ERRATA

Page

58 Normalization factor in eq. (3.2) should be $\frac{1}{\hbar}\sqrt{\frac{m}{2\pi k}}$

59 Normalization factor in eq. (3.3) $\frac{1}{\hbar}\sqrt{\frac{2m}{\pi}}$

61 Eq. (3.5), replace $\frac{2}{\pi}$ by $\frac{2m}{\hbar^2\pi}$

68 Def. of $A_{ij}{}^{k}$, replace $\frac{2}{\pi}$ by $\frac{2m}{\hbar^2\pi}$

69 Last sentence should read "If $\tilde{\underline{\psi}}$ is normalized to a plane wave of one particle per cm^2 per sec

$$d\rho(E) = \frac{mk\ d\Omega}{\hbar^2(2\pi)^3} \qquad \underline{k} = k\underline{n}$$

70 At head of page replace $k^{-1/2}$ by $v^{-1/2}$ outside factor in (3.15) should be

$$\frac{2\pi\hbar^2e^2}{m^2c\nu\omega}$$

Definition of $\tilde{\underline{\psi}}\ (\Gamma_k) = \frac{i}{\hbar}\sqrt{\left(\frac{2m}{\pi}\right)}\sum_{\Gamma_i} \frac{1}{(1 + iR)_{ik}}\ \underline{\psi}_k\ (\Gamma_i)$

eq. (3.16) outside factor should be

$\frac{2\pi\hbar^2e^2}{m^2c\nu\omega}$ and replace $\frac{2}{\pi}$ by $\frac{2m}{\hbar^2\pi}$

71 Eq. (3.17) as eq. (3.16)

72 Eq. (3.19) as eq. (3.16)

73 Eq. (3.20) delete factor $\frac{k}{(2\pi)^3}$ and replace $\frac{2}{\pi}$ by $\frac{2m}{\hbar^2\pi}$

Eq. (3.21) outside factor should be

$$\frac{\hbar^2e^2\ (2S + 1)}{m^2c\nu\omega}\sqrt{\frac{2\pi}{15}}$$

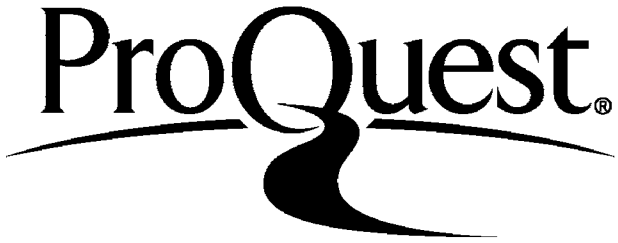
78 Replace $\frac{2}{\pi}$ by $\frac{2m}{\hbar^2\pi}$ in def. of $A_{ij}{}^{k}$

80 As for p. 78

THE SCATTERING OF ELECTRONS BY ATOMIC SYSTEMS

by

Lesley Annette Morgan, B.Sc.



ABSTRACT

The eigenfunction expansion method is used to describe the scattering of low energy electrons by atoms or ions having any number of incomplete subshells. Hartree Fock wave functions are used to describe the target system and allowance is made for the inclusion of any number of excited electronic configurations in the expansion. The continuum electron wave functions are given as the solutions of coupled integro differential equations with prescribed boundary conditions. Expressions for the photoionisation cross sections are also derived within this approximation. The formalism presented in this thesis uses the technique of angular momentum recoupling which greatly simplifies the evaluation of the potential terms which appear in the equations and the expressions for the photoionisation cross sections. This has enabled us to write, for the first time, a computer program for the calculation of the various electron scattering and photoionisation cross sections for a general atomic system, which requires as input only the Hartree Fock functions for the bound orbitals and the parameters needed to specify the terms to be included in the eigenfunction expansion. A program which calculates the necessary recoupling coefficients for any given expansion is described.

ACKNOWLEDGEMENT

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In addition I should like to acknowledge the hospitality of the Physics Department of the University of Nebraska where the latter part of this work was carried out.

CONTENTS

INTRODUCTION

The scattering of low energy electrons by atoms and ions is a process of great importance in astrophysical, high altitude and laboratory plasmas. The knowledge of the various elastic, inelastic and photoionisation crossections is necessary for the interpretation and understanding of the observed phenomena. Recent developments in experimental techniques for the measurement of crossections and the availability of large high speed computers have also helped to stimulate the theoretical study of electron-atom collisions.

In order to estimate the temperature, density and chemical composition of astronomical objects one attempts to interpret their spectra in terms of processes which have been observed in the laboratory or predicted theoretically.

A process of interest to astrophysicists is the excitation of atoms and ions, by collisions with low energy electrons to metastable levels, since these may lie only a few e.v. above the ground state. Depending on the electron density, the atoms either cascade back down to the ground state emitting forbidden quanta or are de-excited by collisions of the second kind. Lines due to these forbidden transitions are often prominent in the spectra of astronomical objects. In particular, the strongest lines in the spectra of planetary nebulae, which are responsible for their pale green appearance, are emitted following the excitation process

$$O^{++}(2p^2\,{}^3P) + e \rightarrow O^{++}(2p\,{}^1D) + e$$

Consequently there have been numerous attempts to predict theoretically, the excitation crossections for these processes.

Alternatively an electron-ion collision may result in the capture of the electron. This may occur directly with the emission of a photon,

$$X^+ + e^- \rightarrow X + h\nu \qquad \text{(radiative recombination)}$$

or by means of a radiationless transition to a quasibound state lying above the ionisation threshold of the atom, which subsequently decays radiatively to a bound state below the ionisation threshold

$$X^+ + e^- \rightarrow X^* \rightarrow X + h\nu$$

This process is known as dielectric recombination. Burgess (1965) has shown that in astrophysical objects of high temperature and low density the rate coefficient for dielectric recombination may exceed that for radiative recombination by several orders of magnitude and that the neglect of dielectric recombination was responsible for the large discrepancy between the observed and calculated temperature of the solar corona.

A process of even greater importance is the absorption of stellar or solar ultraviolet radiation by atoms. This can result in excitation, photoionisation,

$$X + h\nu \rightarrow X^+ + e^-$$

or the excitation of the atom to an autoionising level lying above the ionisation threshold. The atom may then undergo

a radiationless transition from the discrete super-excited state into the state of ion plus free electron

$$X + h\nu \rightarrow X^{*} \rightarrow X^{+} + e^{-} \qquad \text{(autoionisation)}$$

Until recently, there was little astrophysical interest in autoionisation since autoionising lines are most easily observed in absorption and lie in the extreme ultraviolet well below the limit of atmospheric transmission. However the rapidly increasing amount of data from rocket and satelite experiments has stimulated theoretical and laboratory investigation of the processes which give rise to the newly observed lines.

Information on the composition of the earth's atmosphere at different levels may be obtained from an analysis of the absorption of solar radiation. The principal constituents of the upper atmosphere are oxygen and nitrogen and hence the various ionisation, recombination and excitation crossections of these atoms and the molecules formed from them are of particular interest.

In this thesis we consider the scattering of low energy electrons by atoms and ions with a low nuclear charge. That is, the scattering of electrons, having velocities less than those of the atomic electrons, by atoms with $Z < 36$. The Schroedinger equation describing the scattering cannot be solved exactly even for the simplest case of $e^{-}H$ scattering and hence some considerable approximation must be made.

The method we shall use in this thesis is the eigenfunction expansion, or 'close coupling' approximation. This is based on the expansion of the wave function for the system

in terms of the eigenstates of the target Hamiltonian. The expansion coefficients are interpreted as describing the motion of the projectile relative to the unperturbed target. A system of coupled integro differential equations for these coefficients is derived from a variational principle and the scattering parameters can then be obtained from their numerical solutions.

The work of Feshbach (1958, 1962) and Fano (1961) has shown that the autoionising states may be described by the solutions in the closed channels and will give rise to resonances in the open, scattering, channels. In the absence of coupling to the open channels these states would be bound, but in the presence of the coupling they decay, with characteristic lifetimes, into the adjacent continua. An important advantage of the eigenfunction expansion method, therefore lies in its ability to describe autoionisation as well as the scattering of electrons by an atom.

In any calculation one, of course, has to truncate the infinite series and retain in the expansion only those terms which can be expected to play a dominant role in the scattering. The energy range for which a particular expansion is valid is therefore restricted. It has been found that, except for very low energies, the expansion converges slowly (Burke 1963). However good results can be expected if all of the open channels are included and if the coupling to the neglected channels is weak in comparison to the coupling between those retained. The results obtained for e^-He scattering by Burke and co-workers (1965, 1966) and the pre-

diction of autoionising levels in oxygen by Smith, Henry and Burke (1967) are in good agreement with experiment and support this assumption. A serious criticism of the eigenfunction expansion method is that, in expanding the total wave function in a finite number of unperturbed eigenstates of the target, one neglects the distortion of the atom by the incident electron. The explicit antisymmetrisation of the trial wave function partially compensates for the omission of continuum states in the expansion through the introduction of exchange terms. However it has been shown that this is by no means sufficient (Temkin 1957, Callaway 1957, Henry 1968).

The 'Polarised Orbital' method attempts to remedy the neglect of polarisation effects by the expansion of the total wave function in terms of wave functions of the distorted atom (Temkin 1957). The perturbed atomic wave function is expressed as

$$\psi(\underline{X}_A \underline{r}_p) = \phi(\underline{X}_A) + \chi(\underline{X}_A \underline{r}_p)$$

where $\phi(\underline{X}_A)$ is the wave function for the unperturbed atom and $\chi(\underline{X}_A \underline{r}_p)$ describes the distortion produced by a charge at $\underline{r}_p$.

In the adiabatic approximation $\chi(\underline{X}_A \underline{r}_p)$ is found by solving the Hartree Fock equations for the atom in the presence of a stationary external charge, that is for fixed values of $\underline{r}_p$. This approximation neglects dynamic effects and has been found to overestimate the distortion of the target (Temkin , 1962, LaBahn and Callaway 1966). Recent work on the non-adiabatic contributions to the potentials (Kleinman, Hahn

and Spruch 1967, Garrett 1967) has enabled improved results to be obtained for e^+H scattering and is capable of extension to more complex systems. This method should therefore prove to be a useful improvement on the unperturbed eigenfunction expansion. The methods described in this thesis, although applied to an expansion in unperturbed functions are capable of extension to a 'polarised orbitals' expansion without difficulty.

Feshbach has shown that the energies of autoionising states are eigenvalues of the equation

$$(QHQ)\Psi_Q = E_Q\Psi_Q$$

where the operator Q projects out the closed channels of Ψ and are related to the energies E at which resonances are observed in the open channels by $E = E_Q + \Delta_Q$ where Δ_Q is the energy shift caused by the coupling to the open channels. Hence one may predict resonances in electron-atom scattering either by solving the equations which describe the scattering or by finding the eigenvalues of the operator QHQ. The latter method has been used to calculate the position of autoionising or resonance states in H^- and He (O'Malley and Geltman 1965, Altick and Moore 1966, Bhatia and Temkin 1967) and has given good agreement with experiment. The level shifts and widths are given by

$$\Delta = \langle Q\Phi | A_1 | Q\Phi \rangle$$
$$\Gamma = \langle Q\Phi | A_2 | Q\Phi \rangle$$

where A_1 and A_2 are nonlocal but hermitian operators. The solution of the eigenvalue problem is by no means easy even for such simple systems as H^- and He and although good

results have been obtained for the positions of the autoionising states, the values of Δ and Γ calculated from the approximate eigenfunctions $Q\Psi$ have not been in good agreement with experiment. Recently Chen and Rotenburg (1968) have proposed a method by which systematic corrections may be made to Δ and Γ. However it remains to be seen whether this method can be successfully generalised to more complex systems and whether accurate calculation of the level shift and width will not prove to be more difficult than solving the scattering problem to the same degree of accuracy. The main advantage of this method is that it can be used to predict the positions of resonances and hence be used to eliminate the search for them in a scattering calculation.

Numerous other methods have been developed for the calculation of the crossections of particular atomic systems. Many of these methods give more accurate results than those described above but are incapable of generalisation to other, more complex, systems. This is true of many e^-H calculations since the hydrogen wave functions are known exactly and one may use the minimum principle of Hahn, O'Malley and Spruch (1964) to systematically obtain better approximations to the reactance matrix. Other methods which can in principle be extended to many electron systems are made impractical by the great increase in the complexity of the equations.

One of the most accurate calculations to date has been made by Schwartz (1961). He has calculated the elastic e^-H

scattering crossection to an accuracy of probably better than one per cent using Kohns' variational principle and a trial wave function constructed from up to 50 Hylleraas type wave functions. Burke and Taylor (1966, 1967) have calculated e^-H crossections below the n = 3 threshold using as their trial wave function a 3-state close coupling expansion together with up to 20 terms to represent the short range electron-electron correlation. The minimum principle of Hahn, O'Malley and Spruch is used to find the 'best' solution by varying the correlation terms until the maximum eigenphase sum is obtained. Their results for the elastic scattering crossection are comparable to those of Schwartz and the estimated error in their 1s-2s and 1s-2p excitation crossections is less than 10%. The nonadiabatic method of Temkin takes the polarisation of the atom by the incident electron fully into account but is in practice limited to S-wave scattering by hydrogen. Although these methods cannot, successfully, be generalised to more complex atoms, they provide a valuable check on the accuracy of more widely applicable approximation schemes.

