_1, r_2)}{2\lambda + 3} - \frac{M^{\lambda-1}(r_1, r_2)}{2\lambda - 1} \right] \frac{1}{r_2} \frac{\partial}{\partial r_1}, \quad (\text{B3})$$

$$W_3 = -2\alpha^2 \sum_{\lambda > 0} \frac{2\lambda - 1}{\lambda + 1} T^{[\lambda-1;\lambda]}(I) \cdot T^{[\lambda-1;\lambda]}(2) \frac{r_{<}^{\lambda-1}}{r_{>}^{\lambda+2}}, \quad (\text{B4})$$

and

$$W_4 = -\alpha^2 \sum_{\lambda > 0} T^{[\lambda;\lambda]}(I) \cdot T^{[\lambda;\lambda]}(2) \left[ \frac{-\lambda(\lambda + 3)}{2\lambda + 3} \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+3}} + \frac{(\lambda + 1)(\lambda - 2)}{2\lambda - 1} \frac{r_{<}^{\lambda-2}}{r_{>}^{\lambda+1}} \right]. \quad (\text{B5})$$

In (B3),  $M^\lambda$  is defined by

$$M^\lambda(r_1, r_2) = (\lambda - 1) \frac{r_1^\lambda}{r_2^{\lambda+2}} \epsilon(r_2 - r_1) - (\lambda + 2) \frac{r_2^\lambda}{r_1^{\lambda+1}} \epsilon(r_1 - r_2). \quad (\text{B6})$$

The spherical operators  $T^{[\lambda;\lambda]}$  are defined by eqs. (A7) or (A8). Scalar multiplication is denoted by a dot. As usual  $r_{<}$  stands for the smaller and  $r_{>}$  for the bigger of the two radii  $r_1$  and  $r_2$ .

The matrix elements of the operators  $W_i$ , that is  $\langle ab | W_i | cd \rangle$ , can be found using similar techniques to those employed in deriving the matrix elements of  $g_{ij}(so + so')$  (see [6], and Appendix A) and  $g_{ij}(ss')$ . To find the matrix elements of  $C^{[\lambda]}$  or  $T^{[\lambda;\lambda]}$ , one uses eqs. (A9) or (A10), (A11) and (A12) respectively. The  $6j$ -symbols appearing in the matrix elements of  $T^{[\lambda;\lambda]}$  can be written in closed form using eqs. (A14) or (A15) as appropriate. Inspection of (A11) and (A12) shows that  $\langle l_1 m_1 | T^{[\lambda;\lambda]} | l_2 m_2 \rangle$  has the same dependence upon the azimuthal quantum numbers  $m_1$  and  $m_2$  as  $\langle l_1 m_1 | C^{[\lambda]} | l_2 m_2 \rangle$ . On the other hand, the matrix element of  $\langle l_1 m_1 | T^{[\lambda-1;\lambda]} | l_2 m_2 \rangle$  is proportional to  $(-1)^{m_2} d_\lambda(l_1 m_1, l_2 m_2)$ . It therefore follows that the matrix elements of  $W_1$ ,  $W_2$  and  $W_4$  will have the same angular dependence as the inter-electron Coulomb interaction, unlike  $W_3$ . The contributions from  $W_1$ ,  $W_2$  and  $W_4$  can thus be absorbed into the Slater integrals as discussed in 3.4, but those from  $W_3$  need to be considered separately.

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