One of the principal difficulties in the application of the eigenfunction expansion method to complex atomic systems has been the evaluation of the various potential terms when more than one electronic configuration is included in the expansion. Henry and Lipsky (1967) have calculated photoionisation crossections for neon taking into account the possibility of the ejection of one of the 2s electrons. The use of conventional methods to calculate the coupling between the $1s^2 2s^2 2p^5$ and $1s^2 2s 2p^6$ configurations of the ion leads to

laborious evaluations of angular integrals even though each configuration has only one incomplete subshell. Even in the calculations of Smith, Henry and Burke (1966) and Saraph, Seaton and Shemming (1966) on the scattering of electrons by atoms and ions with configurations $1s^2 2s^2 2p^q$ and $1s^2 2s^2 2p^6 3s^2 3p^q$ ($q = 2, 3, 4$) where only the three terms of the ground state configuration are retained in the expansion, the evaluation of the angular integrals appearing in the potential terms was not a simple task. In this thesis we shall show how the scattering equations for these configurations may be obtained directly from our general formalism. The practical difficulties involved in the inclusion of configurations with incomplete inner shells were a particularly great handicap in the use of this method to predict autoionising levels as these often result from inner shell excitations. For example the energies of the autoionising series $ms\,mp^6\,(^2S)\,np\,(^1P)$, $ms\,mp^6\,(^2S)\,ns\,(^{1,3}S)$ of the rare gas atoms, have been measured experimentally by several groups. Also Carroll et. al. (1966) have observed a new Rydberg series in the absorption spectra of atomic nitrogen which they attribute to transitions from the ground state to the autoionising levels $1s^2 2s\,2p^3\,(^5S)\,np(^4P)$

Fano (1965) and Shore (1965) have developed methods which greatly simplify the calculation of matrix elements of one and two electron operators between configurations with any number of incomplete subshells. These methods have enabled us to extend the eigenfunction expansion method to the scattering of electrons by a general atomic system. We expand the total wave function for the system in terms of

target wave functions constructed from one electron Hartree-Fock functions and make allowance for the inclusion of any excited configurations of the target. The scattering equations are derived from a variational principle and the various potential terms are expressed in terms of generalised angular momentum recoupling coefficients. The derivation of these equations and the explicit form of the potentials has been published (Smith and Morgan 1968) and a reprint of this paper is included in this thesis. An algorithm has been developed for the evaluation of the angular momentum recoupling coefficients. This has enabled us to write a computer program for the calculation of the potentials, a task which involves much algebraic manipulation, which needs as input only the parameters needed to specify the target and the quantum number of the states to be included in the expansion. The algorithm and the program for the calculation of the recoupling coefficients are described in Section 4 of this thesis. The program for the potentials and a modified version of the scattering code of Smith, Henry and Burke have been used to construct a program which calculates the continuum wave functions of an electron scattered by a general atomic system and from them derives the various elastic, inelastic and photoionisation crossections. A general expression for the photoionisation crossection is given in Section 3. Throughout this thesis we will use the notation of Smith and Morgan (hereafter referred to as S.M.) and give all expressions in atomic units.

SECTION 2: THE SCATTERING EQUATIONS

2.1. Trial Wave Function

The Hamiltonian for an electron colliding with an atomic system having N electrons and a nuclear charge Z, neglecting magnetic and relativistic effects is, in atomic units,

$$H = \sum_{i=1}^{N+1} H_1(i) + \sum_{i<j}^{N+1} \frac{1}{r_{ij}} \qquad (2.1)$$

where

$$H_1(i) = -\tfrac{1}{2}\left(\nabla_i^2 + \frac{2Z}{r_i}\right)$$

$$r_{ij} = |\underline{r}_i - \underline{r}_j|$$

Since spin-orbit coupling is neglected the total orbital angular momentum and the total spin are separately conserved and hence calculations may be simplified by using a representation which is diagonal in L and S.

As an approximation to the exact solutions of the Schroedinger equation $H\Psi = E\Psi$ we expand the wave function of the total system in terms of the complete set of (assumed known) normalised eigenstates γ_i of the target Hamiltonian H_N where

$$H_N = \sum_{i=1}^{N} H_1(i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \qquad (2.2)$$

The expansion coefficients which are functions of $\underline{x}_{N+1}$ are interpreted as describing the motion of the projectile relative to the target. We write

$$\Psi_u(\underline{X}^{N+1}) = \sum_{\gamma_i} \psi(\gamma_i \underline{X}^N)\, \bar{F}_{\gamma_i}(\underline{x}_{N+1}) \qquad (2.3)$$

where $\sum_{\gamma_i}$ implies integration over the continuous spectrum $E_{\gamma_i} > 0$.

Bound State Hartree-Fock Functions

We choose the target wave functions $\psi(\gamma_i \underline{X}^N)$ to be the Hartree-Fock wavefunctions for the unperturbed atom. That is, we neglect distortion due to the field of the scattered electron.

The Hartree-Fock self-consistent field approximation assumes that each electron may be regarded as being in a stationary state in the field of the nucleus and of the other electrons. Hence we may take as an approximate wave function of N electrons, an antisymmetrised product of N one electron orbitals u_i

Viz $$\Psi(1,2,\cdots N) = \mathcal{A}\left[u_\alpha(1)u_\beta(2)\cdots u_\nu(N)\right]$$

where the u_i are chosen such that $\int d\underline{x}\; u_i^*(\underline{x})\, u_j(\underline{x}) = \delta_{ij}$

There is no restriction since the determinantal wave function is unaltered if u_i is replaced by $u_i + A_{ij}u_j$ where A_{ij} is chosen such that the orthogonality condition is satisfied. If all the electrons are in closed shells then the one electron orbitals will be of the central field type, that is

$$u_i(\underline{x}) \equiv u_i(r,\theta,\phi,\sigma) = R_{n_i l_i}(r)\, Y_{l_i m_i}(\theta\phi)\, \chi_{\frac{1}{2}m_s}(\sigma) \qquad (2.4)$$

where $R_{n_i l_i}(r) = \frac{P_{n_i l_i}(r)}{r}$

If not all the electrons are in closed shells the self consistent field will not be spherically symmetric but we make the approximation that the one electron orbitals may still be represented by central field functions.

For a bound state the u_i must satisfy the boundary conditions $R(r) \to 0$ as $r \to \infty$, $R(r)$ must be everywhere finite and hence $P(0) = 0$. The "best" radial functions R are obtained from the variational principle

$$\delta \langle \Psi | H - E | \Psi \rangle = 0 \tag{2.5}$$

with respect to variations $R \to R + \delta R$, $\delta R \to 0$ as $r \to \infty$ and subject to the constraint $\int d\underline{x}\, u_i^*(\underline{x}) u_j(\underline{x}) = \delta_{ij}$ to ensure that $\langle \Psi | \Psi \rangle = 1$

It can be shown that for the lowest state of a symmetry species, that is, the lowest of the set of states having total quantum numbers $\{\alpha S M_S L M_L\}$ the exact solution to the equation $H\Psi = E\Psi$, where H is the usual approximate Hamiltonian given by (2.1), will give an absolute minimum of the expression $E = \langle \Psi H \Psi \rangle$ Hence we may say that the best approximate wave functions $|\alpha S M_S L M_L\rangle$ are those which give the lowest E. However this is not the only criterion by which we must judge the goodness of the approximate wave function since other properties, such as its asymptotic behaviour, may be of greater importance in particular applications. We note that the individual orbital angular momenta are not good quantum numbers for the true solutions to the Schroedinger equation and therefore the electronic configuration is not used to distinguish symmetry

species. For higher states of a given symmetry species E_{HF} will be a stationary value of E but not an extremum so we must look for other criteria by which we may judge the "goodness" of our trial wave function. If all the electrons are in closed subshells, the N particle wave function may be represented by a single Slater determinant. However as a consequence of the central field approximation, an atomic system with incomplete subshells will be highly degenerate with respect to energy. This implies that several of the Slater determinants (in the usual representation) will correspond to the same energy and that the required wave function will be some linear combination of these determinants. In the absence of spin-orbit coupling the energy levels of an atomic system with a given electronic configuration are specified by the set of total quantum numbers $\{aSL\}$. We shall therefore want to evaluate the matric elements of H in a representation which is diagonal in $\{aSM_S LM_L\}$.

We require a properly antisymmetric wave function $|aLM_L SM_S\rangle$ in this representation. We first construct normalised antisymmetric wave function for each subshell λ from the one electron orbitals u_i

$$\{q_\lambda | nl_\lambda^{N_\lambda} \alpha_\lambda S_\lambda M_{S_\lambda} L_\lambda M_{L_\lambda}) = \sum_{\substack{m_{l_1} \cdots m_{l_n} \\ m_{s_1} \cdots m_{s_n}}} C^{m_{l_1} \cdots m_{l_n} m_{s_1} \cdots m_{s_n}} R(r_{\lambda_1}) \cdots R(r_{\lambda_n}) \times Y_{l_\lambda m_{l_1}}(\hat{r}_{\lambda_1}) \cdots Y_{l_\lambda m_{l_n}}(\hat{r}_{\lambda_n}) \chi_{\frac{1}{2} m_{s_1}}(\sigma_{\lambda_1}) \cdots \chi_{\frac{1}{2} m_{s_n}}(\sigma_{\lambda_n})$$

where $C^{m_{l_1} \cdots m_{s_n}}$ denotes the Clebsch Gordan coefficients and coefficients of fractional parentage needed to couple the spin and orbital angular momenta of the N_λ equivalent particles to give total $\alpha_\lambda S_\lambda M_{S_\lambda} L_\lambda M_{L_\lambda}$ in such a way that the subshell

wave functions is antisymmetric under interchange of any pair of labels $\in q_\lambda$. q_λ denotes the set of labels, subset of {1..N}, of the N_λ electrons in subshell λ.

We next form an unsymmetrised wave function for the N particle system

$$|q\,\alpha LM_L SM_S\rangle = \left[\prod_\lambda \{q_\lambda | n\ell_\lambda^{N_\lambda} \alpha_\lambda S_\lambda M_{S\lambda} L_\lambda M_{L\lambda}\}\right]^{\alpha SM_S LM_L}$$

by coupling the subshell angular momenta to give the required total $aLM_L SM_S$.

Finally we construct a properly antisymmetric normalised N particle wave function

$$|\alpha LM_L SM_S\rangle = \frac{1}{[\eta(N_\lambda)]^{\frac{1}{2}}} \sum_q (-1)^{P_q} |q\,\alpha LM_L SM_S\rangle$$

where $\eta(N_\lambda)$ is the number of possible distributions and P_q is the parity of permutation q.

In order to evaluate the matrix element $\langle aLM_L SM_S|H_N|aLM_L SM_S\rangle$ we first write

$$H_N = \sum_{i=1}^{N} H_1(i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

and consider the matrix elements of the one-electron and two-electron operators separately. The wave functions $|aLM_L SM_S\rangle$ are orthonormal and properly antisymmetric under interchange of any pair of labels 1..N, hence

$$\left\langle \sum_{i=1}^{N} H_1(i) \right\rangle = N \langle H_1(N)\rangle$$

where

$$\langle H_1(N)\rangle = [\eta(N_\lambda)]^{-1} \sum_{q_i q_j} (-1)^{P_{q_i}+P_{q_j}} \langle q_i\,\alpha LM_L SM_S|H_1(N)|q_j\,\alpha LM_L SM_S\rangle \qquad (2.6a)$$

From the orthonormality of the wave functions we see that the matrix element on the r.h.s. will vanish for $q_i \neq q_j$ and

that all distributions of the labels 1..., N-1 will contribute equally hence we may replace

$\sum_{q_i q_j}$ by $\sum_{\rho} \eta(\bar{N}_\lambda)$ where ρ is the subshell containing electron N and

$$\bar{N}_\lambda = N_\lambda \quad \text{for } \lambda \neq \rho$$
$$= N_\rho - 1 \quad \text{for } \lambda = \rho$$

Equation (2.6a) now becomes

$$\langle H_1(N) \rangle = \sum_{\Gamma} \frac{\prod_\lambda N_\lambda!}{N!} \frac{(N-1)!}{\prod_\lambda \bar{N}_\lambda!} \langle \rho \alpha L M_L S M_S | H_1(N) | \rho \alpha L M_L S M_S \rangle$$
$$= \sum_\rho N_\rho \int dr\, P_\rho(r) \left(-\tfrac{1}{2}\right)\left(\frac{d^2}{dr^2} - \frac{l_\rho(l_\rho+1)}{r^2} + \frac{2Z}{r}\right) P_\rho(r) \qquad (2.6)$$

The matrix element $\langle \sum_{i<j} \frac{1}{r_{ij}} \rangle$ is a special case of that studied by Fano (1965) and equals

$$\tfrac{1}{2} \sum_{\lambda\mu} N_\lambda (N_\mu - \delta_{\lambda\mu}) \sum_{\epsilon=0,1} \sum_{\bar{\alpha}_\lambda \cdots \bar{L}_\mu} \left(l_\lambda^{N_\lambda} \alpha_\lambda S_\lambda L_\lambda \| l_\lambda^{\bar{N}_\lambda} \bar{\alpha}_\lambda \bar{S}_\lambda \bar{L}_\lambda \right)^2$$
$$\left(l_\mu^{N_\mu} \alpha_\mu S_\mu L_\mu \| l_\mu^{\bar{N}_\mu} \bar{\alpha}_\mu \bar{S}_\mu \bar{L}_\mu \right)^2 \sum_k \Big\{ \delta_{\epsilon,0} R_k(\lambda\mu, \lambda\mu)$$
$$(l_\lambda k 0 0 | l_\lambda 0)(l_\mu k 0 0 | l_\mu 0) \langle \bar{L}_1 \cdots \bar{L}_\lambda [l_\lambda k (l_\lambda)] L_\lambda \cdots \bar{L}_\mu l_\mu (L_\mu) \cdot L |$$
$$| \bar{L}_1 \cdots \bar{L}_\lambda l_\lambda (L_\lambda) \cdots \bar{L}_\mu [k l_\mu (l_\mu)] L_\mu \cdot L \rangle + \delta_{\epsilon,1} R_k(\lambda\mu, \mu\lambda)$$
$$(l_\lambda k 0 0 | l_\mu 0)^2 \langle \bar{S}_1 \cdots \bar{S}_\lambda \tfrac{1}{2}_{N-1}(S_\lambda) \cdots \bar{S}_\mu \tfrac{1}{2}_N (S_\mu) \cdot S |$$
$$| \bar{S}_1 \cdots \bar{S}_\lambda \tfrac{1}{2}_N (S_\lambda) \cdots \bar{S}_\mu \tfrac{1}{2}_{N-1}(S_\mu) \cdots S \times \bar{L}_1 \cdots \bar{L}_\lambda [l_\mu^{N-1} k (l_\lambda)] L_\lambda \cdots \bar{L}_\mu l_\mu^N (L_\mu) \cdot L |$$
$$| \bar{L}_1 \cdots \bar{L}_\lambda [k l_\mu^N (l_\lambda)] L_\lambda \cdots \bar{L}_\mu l_\mu^{N-1} (L_\mu) \cdots L \rangle \Big\} \qquad (2.7)$$

Applying the variation principle for completely arbitrary variations δP and imposing the orthonormality constraint, using Lagrange multipliers M, gives the Hartree Fock equations:

$$\left[\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{\ell_\lambda(\ell_\lambda+1)}{r^2}\right]P_\lambda(r)-\sum_\mu(N_\mu-\delta_{\mu\lambda})\Big\{\sum_{\bar\alpha_\lambda\bar L_\mu}\big(\ell_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda\|\ell_\lambda^{N_\lambda-1}\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda\big)^2$$
$$\big(\ell_\mu^{N_\mu}\alpha_\mu S_\mu L_\mu\|\ell_\mu^{N_\mu-1}\bar\alpha_\mu\bar S_\mu\bar L_\mu\big)\sum_{\epsilon=0,1}(1-\epsilon\delta_{\mu\lambda})\sum_k(\ell_\lambda k00|\ell_\lambda0)(\ell_\mu k00|\ell_\mu0)$$
$$\langle\bar L_1\cdots\bar L_\lambda\ell_\lambda k(\ell_\lambda)L_\lambda\cdot\bar L_\mu\ell_\mu(L_\mu)\cdots L\,|\,\bar L_1\cdots\bar L_\lambda\ell_\lambda(L_\lambda)\cdots\bar L_\mu k\ell_\mu(\ell_\mu)L_\mu\cdots L\rangle$$
$$y_k(\mu\mu r)P_\lambda(r)+(\ell_\lambda k00|\ell_\mu0)^2\langle\bar S_1\cdots\bar S_\lambda\tfrac12(S_\lambda)\cdot\bar S_\mu\tfrac12'(S_\mu)\cdots S\,|$$
$$|\bar S_1\cdots\bar S_\lambda\tfrac12'(S_\lambda)\cdots\bar S_\mu\tfrac12(S_\mu)\cdots S\rangle\times\langle\bar L_1\cdots\bar L_\lambda\ell_\mu k(\ell_\lambda)L_\lambda\cdots\bar L_\mu\ell_\mu'(L_\mu)\cdots L\,|$$
$$|\bar L_1\cdots\bar L_\lambda k\ell_\mu'(\ell_\lambda)L_\lambda\cdots\bar L_\mu\ell_\mu(L_\mu)\cdots L\rangle y_k(\mu\lambda r)P_\mu(r)$$
$$+\sum_\mu M_{\lambda\mu}P_\mu(r)=0 \qquad (2.8)$$

These are coupled nonlinear integro differential equations for the radial functions $P_\lambda(r)$. For complete subshells μ, λ it can be shown (Hartree 1957) that there is no restriction in choosing $M_{\lambda\mu} = 0 \quad \lambda \neq \mu$. For incomplete subshells we may take $M_{\lambda\mu} = 0$ for $\ell_\lambda \neq \ell_\mu$ since the orthogonality of the one electron orbitals is assured by the orthogonality of the spherical harmonics. However the one electron orbitals are also orthogonal if $\ell_\lambda = \ell_\mu$ but either $m_\lambda \neq m_\mu$ or $m_{s_\lambda} \neq m_{s_\mu}$ As the radial Hartree Fock equations are independent of these quantities the constraint $\int dr\, P_\lambda(r)\, P_\mu(r) = 0, \quad \lambda \neq \mu$ may lead to worse approximations than if it were not imposed. An example of such a case is the wave function for the 1s 2s (^{1}S) state of He like ions where the orthogonality of the 1s and 2s wave functions is assured by the antisymmetry of the spin wave function, [Sharma and Coulson (1962)]. For this system the antisymmetric wave function is

$$\Psi = \frac{1}{\sqrt{2}}\left[u_{1s}^{+}(1)\,u_{2s}^{-}(2) - u_{1s}^{+}(2)\,u_{2s}^{-}(1)\right]$$

where the superscripts refer to the spin orientation. Due to the different spin orientations of the two one particle wave functions we cannot make the substitution $P_{2s}(r) = P_{2s}(r) + A\,P_{1s}(r)$ without altering Ψ and hence have no justification

for imposing the constraint

$$\int P_{1s}(r)\, P_{2s}(r)\, dr = 0.$$

The Hartree-Fock equations may be solved, subject to the boundary conditions $P(0) = 0$, $P(r) \to 0$ as $r \to \infty$, either numerically or by specifying some analytic form of P(r) containing parameters which are varied to obtain the 'best' function. Froese (1963) has written a computer program to numerically solve the Hartree Fock equations for any atomic system with no further approximation, other than taking $M_{\mu\lambda} = 0$, $\mu \neq \lambda$. Numerical solution of the Hartree Fock equations can give greater accuracy than the analytic methods and is more convenient for complex atomic systems since analytic expressions for the radial functions become increasingly more complicated as the numbers of electrons increases. Roothaan and coworkers (1960) have devised a more accurate analytic or expansion method of solving the radial Hartree Fock equations. They make the expansion

$$R_{nl}(r) = \sum_p C_{nlp} [(2n_{lp})!]^{-\frac{1}{2}} (2\zeta_{lp})^{n_{lp}+\frac{1}{2}} r^{n_{lp}-1} e^{-\zeta_{lp} r} \quad (2.9)$$

On substituting this expression in the expression for E and applying the variational principle for variations $C_{nlp} \to C_{nlp} + \delta C_{nlp}$, they obtain pseudo-eigenvalue equations for the vectors C (these will not be true eigenvalue equations because of the self consistancy requirement). Having found a set $\{C_{nlp}\}$ for a particular ζ_{lp} and n_{lp} they then vary ζ_{lp} and n_{lp} to minimise E in such a way that $R_{nl}(r)$ has the correct behaviour for small r (Lowdin 1954). These analytic radial functions have been calculated for a wide range of atomic systems, in most cases to an accuracy comparable

to the numerical results of Froese. They have the advantage of convenience over numerical tabulations, when used as input to scattering programs, since differentiation and integration may be performed analytically in many cases.

Continuum Hartree Fock functions

We expand the wave functions of the continuum electron in central field wave functions as described in S.M. The antisymmetric wave function for the complete system is

$$\Psi(\underline{x}_1 \cdots \underline{x}_{N+1}) = \frac{1}{(N+1)^{\frac{1}{2}}} \sum_{p=1}^{N+1} (-1)^{N+1-p} \sum_{\Gamma} \psi(\Gamma \underline{X} \tilde{\underline{x}}_p) \frac{\tilde{F}_\Gamma(r_p)}{r_p} \quad (2.10)$$

Asymptotically the most general form of the radial function $\tilde{F}$ of the continuum electron is some superposition of incoming and outgoing spherical waves, i.e.,

$$\tilde{F}_\Gamma(r) \underset{r \to \infty}{\sim} A_\Gamma e^{-i\theta_\Gamma} - B_\Gamma e^{i\theta_\Gamma}$$

The coefficients A_Γ and B_Γ are related by

$$B_\Gamma = \sum_{\Gamma'} S_{\Gamma\Gamma'} A_{\Gamma'}$$

where $S_{\Gamma\Gamma'}$ is the scattering matrix and the sum is over all incident channels Γ'. Hence

$$\tilde{F}_\Gamma(r) \sim \sum_{\Gamma'} A_{\Gamma'} \left[\delta_{\Gamma\Gamma'} e^{-i\theta_\Gamma} - S_{\Gamma\Gamma'} e^{i\theta_\Gamma} \right]$$

For numerical calculations it is more convenient to express the asymptotic form of $\tilde{F}_\Gamma$ in terms of the reactance matrix R, which is real and symmetric and is defined by

$$S = \frac{1 + iR}{1 - iR}$$

Making this substitution we obtain

$$\tilde{F}_\Gamma(r) \sim \sum_{\Gamma'} \frac{-2iA_{\Gamma'}}{(1-iR_{\Gamma\Gamma'})} \left[\delta_{\Gamma\Gamma'} \sin\theta_\Gamma + R_{\Gamma\Gamma'} \cos\theta_\Gamma\right] \tag{2.11}$$

for open channels Γ, Γ'. If we choose the continuum wave functions to be normalised to an incident wave of one particle passing through unit area, per unit time

$$\tilde{F}_\Gamma(r) = \sum_{\Gamma'} \frac{2i}{(1-iR)_{\Gamma\Gamma'}} \frac{1}{k_\Gamma^{\frac{1}{2}}} \left[\delta_{\Gamma\Gamma'} \sin\theta_\Gamma + R_{\Gamma\Gamma} \cos\theta_\Gamma\right] \tag{2.12}$$

It will be more convenient to work with real functions

$$\approx{F}_\Gamma(r) = \sum_{\Gamma'} F_{\Gamma\Gamma'}(r) \sim \sum_{\Gamma'} \frac{1}{k_\Gamma^{\frac{1}{2}}} \left[\delta_{\Gamma\Gamma'} \sin\theta_\Gamma + R_{\Gamma\Gamma'} \cos\theta_\Gamma\right] \tag{2.13}$$

In the closed channels

$$F_{\Gamma\Gamma'}(r) \sim \delta_{\Gamma\Gamma'} N_\Gamma \exp\left(-|k_\Gamma| r - \frac{Z-N}{|k_\Gamma|} \log 2|k_\Gamma| r\right)$$

As for the bound states we required that $F_{\Gamma\Gamma'}(r) r^{-1}$ is everywhere finite and hence the boundary condition of the origin is $F_{\Gamma\Gamma'}(0) = 0$. The total wave function may now be written in the form

$$\underline{\Psi}(\underline{x}_1 \cdots \underline{x}_{N+1}) = \frac{1}{(N+1)^{\frac{1}{2}}} \sum_{p=1}^{N+1} (-1)^{N+1-p} \sum_{\Gamma\Gamma'} \mathcal{A}(\Gamma \underline{X} \hat{\underline{x}}_p) \frac{F_{\Gamma\Gamma'}(r_p)}{r_p} \tag{2.14}$$

For the system initially in state Γ_j

$$\underline{\Psi}(\Gamma_j \underline{x}_1 \cdots \underline{x}_{N+1}) = \frac{1}{(N+1)^{\frac{1}{2}}} \sum_{p=1}^{N+1} (-1)^{N+1-p} \sum_{\Gamma_i} \mathcal{A}(\Gamma \underline{X} \hat{\underline{x}}_p) \frac{F_{ij}(r_p)}{r_p} \tag{2.15}$$

We make the assumption that the radial functions $P_\lambda(r)$ used in the construction of $\mathcal{A}(\Gamma \underline{X} \hat{\underline{x}}_p)$ are independent of Γ and depend only on N and Z. The validity of this approximation is discussed in S.M. From the determinantal form of the

wave function (2.15) we see that we may choose F_{ij} such that

$$\delta_{l_i l_\lambda} \int_0^\infty dr\, F_{ij}(r)\, P_{nl_\lambda}(r) = 0 \qquad (2.16)$$

for all closed subshells λ, without imposing any restriction on the total wave function, since Ψ is unaltered if we replace F_{ij} by $F_{ij} + C\, P_{nl_\lambda}$, where C is chosen such that equation (2.16) is satisfied. If $l_i \neq l_\lambda$ then the orthogonality of the continuum orbital and the one electron orbitals of subshell λ is assured by the orthogonality of the spherical harmonics. If λ is an incomplete subshell and $l_i = l_\lambda$ we are not free to impose the constraint (2.16). There are two ways in which we may proceed. The first is to use as our trial wave function that given by equation (2.15) and without making the assumption of orthogonality for the incomplete subshells with $l_\lambda = l_i$. The second method was proposed by Seaton (unpublished notes, 1961) and subsequently used by Smith, Henry and Burke (1966) and Saraph, Seaton and Shemming (1966) in their calculations on electron scattering by atomic systems having incomplete p subshells. Seaton makes the substitution

$$F_{ij}(r) = F'_{ij}(r) + C_{ij}^{\lambda}\, P_{nl_\lambda}(r)\, \delta_{l_i l_\lambda}$$

where

$$\int_0^\infty dr\, F'_{ij}(r)\, P_{nl_\lambda}(r) = 0$$

$$\int_0^\infty dr\, F_{ij}(r)\, P_{nl_\lambda}(r) = C_{ij}^{\lambda}\, \delta_{l_i l_\lambda} \qquad (2.17)$$

This is equivalent to adding to our trial function (2.23) terms of the form $C_\mu^j \overline{\Phi}_\mu(L_j S_j \pi_j)$ where Φ is a properly antisymmetric function of N + 1 electrons constructed from the same radial

Hartree Fock functions as is $\psi(\gamma_i X^N)$. Hence it will not be an eigenfunction of the N + 1 electron Hamiltonian, equation (2.1) but since we have made the approximation that the $P_{nl}(r)$ are independent of configuration it may be regarded as allowing for the virtual capture of the incident electron into the incomplete subshell μ.

In analogy with equation (2.4a) we write

$$\Phi_\mu(q_\mu L S \pi \underline{x}_1 \cdots \underline{x}_{N+1}) = \mathcal{N}(N_\lambda)^{-\frac{1}{2}} \sum_{q_\mu} (-1)^{p_{q_\mu}} \phi_\mu(q_\mu L S \pi \underline{X}^{N+1}) \tag{2.18}$$

We take as our trial function

$$\Psi_t(\Gamma_i \underline{X}^{N+1}) = \Psi(\Gamma_i \underline{X}^{N+1}) + \sum_\mu C_\mu^i \Phi_\mu(L_i S_i \pi_i \underline{X}^{N+1}) \tag{2.19}$$

where $\sum_\mu$ runs over all incomplete subshells in the target configurations included in the eigenfunction expansion. The C_μ^i are arbitrary parameters which together with the $F_{ij}(r)$ will be determined from a variational principle.

In the derivation of the radial equations both methods for handling the non-orthogonality of the continuum orbital and the orbitals of the incomplete subshells λ in the case $\ell_i = \ell_\lambda$ require the evaluation of matrix elements of H which do not occur in the other cases and which lead to additional inhomogeneous terms in the differential equations for the $F_{ij}(r)$. However, for complex atomic systems, Seaton's method leads to considerably more simple expressions for the matrix elements and therefore we have used equation (2.27) as our trial function in S.M. There we used a variational principle to derive differential equations for the radial functions $F_{i\ell}(r)$ subject to constraint, $\delta_{\ell_i \ell_\lambda} \int dr\, P_{n\ell_\lambda}(r) F_{i\ell}(r) = 0$ for all subshells λ. The equations obtained from the direct method using the wave function (2.23)

are discussed in Section 2.3.

2.2. Evaluation of the matrix elements (Case I)

The evaluation of the matrix elements using Ψ defined by equation (2.27) is described in detail in S.M. section 3. In this section we discuss the approximation made in the evaluation of the direct potential, namely, that the target wave functions satisfy the equation

$$\int\cdots\int d\underline{x}_1 \cdots d\underline{x}_N \, \psi(\gamma_i \underline{X})(H_N - \mathcal{E}_j)\psi(\gamma_j \underline{X}) = 0$$

We also give an alternative expression for the terms quadratic in C which is more convenient for machine computations than that given in S.M.

Direct terms

In order to simplify the expression for the direct potential we made the assumption that

$$\int\cdots\int d\underline{x}_1 \cdots d\underline{x}_N \, \psi(\gamma_i \underline{X})(H_N - \mathcal{E}_j)\psi(\gamma_j X) = 0 \qquad (2.20)$$

We have also made the assumption that $\psi(\gamma_i X)$ and $\psi(\gamma_j X)$ may be constructed from the same set of one electron orbitals. The $\psi(\gamma X)$ constructed in the manner described in section (2.1) are orthonormal, hence we may write equation (2.20) in the form:

$$\int\cdots\int d\underline{x}_1 \cdots d\underline{x}_N \, \psi(\gamma_i \underline{X}) H_N \psi(\gamma_j \underline{X}) = 0 \quad i \neq j \qquad (2.20a)$$

$$\int\cdots\int d\underline{x}_1 \cdots d\underline{x}_N \, \psi(\gamma_j \underline{X}) H_N \psi(\gamma_j \underline{X}) = \mathcal{E}_j \qquad (2.20b)$$

Before using the direct potential given in S.M. equation (48) we must therefore consider the validity of equation (2.20a)

for the Hartree Fock functions to be used and the error in ϵ_i incurred by the use of approximate wave functions.

The matrix element $\langle\psi(\gamma_i X)|H_N|\psi(\gamma_j X)\rangle$ may be evaluated in the same way as the diagonal elements, equations (2.6) and (2.7).

$$\left\langle \sum_{i=1}^{N} H_1(i) \right\rangle = N\langle H_1(N)\rangle$$

$$= N\left[\eta(N_\nu^i)\eta(N_\nu^j)\right]^{-\frac{1}{2}} \sum_{q_i q_j} (-1)^{P_{q_i}+P_{q_j}}$$

$$\langle \psi(q_i \gamma_i \underline{X}) \,|\, H_1(N) \,|\, \psi(q_j \gamma_j \underline{X}) \rangle$$

The matrix element on the r.h.s. will vanish if γ_i and γ_j differ by more than one electron jump and the non zero contributions to $\sum_{q_i q_j}$ will come from those $q_i q_j$ which include to the same distribution $\bar{q}$ of labels 1..N-1. Hence we may replace

$$\sum_{q_i q_j} \text{ by } \sum_{\rho_i \rho_j} \prod_{\nu} \delta(N_\nu^i, N_\nu^j + \delta_{\nu\rho_i} - \delta_{\nu\rho_j})\eta(\bar{N}_\nu)$$

where ρ_i is the subshell containing electron N in q_i and ρ_j contains N in q_j. In analogy with S.M. equation (56) we obtain

$$N\langle H_1(N)\rangle = \sum_{\rho_i \rho_j} \prod_{\nu} \delta(N_\nu^i, N_\nu^j + \delta_{\nu\rho_i} - \delta_{\nu\rho_j}) \left[N_{\rho_i} N_{\rho_j}\right]^{\frac{1}{2}}$$

$$(-1)^{\Delta\rho_{ij}} \sum_{\bar{\alpha}_{\rho_i} \cdots \bar{L}_{\rho_j}} \left(\ell_{\rho_i}^{N_{\rho_i}} \alpha_{\rho_i} S_{\rho_i} L_{\rho_i} \| \ell_{\rho_i}^{\bar{N}_{\rho_i}} \bar{\alpha}_{\rho_i} \bar{S}_{\rho_i} \bar{L}_{\rho_i}\right)\left(\ell_{\rho_j}^{N_{\rho_j}} \alpha_{\rho_j} S_{\rho_j} L_{\rho_j} \| \ell_{\rho_j}^{\bar{N}_{\rho_j}} \bar{\alpha}_{\rho_j} \bar{S}_{\rho_j} \bar{L}_{\rho_j}\right)$$

$$\langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2}_N (S_{\rho_i}) \cdots \bar{S}_{\rho_j} \cdots S \,|\, \bar{S}_1 \cdots \bar{S}_{\rho_i} \cdots \bar{S}_{\rho_j} \tfrac{1}{2}_N (S_{\rho_j}) \cdots S\rangle$$

$$\langle \bar{L}_1 \cdots \bar{L}_{\rho_i} \ell^N(L_{\rho_i}) \cdots L \,|\, \bar{L}_1 \cdots \bar{L}_{\rho_j} \ell^N(L_{\rho_j}) \cdots L\rangle \int dr\, P_{\rho_i}\left[-\tfrac{1}{2}\frac{d^2}{dr^2} - \ell_{\rho_i}\frac{(\ell_{\rho_i}+1)}{r} - \frac{2Z}{r}\right] P_{\rho_j}(r) \qquad (2.21a)$$

The matrix element

$$\left\langle \sum_{i<j}^{N} \frac{1}{r_{ij}} \right\rangle = \tfrac{1}{2} N(N-1) \left\langle \frac{1}{r_{N-1,N}} \right\rangle$$

and $\left\langle \frac{1}{r_{N-1,N}} \right\rangle$ is the N particle analogue of the matrix element on the l.h.s. of S.M. equation (62). Hence from equation (2.21a) and S.M. equation (62a) we obtain

$$
\begin{aligned}
&\langle \psi(\gamma_i \underline{X}) \,|\, H_N \,|\, \psi(\gamma_j \underline{X}) \rangle \\
&= \sum_{\rho_i \rho_j} \prod_{\lambda}{}' \delta(N_{\lambda i}, N_{\lambda j} + \delta_{\lambda \rho_i} - \delta_{\lambda \rho_j}) [N_{\rho_i} N_{\rho_j}]^{\frac{1}{2}} (-\tfrac{1}{2}) \int dr\, P_{\rho_i}(r) \\
&\left[\frac{d^2}{dr^2} - \frac{l_{\rho_i}(l_{\rho_i}+1)}{r^2} + \frac{2Z}{r} \right] \delta_{l_{\rho_i} l_{\rho_j}} (-1)^{\Delta \rho_{ij}} \sum_{\bar{\alpha}_{\rho_i} \cdots \bar{L}_{\rho_j}} (l_{\rho_i}^{N_{\rho_i}} \alpha_{\rho_i} S_{\rho_i} L_{\rho_i} \| l_{\rho_i}^{\bar{N}_{\rho_i}} \bar{\alpha}_{\rho_i} \bar{S}_{\rho_i} \bar{L}_{\rho_i}) \\
&(l_{\rho_j}^{N_{\rho_j}} \alpha_{\rho_j} S_{\rho_j} L_{\rho_j} \| l_{\rho_j}^{\bar{N}_{\rho_j}} \bar{\alpha}_{\rho_j} \bar{S}_{\rho_j} \bar{L}_{\rho_j}) \langle \bar{L}_1 \cdots \bar{L}_{\rho_i} l_{\rho_i}^{N+1}(L_{\rho_i}) \cdots L_i \,| \\
&| \bar{L}_1 \cdots \bar{L}_{\rho_j} l_{\rho_j}^{N+1}(L_{\rho_j}) \cdots L_j \rangle \langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2}_{N+1}(S_{\rho_i}) \cdots S_i \,|\, \bar{S}_1 \cdots \bar{S}_{\rho_j} \tfrac{1}{2}_{N+1}(S_{\rho_j}) \cdots S \rangle \\
&\delta_{L_i L_j} \delta_{M_{L_i} M_{L_j}} \delta_{S_i S_j} \delta_{M_{S_i} M_{S_j}} \quad + \sum_{\substack{\rho_i \le \sigma_i \\ \rho_j \le \sigma_j}} \prod_{\lambda}{}' \\
&\delta(N_{\lambda}^{i}, N_{\lambda}^{j} + \delta_{\lambda \rho_i} + \delta_{\lambda \sigma_i} - \delta_{\lambda \rho_j} - \delta_{\lambda \sigma_j}) [N_{\rho_i} (N_{\sigma_i} - \delta_{\rho_i \sigma_i}) N_{\rho_j} \\
&(N_{\sigma_j} - \delta_{\rho_j \sigma_j})]^{\frac{1}{2}} (-1)^{\Delta \rho_{ij}} \sum_{\bar{\alpha}_{\rho_i} \cdots \bar{L}_{\rho_j}} (l_{\rho_i}^{N_{\rho_i}} \alpha_{\rho_i} S_{\rho_i} L_{\rho_i} \| l_{\rho_i}^{\bar{N}_{\rho_i}} \bar{\alpha}_{\rho_i} \bar{S}_{\rho_i} \bar{L}_{\rho_i}) \\
&(l_{\rho_j}^{N_{\rho_j}} \alpha_{\rho_j} S_{\rho_j} L_{\rho_j} \| l_{\rho_j}^{\bar{N}_{\rho_j}} \bar{\alpha}_{\rho_j} \bar{S}_{\rho_j} \bar{L}_{\rho_j}) (l_{\sigma_i}^{N_{\sigma_i}} \alpha_{\sigma_i} S_{\sigma_i} L_{\sigma_i} \| l_{\sigma_i}^{\bar{N}_{\sigma_i}} \bar{\alpha}_{\sigma_i} \bar{S}_{\sigma_i} \bar{L}_{\sigma_i}) \\
&(l_{\sigma_j}^{N_{\sigma_j}} \alpha_{\sigma_j} S_{\sigma_j} L_{\sigma_j} \| l_{\sigma_j}^{\bar{N}_{\sigma_j}} \bar{\alpha}_{\sigma_j} \bar{S}_{\sigma_j} \bar{L}_{\sigma_j}) \sum_{\epsilon \epsilon' = 0,1} (1 - \epsilon \delta_{\rho_i \sigma_i})(1 - \epsilon' \delta_{\rho_j \sigma_j}) \\
&(-1)^{\epsilon - \epsilon'} \langle S_i | S_j \rangle \sum_k \Big\{ \delta_{\epsilon \epsilon'} R_k(\rho_i \sigma_i \rho_j \sigma_j)(l_{\rho_i} k\, 0\, 0 \,|\, l_{\rho_j} 0) \\
&(l_{\sigma_j} k\, 0\, 0 \,|\, l_{\sigma_i} 0) \langle L_i | L_j \rangle^{\rightarrow} + (1 - \delta_{\epsilon \epsilon'}) R_k(\rho_i \sigma_i \sigma_j \rho_j) \\
&(l_{\rho_i} k\, 0\, 0 \,|\, l_{\sigma_j} 0)(l_{\rho_j} k\, 0\, 0 \,|\, l_{\sigma_i} 0) \langle L_i | L_j \rangle^{\in} \Big\} \delta_{L_i L_j} \delta_{S_i S_j} \delta_{M_{L_i} M_{L_j}} \delta_{M_{S_i} M_{S_j}}
\end{aligned}
$$

(2.21)

$$
\begin{aligned}
\langle S_i | S_j \rangle &= \langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2}_{N+\epsilon}(S_{\rho_i}) \cdots \bar{S}_{\sigma_i} \tfrac{1}{2}_{N+1-\epsilon}(S_{\sigma_i}) \cdots S_i \,| \\
&\quad | \bar{S}_1 \cdots \bar{S}_{\rho_j} \tfrac{1}{2}_{N+1+\epsilon'}(S_{\rho_j}) \cdots \bar{S}_{\sigma_j} \tfrac{1}{2}_{N+1-\epsilon'}(S_{\sigma_j}) \cdots S_j \rangle \\
\langle L_i | L_j \rangle^{\rightarrow} &= \langle \bar{L}_1 \cdots \bar{L}_{\rho_i} [l_{\rho_j} k(l_{\rho_i})] L_{\rho_i} \cdots \bar{L}_{\sigma_i} l_{\sigma_i}(L_{\sigma_i}) \cdots L_i \,| \\
&\quad | \bar{L}_1 \cdots \bar{L}_{\rho_j} l_{\rho_j}(L_{\rho_j}) \cdots \bar{L}_{\sigma_j} [k\, l_{\sigma_i}(l_{\sigma_j}) L_{\sigma_j}] \cdots L_j \rangle \\
\langle L_i | L_j \rangle^{\in} &= \langle \bar{L}_1 \cdots \bar{L}_{\rho_i} [l_{\sigma_j} k(l_{\rho_i})] L_{\rho_i} \cdots \bar{L}_{\sigma_i} l_{\sigma_i}(L_{\sigma_i}) \cdots L_i \,| \\
&\quad | \bar{L}_1 \cdots \bar{L}_{\rho_j} [k\, l_{\sigma_i}(l_{\rho_j})] L_{\rho_j} \cdots \bar{L}_{\sigma_j} l_{\sigma_j}(L_{\sigma_j}) \cdots L_j \rangle
\end{aligned}
$$

From equation (2.21) we see that the matrix element is diagonal in the quantum numbers $\alpha S M_S L M_L \pi$. The off diagonal elements will not vanish for $\gamma_i \gamma_j$ having the same total quantum numbers for different electronic configurations. An example of a non-vanishing off diagonal matrix element is one of the form $\langle 1s^2 2s^2 2p^4 | H_N | 1s^2 2s^2 2p^3 3p \rangle$. However, in many applications of the eigenfunction expansion method the off diagonal terms will vanish and in other cases they will be small in comparison with the diagonal matrix elements. Therefore the equation

$$\int \cdots \int d\underline{x}_1 \cdots d\underline{x}_N \, \psi(\gamma_i \underline{X}) \, H_N \, \psi(\gamma_j \underline{X}) = 0$$

will be exact in many applications and may be considered a good approximation in others.

The error in $\mathcal{E}_i$ incurred by assuming that $\psi(\gamma_i X)$ and $\psi(\gamma_j X)$ may be constructed from the same set of Hartree Fock functions $P_\lambda(r)$, for all γ retained in the eigenfunction expansion can be expected to be small if the exact energy differences $(E_{\gamma_i} - E_{\gamma_j})$ are also small.

In practice, the most reliable results are obtained if the electron energies in the inelastic channels are calculated using experimentally determined energy differences rather than Hartree Fock energies.

C^2 term

In S.M. we expressed the matrix elements $\langle \Phi_\mu (L_k S_k \pi_k) | H_{N+1} | \Phi \; (L_\ell S_\ell \pi_\ell) \rangle$ in terms of the matrix elements of $H_1(N+1)$ and $\sum_{\alpha=1}^{N} \frac{1}{r_{\alpha,N+1}}$ together with the Hartree Fock energies of the N electron target. Φ is properly antisymmetric under interchange of any pair of labels 1..N+1.

Hence we had to consider all possible configurations of the N electron system resulting from the removal of one electron from the configuration described by Φ and not merely the target configurations included in the eigenfunction expansion. Although the error incurred, by assuming that all the $\psi(\gamma_i X)$ included in the eigenfunction expansion may be constructed from the same set of radial functions $P_\lambda(r)$, may be small, the error in the Hartree Fock energies $E^{\tilde{L},\tilde{S}}$ of S.M. equation(72)for the highly excited configurations may be considerable. An alternative expression for the matrix element

$$\langle \Phi_\mu(L_k S_k \pi_k) | H_{N+1} | \Phi_\nu(L_\ell S_\ell \pi_\ell) \rangle \qquad (2.22)$$

may be obtained by noting that, although the Φ_μ are neither eigenfunctions of H_{N+1} nor constructed from the appropriate Hartree Fock functions for the N+1 electron system, they are properly antisymmetric under interchange of any pair of the N+1 labels and are constructed in the same way and from the same set of radial functions as the target function $\psi(\gamma \underline{X})$. Hence the expression for the matrix element (2.22) is exactly analogous to that given in equation (2.21) with N_λ now representing the number of electrons in subshell λ in the N+1 electron wave function.

The expression given in equation (2.21) is no more difficult to compute than the expressions given in S.M. equations (62a), (67) and (72) and does not require any Hartree Fock energies as input.

Evaluation of the Matrix Elements (Case II)

We wish to evaluate

$$L_{k\ell} = \langle \Psi_k | H - E | \Psi_\ell \rangle$$

when Ψ_k is of the form

$$\Psi_k = \frac{1}{(N+1)!} \sum_{p=1}^{N+1} (-1)^{N+1-p} \sum_{\Gamma_i} \psi(\Gamma_i \, \underline{X} \, \hat{x}_p) \frac{F_{ik}(r_p)}{r_p} \qquad (2.30)$$

and

$$\delta_{\ell_i \ell_\lambda} \int_0^\infty dr \, F_{ik}(r) P_\lambda(r) = 0 \qquad (2.31)$$

only if λ is a closed subshell.

The evaluation of $L_{k\ell}$ is equivalent to the evaluation of the C independent terms of S.M. section 3, but without the orthogonality condition (2.31) for incomplete subshells λ with $\ell_\lambda = \ell_i$.

It is clear that the direct terms (S.M. equation 42) are not affected by the orthogonality requirement since electron label N+1 is in the continuum orbital on both sides of the matrix element. However, the exchange term will not simplify to the expression given by S.M. equation (41). The exchange term is

$$L^E_{ik,j\ell} = -N \int \cdots \int d\underline{x}_1 \cdots d\underline{x}_{N+1} \, \psi(\Gamma_i \, \underline{X} \, \hat{x}_{N+1}) \frac{F_{jk}(r_{N+1})}{r_{N+1}} [H - E]$$
$$\psi(\Gamma_j \, \underline{X} \, \hat{x}_N) \frac{F_{j\ell}(r_N)}{r_N}$$

We consider first the matrix element of the one electron operators

$$\langle H_1 \rangle = -N \int\cdots\int d\underline{x}_1 \cdots d\underline{x}_{N+1} \frac{1}{[\eta(N_>^i)\eta(N_>^j)]^{\frac{1}{2}}} \sum_{q_i q_j} (-1)^{\rho_{q_i}+\rho_{q_j}}$$
$$\psi(q_i \Gamma_i \underline{X} \hat{x}_{N+1}) \underline{F_{i\kappa}(r_{N+1})}_{r_{N+1}} \sum_{\alpha=1}^{N+1} H_1(\alpha) \psi(q_j \Gamma_j \underline{X} \hat{x}_N) \underline{F_{j\ell}(r_N)}_{r_N}$$

The orthogonality constraint may be expressed in the form

$$\int dr\, F_{ij}(r) P_\lambda(r) = C_{ij}^\lambda \delta_{\ell_i \ell_\lambda} \qquad C_{ij}^\lambda \neq 0 \qquad (2.32)$$

Although, strictly speaking, electrons 1..a-1, a+1, ..., N+1 are 'spectators' for $H_1(a)$, only electrons 1..a-1, a+1, ...N-1 are 'spectators' in the sense that the various distributions of these labels contribute equally to the matrix element. For $a \neq N$, N+1 the matrix element $\langle H_1(a) \rangle$ may be non-zero if $\gamma_i \gamma_j$ differ by two or less electron jumps. We define μ_i and μ_j to be the subshells containing electrons N and N+1 in distributions q_i and q_j respectively.

$$\left\langle \sum_{\alpha=1}^{N-1} H_1(\alpha) \right\rangle = -N(N-1)\left[\eta(N_>^i)\eta(N_>^j)\right]^{-\frac{1}{2}} \sum_{q_i q_j} (-1)^{\rho_{q_i}+\rho_{q_j}}$$
$$\int\cdots\int d\underline{x}_1 \cdots d\underline{x}_{N+1}\, \psi_\kappa(q_i \Gamma_i \underline{X} \hat{x}_{N+1}) \underline{F_{i\kappa}(r_{N+1})}_{r_{N+1}} H_1(N-1)$$
$$\times \psi(q_j \Gamma_j \underline{X} \hat{x}_N) \underline{F_{j\ell}(r_N)}_{r_N}$$
$$= -N(N-1)\left[\eta(N_>^i)\eta N_>^j\right]^{-\frac{1}{2}} \sum_{\mu_i \mu_j \rho_i \rho_j} \prod_> \eta(\bar{N}_>)$$
$$\delta(N_>^i, N_>^j + \delta_{>\rho_i} + \delta_{>\mu_i} - \delta_{>\rho_j} - \delta_{>\mu_j})(-1)^{\Delta\rho_{ij}} \langle H_1(N-1) \rangle_{\mu_i \mu_j \rho_i \rho_j}$$

where

$$\eta(\bar{N}_>) = (N-2)! / \prod_> (\bar{N}_>!)$$

$$\Delta\rho_{ij} = \sum_{>=\min(\rho_i,\mu_i)}^{\max(\rho_i,\mu_i)} \bar{N}_> + \sum_{>=\min(\rho_j,\mu_j)+1}^{\max(\rho_j,\mu_j)} \bar{N}_>$$
$$+ \operatorname{sign}(\mu_i - \rho_i) + \operatorname{sign}(\mu_j - \rho_j)$$

the outside factor now becomes

$$(-1)\left[N_{\rho_i}(N_{\mu_i}-\delta_{\rho_i\mu_i})\,N_{\rho_j}(N_{\mu_j}-\delta_{\rho_j\mu_j})\right]^{\frac{1}{2}}$$

and the complete matrix element is, in analogy with S.M. Equation (56)

$$\begin{aligned}
&\Big\langle \sum_{\alpha=1}^{N-1} H_1(\alpha)\Big\rangle = \sum_{\rho_i\rho_j\mu_i\mu_j} \prod_{\lambda} \delta\left(N_\lambda^i N_\lambda^j + \delta_{\lambda\rho_i} - \delta_{\lambda\rho_j} + \delta_{\lambda\mu_i} - \delta_{\lambda\mu_j}\right) \\
&(-1)^{\Delta\rho_{ij}+1}\left[N_{\rho_i}(N_{\mu_i}-\delta_{\rho_i\mu_i})\,N_{\rho_j}(N_{\mu_j}-\delta_{\rho_j\mu_j})\right]^{\frac{1}{2}} \sum_{\bar\alpha_{\rho_i}\bar L_{\mu_j}} \left(l_{\rho_i}^{N_{\rho_i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\|l_{\rho_i}^{\bar N_{\rho_i}}\bar\alpha_{\rho_i}\bar S_{\rho_i}\bar L_{\rho_i}\right) \\
&\left(l_{\rho_j}^{N_{\rho_j}}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j}\|l_{\rho_j}^{\bar N_{\rho_j}}\bar\alpha_{\rho_j}\bar S_{\rho_j}\bar L_{\rho_j}\right)\left(l_{\mu_i}^{N_{\mu_i}}\alpha_{\mu_i}S_{\mu_i}L_{\mu_i}\|l_{\mu_i}^{\bar N_{\mu_i}}\bar\alpha_{\mu_i}\bar S_{\mu_i}\bar L_{\mu_i}\right) \\
&\left(l_{\mu_j}^{N_{\mu_j}}\alpha_{\mu_j}S_{\mu_j}L_{\mu_j}\|l_{\mu_j}^{\bar N_{\mu_j}}\bar\alpha_{\mu_j}\bar S_{\mu_j}\bar L_{\mu_j}\right)\Big\langle \bar S_1\cdots\bar S_{\rho_i}\tfrac{1}{2N-1}(S_{\rho_i})\cdots\bar S_{\mu_i}\tfrac{1}{2N}(S_{\mu_i})\cdots S_i\tfrac{1}{2N+1}S\,\Big| \\
&\Big|\bar S_1\cdots\bar S_{\rho_j}\tfrac{1}{2N-1}(S_{\rho_j})\cdots\bar S_{\mu_j}\tfrac{1}{2N+1}(S_{\mu_j})\cdots S_j\tfrac{1}{2N}S\Big\rangle\Big\langle \bar L_1\cdots\bar L_{\rho_i}l_{\rho_i}^{N-1}(L_{\rho_i})\cdots\bar L_{\mu_i}l_{\mu_i}^{N}(L_{\mu_i})\cdots L_i l_i^{N+1}L\,\Big| \\
&\Big|\bar L_1\cdots\bar L_{\rho_j}l_{\rho_j}^{N}(L_{\rho_j})\cdots\bar L_{\mu_j}l_{\mu_j}^{N+1}(L_{\mu_j})\cdots L_j l_j^{N}L\Big\rangle\,\delta_{l_{\rho_i}l_{\rho_j}}\,\delta_{l_{\mu_i}l_j}\,\delta_{l_i l_{\mu_j}} \\
&\int dr\,P_{\mu_i}(r)\,F_{jl}(r)\int dr\,F_{ik}(r)\,P_{\mu_j}(r)\left(-\tfrac{1}{2}\right)\int dr\,P_{\rho_i}(r) \\
&\left[\frac{d^2}{dr^2}-\frac{l_{\rho_j}(l_{\rho_j}+1)}{r^2}+\frac{2Z}{r}\right]P_{\rho_i}(r)
\end{aligned}\tag{2.33}$$

We are free to impose the constraint (2.31) for μ_i or μ_j a closed subshell hence the summation over μ_i and μ_j need only run over the incomplete subshells.

Similarly

$$\begin{aligned}
&\langle H_1(N)\rangle = \sum_{\mu_i\mu_j} \prod_{\lambda} \delta\left(N_\lambda^i N_\lambda^j + \delta_{\lambda\mu_i} - \delta_{\lambda\mu_j}\right)(-1)^{\Delta\rho_{ij}+1} \\
&\left[N_{\mu_i}N_{\mu_j}\right]^{\frac{1}{2}}\sum_{\bar\alpha_{\mu_i}\bar L_{\mu_j}}\left(l_{\mu_i}^{N_{\mu_i}}\alpha_{\mu_i}S_{\mu_i}L_{\mu_i}\|l_{\mu_i}^{\bar N_{\mu_i}}\bar\alpha_{\mu_i}\bar S_{\mu_i}\bar L_{\mu_i}\right)\left(l_{\mu_j}^{N_{\mu_j}}\alpha_{\mu_j}S_{\mu_j}L_{\mu_j}\|l_{\mu_j}^{\bar N_{\mu_j}}\bar\alpha_{\mu_j}\bar S_{\mu_j}\bar L_{\mu_j}\right) \\
&\Big\langle \bar S_1\cdots\bar S_{\mu_i}\tfrac{1}{2N}(S_{\mu_i})\cdots\bar S_{\mu_j}\cdots S_i\tfrac{1}{2N+1}S\,\Big|\,\bar S_1\cdots\bar S_{\mu_i}\cdots\bar S_{\mu_j}\tfrac{1}{2N+1}(S_{\mu_j})\cdots S_j\tfrac{1}{2N}S\Big\rangle \\
&\Big\langle \bar L_1\cdots\bar L_{\mu_i}l_{\mu_i}^{N}(L_{\mu_i})\cdots\bar L_{\mu_j}\cdots L_j l_i^{N+1}L\,\Big|\,\bar L_1\cdots\bar L_{\mu_i}\cdots\bar L_{\mu_j}l_{\mu_j}^{N+1}(L_{\mu_j})\cdots L_j l_j^{N}L\Big\rangle \\
&\delta_{l_i l_{\mu_j}}\,\delta_{l_{\mu_i}l_j}\int dr\,F_{ik}(r)\,P_{\mu_j}(r)\left(-\tfrac{1}{2}\right)\int dr\,P_{\mu_i}(r)\left[\frac{d^2}{dr^2}-\frac{l_j(l_j+1)}{r^2}\right. \\
&\left.+\frac{2Z}{r}\right]F_{jl}(r)
\end{aligned}\tag{2.34}$$

Now

$$\int_0^\infty dr\ P_{\mu_i}(r)\left[\frac{d^2}{dr^2} - \frac{l_j(l_j+1)}{r^2} + \frac{2Z}{r}\right] F_{jl}(r)$$

$$= \int_0^\infty dr\ F_{jl}(r)\left[\frac{d^2}{dr^2} - \frac{l_j(l_j+1)}{r^2} + \frac{2Z}{r}\right] P_{\mu_i}(r)$$

from Green's theorem and the boundary conditions

$P_\mu(0) = 0 = F_{jl}(0)$, $P_\mu(r) \to 0$ and $P'_\mu(r) \to 0$ as $r \to \infty$.

Hence we may write this matrix element in the form

$$\langle H_i(N)\rangle = \sum_{\mu_i\mu_j} D^{ij}_{\mu_i\mu_j} \int_\epsilon^\infty dr\ F_{in}(r)\, P_{\mu_j}(r) \int_0^\infty dr\ F_{jl}(r)$$

$$\left[\frac{d^2}{dr^2} - \frac{l_j(l_j+1)}{r^2} + \frac{2Z}{r}\right] P_{\mu_i}(r)$$

(2.35)

In exact analogy

$$\langle H_i(N+1)\rangle = \sum_{\mu_i\mu_j} D^{ij}_{\mu_i\mu_j} \int_0^\infty dr\ P_{\mu_i}(r)\, F_{jl}(r) \int dr\ F_{in}(r)$$

$$\left[\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2Z}{r}\right] P_{\mu_j}(r)$$

(2.35a)

Also, in more compact notation

$$\left\langle \sum_{\alpha=1}^{N-1} H_i(\alpha) \right\rangle = \sum_{\rho_i\rho_j\mu_i\mu_j} C^{ij}_{\rho_i\rho_j\mu_i\mu_j} \int dr\ P_{\mu_i}(r)\, F_{jl}(r)$$

$$\int dr\ F_{ik}(r)\, P_{\mu_j}(r) \int dr\ P_{\rho_i}(r)\left[\frac{d^2}{dr^2} - \frac{l_{\rho_j}(l_{\rho_j}+1)}{r^2} + \frac{2Z}{r}\right] P_{\rho_j}(r)$$

(2.36)

We have four types of two electron operators to consider

$$\sum_{i<j}^{N+1}\left\langle \frac{1}{r_{ij}}\right\rangle = \sum_{i<j}^{N-1}\left\langle \frac{1}{r_{ij}}\right\rangle + \sum_{i=1}^{N-1}\left\langle \frac{1}{r_{i,N}}\right\rangle + \sum_{i=1}^{N-1}\left\langle \frac{1}{r_{i,N+1}}\right\rangle + \left\langle \frac{1}{r_{N,N+1}}\right\rangle$$

The matrix element $\left\langle \frac{1}{r_{N,N+1}}\right\rangle$ is given by S.M. equation (41) and is of the form

$$\left\langle \frac{1}{r_{N+1,N}} \right\rangle = \sum_{\mu_i \mu_j t} E^{ij}_{\mu_i \mu_j t} R_t(\mu_i F_{ik} F_{je} \mu_j)$$

(2.37)

$$\left\langle \sum_{i=1}^{N-1} \frac{1}{r_{iN}} \right\rangle = -N(N-1) \left\langle \frac{1}{r_{N,N-1}} \right\rangle$$

$$= \sum_{\rho_i \rho_j \mu_i \mu_j} \prod_{\lambda} \delta(N^i_\lambda, N^j_\lambda + \delta_{\lambda\rho_i} + \delta_{\lambda\mu_i} - \delta_{\lambda\rho_j} - \delta_{\lambda\mu_j})(-1)^{\Delta\rho_j + 1}$$

$$[N_{\rho_i}(N_{\mu_i} - \delta_{\rho_i\mu_i}) N_{\rho_j}(N_{\mu_j} - \delta_{\rho_j\mu_j})]^{\frac{1}{2}} \sum_{\bar{\alpha}_{\rho_i} \bar{L}_{\mu_j}} (l_{\rho_i}^{N_{\rho_i}} \alpha_{\rho_i} S_{\rho_i} L_{\rho_i} \| l_{\rho_i}^{\bar{N}_{\rho_i}} \bar{\alpha}_{\rho_i} \bar{S}_{\rho_i} \bar{L}_{\rho_i})$$

$$(l_{\rho_j}^{N_{\rho_j}} \alpha_{\rho_j} S_{\rho_j} L_{\rho_j} \| l_{\rho_j}^{\bar{N}_{\rho_j}} \bar{\alpha}_{\rho_j} \bar{S}_{\rho_j} \bar{L}_{\rho_j})(l_{\mu_i}^{N_{\mu_i}} \alpha_{\mu_i} S_{\mu_i} L_{\mu_i} \| l_{\mu_i}^{\bar{N}_{\mu_i}} \bar{\alpha}_{\mu_i} \bar{S}_{\mu_i} \bar{L}_{\mu_i})$$

$$(l_{\mu_j}^{N_{\mu_j}} \alpha_{\mu_j} S_{\mu_j} L_{\mu_j} \| l_{\mu_j}^{\bar{N}_{\mu_j}} \bar{\alpha}_{\mu_j} \bar{S}_{\mu_j} \bar{L}_{\mu_j})$$

$$\langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2N-1}(S_{\rho_i}) \cdot \bar{S}_{\mu_i} \tfrac{1}{2N}(S_{\mu_i}) \cdots S_i \tfrac{1}{2N+1} S |$$

$$| \bar{S}_1 \cdots \bar{S}_{\rho_j} \tfrac{1}{2N-1}(S_{\rho_j}) \cdot \bar{S}_{\mu_j} \tfrac{1}{2N+1}(S_{\mu_j}) \cdots S_j \tfrac{1}{2N} S \rangle$$

$$\sum_t \langle \bar{L}_1 \cdots \bar{L}_{\rho_i} [l_{\rho_j}^{N-1} t(l_{\rho_i})] L_{\rho_i} \cdots \bar{L}_{\mu_i} l_{\mu_i}^{N}(L_{\mu_i}) \cdots L_i (l_i^{N+1} L |$$

$$| L_1 \cdots \bar{L}_{\rho_j} l_{\rho_j}(L_{\rho_j}) \cdots \bar{L}_{\mu_j} l_{\mu_j}^{N+1}(L_{\mu_j}) \cdots L_j \, t l_i^{N+1}(l_j) \, L \rangle$$

$$(l_{\rho_i} t \, 00 \, | \, l_{\rho_j} 0)(l_j t \, 00 \, | \, l_{\mu_i} 0) \int dr \, F_{ik}(r) P_{\mu_j}(r)$$

$$l_i l_{\mu_j} R_t(\rho_i \mu_i \rho_j F_{je})$$

$$= \sum_{\rho_i \rho_j \mu_i \mu_j t} \bar{C}^{ij}_{\rho_i \rho_j \mu_i \mu_j t} \int dr \, F_{ik}(r) P_{\mu_j}(r)$$

$$R_t(\rho_i \mu_i, \rho_j F_{je})$$

(2.38)

Similarly

$$\left\langle \sum_{i=1}^{N-1} \frac{1}{r_{i,N+1}} \right\rangle = \sum_{\rho_i \rho_j \mu_i \mu_j t} \bar{\bar{C}}^{ij}_{\rho_i \rho_j \mu_i \mu_j t} \int dr\, F_{je}(r) P_{\mu_i}(r) \, R_t(\rho_i F_{ik} \rho_j \mu_j) \tag{2.38a}$$

where

$$\bar{\bar{C}}_{\rho_i \rho_j \mu_i \mu_j t} = \prod_{\lambda} \delta(N^i_\lambda, N^j_\lambda + \delta_{\lambda \rho_i} + \delta_{\lambda \mu_i} - \delta_{\lambda \rho_j} - \delta_{\lambda \mu_j})$$

$$(-1)^{\Delta \rho_{ij}+1} \left[N_{\rho_i}(N_{\mu_i} - \delta_{\rho_i \mu_i}) N_{\rho_j}(N_{\mu_j} - \delta_{\rho_j \mu_j}) \right]^{\frac{1}{2}}$$

$$\sum_{\bar{\alpha}_{\rho_i} \bar{L}_{\mu_j}} (l_{\rho_i}^{N_{\rho_i}} \alpha_{\rho_i} S_{\rho_i} L_{\rho_i} \| l_{\rho_i}^{\bar{N}_{\rho_i}} \bar{\alpha}_{\rho_i} \bar{S}_{\rho_i} \bar{L}_{\rho_i})(l_{\rho_j}^{N_{\rho_j}} \alpha_{\rho_j} S_{\rho_j} L_{\rho_j} \| l_{\rho_j}^{\bar{N}_{\rho_j}} \bar{\alpha}_{\rho_j} \bar{S}_{\rho_j} \bar{L}_{\rho_j})$$

$$(l_{\mu_i}^{N_{\mu_i}} \alpha_{\mu_i} S_{\mu_i} L_{\mu_i} \| l_{\mu_i}^{\bar{N}_{\mu_i}} \bar{\alpha}_{\mu_i} \bar{S}_{\mu_i} \bar{L}_{\mu_i})(l_{\mu_j}^{N_{\mu_j}} \alpha_{\mu_j} S_{\mu_j} L_{\mu_j} \| l_{\mu_j}^{\bar{N}_{\mu_j}} \bar{\alpha}_{\mu_j} \bar{S}_{\mu_j} \bar{L}_{\mu_j})$$

$$\langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2N-1}(S_{\rho_i}) \cdots \bar{S}_{\mu_i} \tfrac{1}{2N}(S_{\mu_i}) \cdots S_i \tfrac{1}{2N+1} S |$$

$$| \bar{S}_1 \cdots \bar{S}_{\rho_j} \tfrac{1}{2N-1}(S_{\rho_j}) \cdots \bar{S}_{\mu_j} \tfrac{1}{2N+1}(S_{\mu_j}) \cdots S_j \tfrac{1}{2N} S \rangle$$

$$\langle \bar{L}_1 \cdots \bar{L}_{\rho_i} [l_{\rho_j}^{N-1} t(l_{\rho_i})] L_{\rho_i} \cdots \bar{L}_{\mu_i} l_{\mu_i}^{N}(L_{\mu_i}) \cdots L_i l_i^{N+1} L |$$

$$| \bar{L}_1 \cdots \bar{L}_{\rho_j} l_{\rho_j}^{N-1}(L_{\rho_j}) \cdots \bar{L}_{\mu_j} [l_i^{N+1} t(l_{\mu_j})] L_{\mu_j} \cdots L_j l_j^{N} L \rangle$$

$$(l_{\rho_i} t \cdots 0 | l_{\rho_j} 0)(l_{\mu_j} t \cdots 0 | l_i 0) \delta_{l_j l_{\mu_i}}$$

and

$$\left\langle \sum_{i<j}^{N-1} \frac{1}{r_{ij}} \right\rangle = -\frac{N}{2}(N-1)(N-2) \left\langle \frac{1}{r_{N-2,N-1}} \right\rangle$$

$$= \sum_{\rho_i \rho_j \sigma_i \sigma_j \mu_i \mu_j t} G^{ij}_{\rho_i \rho_j \sigma_i \sigma_j \mu_i \mu_j t} R_t(\rho_i \sigma_i \rho_j \sigma_j)$$

$$\int dr\, F_{ik}(r) P_{\mu_j}(r) \int dr\, P_{\mu_i}(r) F_{ik}(r) \tag{2.38b}$$

where σ denotes the subshell containing electron N-2 and

$$G^{ij}_{\rho_i\rho_j\sigma_i\sigma_j\mu_i\mu_j} = \frac{1}{2}\prod_\lambda \delta(N^i_\lambda, N^j_\lambda + \delta_{\lambda\rho_i} + \delta_{\lambda\mu_i} + \delta_{\lambda\sigma_i} - \delta_{\lambda\rho_j} - \delta_{\lambda\sigma_j} - \delta_{\lambda\mu_j})\left[N_{\rho_i}(N_{\sigma_i} - \delta_{\rho_i\sigma_i})(N_{\mu_i} - \delta_{\rho_i\mu_i} - \delta_{\sigma_i\mu_i})N_{\rho_j}(N_{\sigma_j} - \delta_{\rho_j\sigma_j})(N_{\mu_j} - \delta_{\mu_j\rho_j} - \delta_{\mu_j\sigma_j})\right]^{\frac{1}{2}}$$

$$\sum_{\alpha_{\rho_i}\cdots L_{\mu_j}} (l_{\rho_i}^{N_{\rho_i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i} \| l_{\rho_i}^{N_{\rho_i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i})(l_{\sigma_i}^{N_{\sigma_i}}\alpha_{\sigma_i}S_{\sigma_i}L_{\sigma_i} \| l_{\sigma_i}^{\bar{N}_{\sigma_i}}\bar{\alpha}_{\sigma_i}\bar{S}_{\sigma_i}\bar{L}_{\sigma_i})$$
$$(l_{\mu_i}^{N_{\mu_i}}\alpha_{\mu_i}S_{\mu_i}L_{\mu_i} \| l_{\mu_i}^{\bar{N}_{\mu_i}}\bar{\alpha}_{\mu_i}\bar{S}_{\mu_i}\bar{L}_{\mu_i})(l_{\rho_j}^{N_{\rho_j}}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j} \| l_{\rho_j}^{\bar{N}_{\rho_j}}\bar{\alpha}_{\rho_j}\bar{S}_{\rho_j}\bar{L}_{\rho_j})$$
$$(l_{\sigma_j}^{N_{\sigma_j}}\alpha_{\sigma_j}S_{\sigma_j}L_{\sigma_j} \| l_{\sigma_j}^{\bar{N}_{\sigma_j}}\bar{\alpha}_{\sigma_j}\bar{S}_{\sigma_j}\bar{L}_{\sigma_j})(l_{\mu_j}^{N_{\mu_j}}\alpha_{\mu_j}S_{\mu_j}L_{\mu_j} \| l_{\mu_j}^{\bar{N}_{\mu_j}}\bar{\alpha}_{\mu_j}\bar{S}_{\mu_j}\bar{L}_{\mu_j})$$
$$(-1)^{\Delta\rho_{ij}+1}\langle S_i \| S_j\rangle (l_{\rho_i} t\,oo \| l_{\rho_j} 0)$$
$$(l_{\sigma_j} t\,oo \| l_{\sigma_i} 0)\langle L_i \| L_j\rangle_t\, \delta_{l_{\mu_i}l_j}\,\delta_{l_i l_{\mu_j}}$$

Here

$$\Delta\rho_{ij} = \sum_{\lambda=\rho_i+1}^{b_i}\bar{N}_\lambda + \sum_{\lambda=\sigma_i+1}^{b_i}\bar{N}_\lambda + \sum_{\lambda=\mu_i+1}^{b_i}\bar{N}_\lambda + \sum_{\lambda=\rho_j+1}^{b_j}\bar{N}_\lambda + \sum_{\lambda=\sigma_j+1}^{b_j}\bar{N}_\lambda + \sum_{\lambda=\mu_j+1}^{b_j}\bar{N}_\lambda$$

$$\langle S_i \| S_j\rangle = \langle \bar{S}_1\cdots\bar{S}_{\sigma_i}\tfrac{1}{2N-2}(S_{\sigma_i})\cdots\bar{S}_{\rho_i}\tfrac{1}{2N-1}(S_{\rho_i})\cdots\bar{S}_{\mu_i}\tfrac{1}{2N}(S_{\mu_i})\cdots S_i\tfrac{1}{2N+1}S \|$$
$$\|\bar{S}_1\cdots\bar{S}_{\sigma_j}\tfrac{1}{2N-2}(S_{\sigma_j})\cdots\bar{S}_{\rho_j}\tfrac{1}{2N-1}(S_{\rho_j})\cdots\bar{S}_{\mu_j}\tfrac{1}{2N+1}(S_{\mu_j})\cdots S_j\tfrac{1}{2N}S\rangle$$

$$\langle L_i \| L_j\rangle = \langle \bar{L}_1\cdots\bar{L}_{\sigma_i}[l_{\sigma_j}^{N-2}\, t(l_{\sigma_i})]L_{\sigma_i}\;\bar{L}_{\rho_i}l_{\rho_i}^{N-1}(L_{\rho_i})\cdots$$
$$\bar{L}_{\mu_i}l_{\mu_i}^{N}(L_{\mu_i})\cdots L_i l_i^{N+1}L \,\|\, \bar{L}_1\cdots\bar{L}_{\sigma_j}l_{\sigma_j}^{N-2}(L_{\sigma_j})\cdots$$
$$\bar{L}_{\rho_j}[t\,l_{\rho_i}^{N-1}(l_{\rho_j})]L_{\rho_j}\cdots\bar{L}_{\mu_j}l_{\mu_j}^{N+1}(L_{\mu_j})\cdot L_j l_j^{N} L\rangle$$

The variational principle (S.M. equation 73) now becomes

$$\delta\Big[\sum_{i,j}\int dr\, F_{ik}(r)\,\mathcal{L}_{ij}(r)\,F_{jl} + \sum_{i,j}\int dr\, F_{ik}(r)\,X^{l}_{ij}(r) + \sum_{\substack{\lambda\\ \text{closed}}} M_\lambda \int dr\, P_\lambda(r) F_{ik}(r) + \sum_{\substack{\lambda\\ \text{closed}}} M'_\lambda \int dr\, P_\lambda(r) F_{jl}(r) - \frac{1}{2} R_{kl}\Big] = 0$$

for variations $\delta F_{mn} \sim k_m^{-1/2}\,\delta R_{mn}\cos\theta_m$
(M_λ is the Lagrange multiplier chosen to ensure the orthogonality of the continuum and the closed subshells). This yields the radial equations

$$\sum_j \mathcal{L}_{ij}(r)\,F_{jl}(r) + \sum_j X^{l}_{ij}(r) + \sum_{\lambda\,\text{closed}} M_\lambda P_\lambda(r) = 0 \qquad (2.39)$$

where $\mathcal{L}_{ij}(r)$ is defined by S.M. equation (74) and the inhomogeneous term X^{l}_{ij} is given by

$$\begin{aligned} X^{l}_{ij}(r) = \sum_{\mu_i\mu_j}\Bigg\{ & D^{ij}_{\mu_i\mu_j} P_{\mu_j}(r)\int dr\, F_{jl}(r)\Big[\frac{d^2}{dr^2} - \frac{l_j(l_j+1)}{r^2} + \frac{2Z}{r}\Big]P_{\mu_i}(r) \\ & + D^{ij}_{\mu_i\mu_j}\Big[\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2Z}{r}\Big]P_{\mu_j}(r)\int dr\, F_{jl}(r)\,P_{\mu_i}(r) \\ & + \sum_{\rho_i\rho_j} C^{ij}_{\mu_i\mu_j\rho_i\rho_j} P_{\mu_j}(r)\int dr\, F_{jl}(r) P_{\mu_i}(r)\int dr\, P_{\rho_i}(r) \\ & \Big[\frac{d^2}{dr^2} - \frac{l_{\rho_j}(l_{\rho_j}+1)}{r^2} + \frac{2Z}{r}\Big]P_{\rho_j}(r) + \sum_{\rho_i\rho_j t} \bar{C}^{ij}_{\rho_i\rho_j\mu_i\mu_j t} \\ & \times P_{\mu_j}(r)\,R_t(\rho_i\mu_i\rho_j F_{jl}) + \sum_{\rho_i\rho_j t} \bar{\bar{C}}^{ij}_{\rho_i\rho_j\mu_i\mu_j t} P_{\mu_j}(r) \\ & \times y_t(\rho_i\rho_j r)\int dr\, F_{jl}(r) P_{\mu_i}(r) + \sum_{\rho_i\rho_j\sigma_i\sigma_j t} G^{ij}_{\rho_i\rho_j\sigma_i\sigma_j\mu_i\mu_j t} \\ & \times P_{\mu_j}(r)\int dr\, F_{jl}(r) P_{\mu_i}(r)\cdot R_t(\rho_i\sigma_i\rho_j\sigma_j)\Bigg\} \end{aligned} \qquad (2.40)$$

This may be condensed into the form

$$X^{\ell}_{ij}(r) = \sum_{\mu_i\mu_j} \Big\{ \mathcal{G}^{ij}_{\mu_i\mu_j}(r) \int dr\, F_{j\ell}(r)\, P_{\mu_i}(r) + \bar{\mathcal{G}}^{ij}_{\mu_i\mu_j}(r) \int dr\, F_{j\ell}(r) \Big[\frac{d^2}{dr^2} - \ell_j(\ell_j+1) + \frac{2Z}{r}\Big] P_{\mu_i}(r) + \sum_{\rho_i\rho_j t} \bar{\bar{\mathcal{G}}}^{ij}_{\mu_i\mu_j\rho_i\rho_j t}(r)\, R_t(\rho_i\mu_i\rho_j F_{j\ell}) \qquad (2.41)$$

Each of the constituent terms of X are of the form $\mathcal{G}^{ij}(r)A^{\ell}_{ij}$ where $\mathcal{G}^{ij}(r)$ is a known function of r and A^{ℓ}_{ij} is an unknown constant depending upon $F_{j\ell}$. As before, the radial equations form a system of coupled integro differential equations.

Numerical Method

In order to solve the radial equations we use the method of Smith, Henry and Burke to generate the independent solutions of the homogeneous system. If there is a total of NV inhomogeneous terms of the form $\mathcal{G}^{ij}(r)A^{\ell}_{ij}$, we may generate NV particular solutions of the innomogeneous system by setting each of the constants A^{ℓ}_{ij} in turn to unity, and the rest to zero. If $\mathcal{J}_h$ denotes the homogeneous solution and $\mathcal{J}^{a}_{inh}$ denotes a particular solution of the inhomogeneous system generated in the above manner, then the required solutions of the system of the equations are of the form

$$F = \mathcal{J}_h + \sum_{\alpha=1}^{NV} A_\alpha \mathcal{J}^{\alpha}_{inh} \qquad (2.42)$$

where the A_a are defined by the equations

$$A_\alpha = \begin{cases} \int dr\, F(r)\, P_\lambda(r) \\ \int dr\, F(r) \Big[\frac{d^2}{dr^2} - \ell_\lambda(\ell_\lambda+1) + \frac{2Z}{r}\Big] P_\lambda(r) \\ R_t(\rho\mu\rho' F) \end{cases}$$

Substituting equation (2.42) into these equations yields the coupled algebraic equations for the A_α

$$A_\lambda = \int dr \left[\mathcal{F}_h(r) + \sum_{\alpha=1}^{NV} A_\alpha \mathcal{F}_{inh}^{\alpha}(r) \right] P_\lambda(r) \qquad \lambda = 1 \cdots \mu$$

$$A_{\lambda+\mu} = \int dr \left[\mathcal{F}_h(r) + \sum_{\alpha=1}^{NV} A_\alpha \mathcal{F}_{inh}^{\alpha}(r) \right] \left[\frac{d^2}{dr^2} - \ell_\lambda(\ell_\lambda+1) + \frac{2Z}{r} \right] P_\lambda(r)$$

$$A_\beta = \int dr \left[\mathcal{F}_h(r) + \sum_{\alpha=1}^{NV} A_\alpha \mathcal{F}_{inh}^{\alpha}(r) \right] P_\lambda(r) \, \mathcal{Y}_k(\rho\rho' r)$$

$$\beta = 2\mu+1, \cdots NV$$

where μ is the number of incomplete subshells. The matching parameters of the N independent homogeneous solutions may be determined using the method described by Smith, Henry and Burke.

The method described above has the advantage that trial function $\Psi(x_1 \cdots x_{N+1})$ has a more general form than that used in S.M. and the F_{ij} may be varied subject only to the constraints that they satisfy the same boundary conditions as the exact solutions and that they are orthogonal to the wave functions of the closed subshells. However it is clear that the radial equations obtained for this form of Ψ are considerably more complex then those given in S.M. For example if we retain the ground state terms of carbon in our trial wave function for e^-C scattering and consider the case when the system has total quantum numbers L = 0, S = 3/2, π = odd, (2.39) will reduce to a single equation (see SHB II). There is only one incomplete subshell μ = 2p and hence S.M. equation 77 contains two inhomogeneous terms, $C_1^1 V_{1,1}(r)$ and $M_{2p} P_{2p}(r)$. Equation (2.39), on the other hand, will contain six inhomogeneous terms, one of the form $\mathcal{Y}(r)A_\lambda$, one of the form $\bar{\mathcal{Y}}(r)A_{\lambda+\mu}$ and four of the form $\bar{\bar{\mathcal{Y}}} A_\beta$.

2.4: Radial Equations for the Case of an Atomic System with Configuration $2p^q$ or $3p^q$

A large number of calculations have been made recently on the scattering of electrons by atomic systems with configurations $1s^2 2s^2 2p^q$ or $1s^2 2s^2 2p^6 3s^2 3p^q$ since there is considerable astrophysical interest in the forbidden lines arising from transitions between the three spectrascopic terms of many of the atoms and ions having configurations $2p^q$ or $3p^q$ for q = 2, 3, 4. These lines can be excited by electron impact.

The eigenfunction expansion method has been used by Smith, Henry and Burke (S.H.B. 1966), Saraph, Seaton and Shemming (S.S.S. 1966) and Myerscough and McDowell (1964) in their calculations. These authors include only the terms of the ground state configuration in their expansion and impose the constraint $\delta_{\lambda,1}\int dr\, F_{ij}(r)P_{np}(r) = 0$. S.H.B. and S.S.S. compensate for this restriction by adding a term $C_j\Phi(2p^{q+1}LS\pi)$ to their trial solution as in S.M. equation (14). A valuable check on the derivation of the expressions for the potentials is, therefore, a comparison of the potentials given by these authors with those obtained from the general formulae of S.M. section 3.

If we include only the terms with configurations $1s^2 2s^2 \ldots 2p^q$ in our expansion the direct potential, equation (S.M. 48), is

$$V_{ij}(r) = \sum_{\bar{c}} \prod_{\lambda} \delta(N_\lambda^i, N_\lambda^j + \delta_{\lambda\rho_i} - \delta_{\lambda\rho_j})[N_{\rho_i} N_{\rho_j}]^{\frac{1}{2}}$$
$$(-1)^{\Delta\rho_{ij}} \sum_{\bar{\alpha}_{\rho_i}\bar{L}_{\rho_j}} (l_{\rho_i}^{N_{\rho_i}} \alpha_{\rho_i} S_{\rho_i} L_{\rho_i} \| l_{\rho_i}^{\bar{N}_{\rho_i}} \bar{\alpha}_{\rho_i} \bar{S}_{\rho_i} \bar{L}_{\rho_i})$$
$$(l_{\rho_j}^{N_{\rho_j}} \alpha_{\rho_j} S_{\rho_j} L_{\rho_j} \| l_{\rho_j}^{\bar{N}_{\rho_j}} \bar{\alpha}_{\rho_j} \bar{S}_{\rho_j} \bar{L}_{\rho_j}) \langle S_i | S_j \rangle^2 \sum_t$$
$$y_t(nl_{\rho_i} nl_{\rho_j} r)(l_{\rho_i} t\, 0\, 0 | l_{\rho_j} 0)(l_j t\, 0\, 0 | l_i 0) \langle L_i | L_j \rangle^2$$

where if Γ_i and Γ_j both correspond to the configurations $1s^2 2s^2 \ldots np^q$ $\sum_C^{\Sigma}$ becomes $\sum_{\lambda=1s}^{np}$, $\rho_i = \rho_j = \lambda$ and $\Delta P_{ij} = 0$.

Also

$$\langle S_i | S_j \rangle_\lambda^D = \langle \bar{S}_1 \cdots \bar{S}_\lambda \tfrac{1}{2}_N(S_\lambda) \cdot S_i \tfrac{1}{2}_{N+1} S \,|\, \bar{S}_1 \cdots \bar{S}_\lambda \tfrac{1}{2}_N(S_\lambda) \cdots S_j \tfrac{1}{2}_{N+n} S \rangle$$

$$= \delta_{S_i S_j}$$

$$\langle L_i | L_j \rangle_\lambda^D = \langle \bar{L}_1 \cdots \bar{L}_\lambda [l_\lambda t(l_\lambda)] L_\lambda^i \quad L_i l_i L \,|$$
$$| \bar{L}_1 \cdots \bar{L}_\lambda l_\lambda(L_\lambda^j) \cdots L_j, t l_i(l_j) L \rangle$$

so that

$$V_{ij} = \sum_\lambda N_\lambda \sum_{\bar{S}_\lambda \bar{L}_\lambda} (l_\lambda^{N_\lambda} S_\lambda^i L_\lambda^i \,||\, l_\lambda^{\bar{N}_\lambda} \bar{S}_\lambda \bar{L}_\lambda)(l_\lambda^{N_\lambda} S_\lambda^i L_\lambda^i \,||\, l_\lambda^{\bar{N}_\lambda} \bar{S}_\lambda \bar{L}_\lambda)$$
$$\sum_t (l_\lambda t \infty | l_\lambda 0)(l_j t \infty | l_i 0) \langle L_i | L_j \rangle_\lambda^D \, y_t(\lambda, \lambda, r)$$

If λ refers to a closed subshell

$$N_\lambda = 2(2l_\lambda + 1)$$

the C.F.P.'s = 1

$$\langle L_i | L_j \rangle_\lambda^D = \langle \bar{L}_\lambda (l_\lambda t(l_\lambda)) 0 \, L_i l_i L \,|\, \bar{L}_\lambda l_\lambda(0) L_j, t l_i(l_j) L \rangle \delta_{L_i L_j}$$

$$= \langle \bar{L}_\lambda l_\lambda t(l_\lambda) 0 \,|\, \bar{L}_\lambda l_\lambda(0) t 0 \rangle$$
$$\langle \bar{L}_\lambda l_\lambda(0) t(0) L_i l_i L \,|\, \bar{L}_\lambda l_\lambda(0) L_i, t l_i(l_j) L \rangle \delta_{L_i L_j}$$

$$= \delta_{t0} \delta_{l_i l_j} \delta_{L_i L_j}$$

(For a discussion of the methods used to evaluate the recoupling coefficients, see section 4). Therefore the contribution $\bar{V}_{ij}$ from the closed subshells to V_{ij}, is

$$\bar{V}_{ij} = \delta_{ij} \sum_{\lambda \text{ closed}} 2(2l_\lambda + 1) y_0(\lambda, \lambda, r)$$

If $\lambda = np$, the incomplete subshell, $N_\lambda = q$

$$\langle L_i | L_j \rangle^{D}_{np} = \langle \bar{L}_{np} [l_{np} t (l_{np})] L_i l_i L | \bar{L}_{np} l_{np} (L_j) t l_i (l_j) L \rangle$$

$$= \langle \bar{L}_{np} l_{np} t (l_{np}) L_i | \bar{L}_{np} l_{np} (L_j) t L_i \rangle$$

$$\langle L_j t (L_i) l_i L | L_j t l_i (l_j) L \rangle$$

$$= [3 (2 l_j + 1)(2 L_i + 1)(2 L_j + 1)]^{\frac{1}{2}} W (\bar{L}_{np} | L_i t, L_j l)$$

$$W (L_j t L l_i, L_i l_j)$$

so that

$$V_{ij}(r) = \delta_{ij} \left[\sum_{\lambda \text{ closed}} 2 (2 l_\lambda + 1) y_0 (\lambda \lambda r) \right] + \delta_{s_i s_j} q [3 (2 l_j + 1)$$

$$(2 L_i + 1)(2 L_j + 1)]^{\frac{1}{2}} \sum_t (1 t 0 0 | 1 0)(l_j t 0 0 | l_i 0)$$

$$W (L_j t L l_i, L_i L_j) \sum_{L \bar{S}} (p^q S_i L_i \| p^{q-1} \bar{S} L)$$

$$(p^q S_j L_j \| p^{q-1} \bar{S} L) W (\bar{L} l L_i l L_j l) y_t (n_p n_p r)$$

$$= \delta_{ij} \left[\sum_{\lambda \text{ closed}} 2 (2 l_\lambda + 1) y_0 (\lambda \lambda, r) \right] + \delta_{s_i s_j} 3 q [(2 l_i + 1)(2 l_j + 1)$$

$$(2 L_i + 1)(2 L_j + 1)]^{\frac{1}{2}} \sum_t (2 t + 1)^{-1} (1 1 0 0 | t 0)(l_i l_j 0 0 | t 0)$$

$$W (l_i L_i l_j L_j, L t) \sum_{L \bar{S}} (p^q S_i L_i \| p^{q-1} \bar{S} L)(p^q S_i L_i \| p^{q-1} \bar{S} L)$$

$$(-1)^{\bar{L} + L_i + L_j + L} W (l L_i l L_j, \bar{L} t) y_t (n_p n_p, r)$$

which is exactly that obtained by Smith, Henry and Burke equation (19).

The exchange term, equation (S.M. 41) is (dropping the subscript ℓ)

$$W_j F_j = \sum_{\bar{c}} \prod_{\lambda} \delta (N^i_\lambda, N^j_\lambda + \delta_{\lambda p_i} - \delta_{\lambda p_j}) [N_{p_i} N_{l_j}]^{\frac{1}{2}} (-1)^{\Delta p_j + 1}$$

$$\sum_{\bar{S}_{p_i} \bar{L}_{p_j}} (l_{p_i}^{N_{p_i}} S_{l_i} L_{p_i} \| l_{p_i}^{\bar{N}_{p_i}} \bar{S}_{p_i} \bar{L}_{p_i})(l_{p_j}^{N_{p_j}} S_{p_j} L_{p_j} \| l_{p_j}^{\bar{N}_{p_j}} \bar{S}_{p_j} \bar{L}_{p_j})$$

$$\langle S_i | S_j \rangle^{E} \sum_t (l_{p_i} t 0 0 | l_j 0)(l_{p_j} t 0 0 | l_i 0) \langle L_i | L_j \rangle^{E}$$

$$y_t (p_i F_j r) P_{p_j}(r)$$

where as before

$$\sum_{\bar{c}} \rightarrow \sum_{\lambda}, \quad \Delta\rho_{ij} = 0, \quad \rho_i = \rho_j = \lambda$$

$$\langle S_i | S_j \rangle^{\varepsilon}_{\lambda} = \langle \bar{S}_1 \cdots \bar{S}_\lambda \tfrac{1}{2N}(S^i_\lambda) \cdot S_i \tfrac{1}{2N+1} S \,|\, \bar{S}_1 \cdots \bar{S}_\lambda \tfrac{1}{2N+1}(S^j_\lambda) \cdots S_j \tfrac{1}{2N} S \rangle$$

$$\langle L_i | L_j \rangle^{\varepsilon}_{\lambda} = \langle \bar{L}_1 \cdots \bar{L}_\lambda [l_j t(l_\lambda)] L^i_\lambda \; L_i l_i L \,|$$
$$|\bar{L}_1 \cdots \bar{L}_\lambda [t l_i(l_\lambda)] L^j_\lambda \cdots L_j l_j L \rangle$$

The contribution for the closed shells

$$\bar{W}_{ij} F_j = \sum_{\lambda \text{ closed}} -2(2l_\lambda+1) \langle S_i | S_j \rangle^{\varepsilon}_{\lambda} \sum_t (l_\lambda t\, 0\, 0 | l_j 0)$$
$$(l_\lambda t\, 0\, 0 | l_i 0) \langle L_i | L_j \rangle^{\varepsilon}_{\lambda} y_t(\lambda F_j r) P_\lambda(r)$$

where

$$\langle S_i | S_j \rangle^{\varepsilon}_{\lambda} = \langle \bar{S}_\lambda \tfrac{1}{2N}(0) S_i \tfrac{1}{2N+1} S \,|\, \bar{S}_\lambda \tfrac{1}{2N+1}(0) S_j \tfrac{1}{2N} S \rangle \delta_{S_i S_j}$$
$$= \tfrac{1}{2} \delta_{S_i S_j}$$

$$\langle L_i | L_j \rangle^{\varepsilon}_{\lambda} = \langle \bar{L}_\lambda l_j t(l_\lambda) 0 L_i l_i L \,|\, \bar{L}_\lambda t l_i(l_\lambda) 0 L_j l_j L \rangle \delta_{L_i L_j}$$
$$= (2l_i+1)^{-1} \delta_{L_i L_j} \delta_{l_i l_j}$$

hence

$$\bar{W}_{ij} F_j = -\delta_{ij} \sum_{\lambda \text{ closed}, t} \left(\frac{2l_i+1}{2l_i+1}\right) (l_\lambda t\, 0\, 0 | l_i 0)^2 y_t(\lambda F_j r) P_\lambda(r)$$

The contribution from the incomplete np shell includes the recoupling coefficients

$$\langle S_i | S_j \rangle^{\varepsilon}_{np} = \langle \bar{S}_{np} \tfrac{1}{2N}(S_i) \tfrac{1}{2N+1} S \,|\, \bar{S}_{np} \tfrac{1}{2N+1}(S_j) \tfrac{1}{2N} S \rangle$$
$$= [(2S_i+1)(2S_j+1)]^{\frac{1}{2}} W(S_j \tfrac{1}{2} \tfrac{1}{2} S_i \bar{S}_{np} S)$$

$$\langle L_i | L_j \rangle^{\varepsilon}_{np} = \langle \bar{L}_{np} l_j t(l_{np}) L_i l_i L \,|\, \bar{L}_{np} t l_i(l_{np}) L_j l_j L \rangle$$
$$= 3[(2L_i+1)(2L_j+1)]^{\frac{1}{2}} \begin{pmatrix} \bar{L}_{np} & 1 & L_i \\ 1 & t & l_i \\ L_j & l_j & L \end{pmatrix}$$

and the complete exchange term is

$$W_{ij} F_j = -\delta_{ij}\Big[\sum_{\lambda \text{ closed},\, t}\Big(\frac{2\ell_\lambda+1}{2\ell_i+1}\Big)(\ell_\lambda\, t\, 0\,0|\ell_i 0)^2 y_t(\lambda F_j r) P_\lambda(r)\Big]$$
$$-3q\big[(2L_i+1)(2L_j+1)(2S_i+1)(2S_j+1)(2\ell_i+1)(2\ell_j+1)\big]^{\frac{1}{2}}$$
$$\sum_{\bar{L}\bar{S}} (np^q L_i S_i \,\}\, np^{q-1}\bar{L}\bar{S})(np^q L_j S_j \,\}\, np^{q-1}\bar{L}\bar{S})$$
$$W(S_j \tfrac{1}{2}\tfrac{1}{2} S_i, \bar{S} S)\sum_t (2t+1)^{-1}(\ell_j 0\,0\,|\,t\,0)\begin{pmatrix} \bar{L} & 1 & L_i \\ 1 & t & \ell_i \\ L_j & \ell_j & L \end{pmatrix}$$
$$(\ell_i 0\,0\,|\,t\,0)\, y_t(np_i F_j r)\, P_{np}(r)$$

which also agrees exactly with S.H.B. equation (22).

It is useful to note that

(1) any recoupling coefficients of the form

$$\langle \bar{S}_1 \cdots \bar{S}_\rho \tfrac{1}{2w}(S_\rho)\cdots \bar{S}_\sigma \tfrac{1}{2w+1}(S_\sigma)\cdots S \,|\, \bar{S}_1 \cdots \bar{S}_\rho \tfrac{1}{2w}(S_\rho)\cdots \bar{S}_\sigma \tfrac{1}{2w+1}(S_\sigma)\cdots S\rangle$$
$$\equiv 1$$

(2) if all subshells except the outermost are closed

$$L_{1s} = L_{2s} = \cdots L_{b-1} = 0, \quad L_b = L$$

the direct type recoupling coefficient

$$\langle \bar{L}_1 \cdots \bar{L}_\rho [\ell_\rho k(\ell_\rho)] L_\rho \cdots \bar{L}_\sigma \ell_\sigma(L_\sigma)\cdots L \,|\, \bar{L}_1 \cdots \bar{L}_\rho \ell_\rho(L_\rho)\cdots \bar{L}_\sigma k\ell_\sigma(\ell_\sigma) L_\sigma \cdots L\rangle$$

for $\rho \le \sigma$ and $\rho \neq b$ equals

$$\langle \bar{L}_\rho [\ell_\rho k(\ell_\rho)] 0\, \bar{L}_\sigma \ell_\sigma\, L_\sigma \,|\, \bar{L}_\rho \ell_\rho(0)\, \bar{L}_\sigma [k \ell_\sigma(\ell_\sigma)] L_\sigma\rangle$$
$$= \langle \bar{L}_\rho \ell_\rho k(\ell_\rho) 0 \,|\, \bar{L}_\rho \ell_\rho(0) k 0\rangle \langle k, \bar{L}_\sigma \ell_\sigma(L_\sigma) L_\sigma \,|\, \bar{L}_\sigma k \ell_\sigma(\ell_\sigma) L_\sigma\rangle$$
$$= \delta_{k0}$$

for $\rho = \sigma = b$ this equals

$$\langle \bar{\bar{L}}_\rho \ell_\rho k(\ell_\rho) \bar{L}_\rho^i \ell_\rho L_\rho \,|\, \bar{\bar{L}}_\rho \ell_\rho(\bar{L}_\rho^j) k \ell_\rho(\ell_\rho) L_\rho\rangle$$
$$= \langle \bar{\bar{L}}_\rho \ell_\rho k(\ell_\rho) \bar{L}_\rho^i \,|\, \bar{\bar{L}}_\rho \ell_\rho(\bar{L}_\rho^j) k \bar{L}_\rho^i\rangle$$
$$\langle \bar{L}_\rho^j k(\bar{L}_\rho^i) \ell_\rho L_\rho \,|\, \bar{L}_\rho^j, k \ell_\rho(\ell_\rho) L_\rho\rangle$$
$$= (2\ell_\rho+1)\big[(2\bar{L}_\rho^i+1)(2\bar{L}_{\rho_j}+1)\big]^{\frac{1}{2}} W(\bar{\bar{L}}_\rho \ell_\rho\, \bar{L}_\rho^i\, k, \bar{L}_\rho^j \ell_\rho)$$
$$\times W(\bar{L}_\rho^j k L \ell_\rho, \bar{L}_\rho^i \ell_\rho)$$

(3) the exchange type recoupling coefficients for $\rho \le \sigma$ $\rho \neq b$ are

$$\langle \bar{S}_1 \cdots \bar{S}_\rho \tfrac{1}{2}_N(S_\rho) \cdot \bar{S}_\sigma \tfrac{1}{2}_{N+1}(S_\sigma) \cdot S \,|\, \bar{S}_1 \cdots \bar{S}_\rho \tfrac{1}{2}_{N+1}(S_\rho) \cdots \bar{S}_\sigma \tfrac{1}{2}_N(S_\sigma) \cdot S \rangle$$

$$= \langle \bar{S}_\rho \tfrac{1}{2}_N(0)\, \bar{S}_\sigma \tfrac{1}{2}_{N+1}(S_\sigma)\, S_\sigma \,|\, \bar{S}_\rho \tfrac{1}{2}_{N+1}(0)\, \bar{S}_\sigma \tfrac{1}{2}_N(S_\sigma)\, S_\sigma \rangle$$

$$= (2S_\sigma+1) \begin{pmatrix} \bar{S}_\rho & \frac{1}{2} & 0 \\ \frac{1}{2} & \bar{S}_\sigma & S_\sigma \\ 0 & S_\sigma & S_\sigma \end{pmatrix}$$

$$= \frac{1}{2}$$

and

$$\langle \bar{L}_1 \cdots \bar{L}_\rho [l_\sigma^N k(l_\rho)] L_\rho \cdots \bar{L}_\sigma l_\sigma^{N+1}(L_\sigma) \cdot L \,|\, \bar{L}_1 \cdots \bar{L}_\rho [k l_\sigma^{N+1}(l_\rho)] L_\rho \cdots \bar{L}_\sigma l_\sigma^N(L_\sigma) \cdot L \rangle$$

$$= \langle \bar{L}_\rho l_\sigma^N k(l_\rho) 0\, \bar{L}_\sigma l_\sigma^{N+1} L_\sigma \,|\, \bar{L}_\rho k l_\sigma^{N+1}(l_\rho) 0\, \bar{L}_\sigma l_\sigma^N L_\sigma \rangle$$

$$= \langle \bar{L}_\rho k l_\sigma(l_\rho) 0 \,|\, \bar{L}_\rho k(l_\sigma) l_\sigma 0 \rangle^2 \quad \text{since } |l_\sigma^N| = |l_\sigma^{N+1}|$$

$$\langle l_\sigma l_\sigma^N(0) \bar{L}_\sigma l_\sigma^{N+1} L_\sigma \,|\, l_\sigma l_\sigma^{N+1}(0) \bar{L}_\sigma l_\sigma^N L_\sigma \rangle$$

$$= (2l_\rho+1)(2l_\sigma+1)(2L_\sigma+1)[W(\bar{L}_\rho k 0 l_\sigma, l_\sigma l_\rho)]^2 \begin{pmatrix} l_\sigma & l_\sigma & 0 \\ \bar{L}_\sigma & l_\sigma & L_\sigma \\ L_\sigma & 0 & L_\sigma \end{pmatrix}$$

$$= (2l_\sigma+1)^{-1}$$

(4) the exchange type recoupling coefficients for $\rho = \sigma = b$ are

$$\langle \bar{\bar{S}}_\rho \tfrac{1}{2}_N(\bar{S}_\rho^i) \tfrac{1}{2}_{N+1} S_\rho \,|\, \bar{\bar{S}}_\rho \tfrac{1}{2}_{N+1}(\bar{S}_\rho^j) \tfrac{1}{2}_N S_\rho \rangle$$

$$= [(2\bar{S}_\rho^i+1)(2\bar{S}_\rho^j+1)]^{\frac{1}{2}} W(\bar{S}_\rho^j \tfrac{1}{2} \tfrac{1}{2} \bar{S}_\rho^i, \bar{\bar{S}}_\rho S_\rho)$$

and

$$\langle \bar{\bar{L}}_\rho k l_\rho^N(l_\rho) \bar{L}_\rho^i l_\rho^{N+1} L_\rho \,|\, \bar{\bar{L}}_\rho l_\rho^{N+1} k(l_\rho) \bar{L}_\rho^j l_\rho^N L_\rho \rangle$$

$$= (2l_\rho+1)[(2\bar{L}_\rho^i+1)(2\bar{L}_\rho^j+1)]^{\frac{1}{2}} \begin{pmatrix} \bar{\bar{L}}_\rho & l_\rho & \bar{L}_\rho^i \\ l_\rho & k & l_\rho \\ \bar{L}_\rho^j & l_\rho & L_\rho \end{pmatrix}$$

The terms linear in C are given by (S.M. equation 53a)

$$L^C_{il,jk} = \sum_\mu C^k_\mu \left\{ \langle il | H_1 | \mu \rangle + \langle il | \tfrac{1}{r} | \mu \rangle \right\}$$

where μ runs over all the incomplete subshells of the config-

urations included in the eigenfunction expansion. The configurations considered in this section have an incomplete outer np subshell, hence only the term $\mu = np$ will appear in the above sum. We have, (S.M. 56)

$$\begin{aligned}\langle H_1 \rangle = \sum_{\rho} \prod_{\lambda} \delta(N_\lambda^i, N_\lambda^\mu - \delta_{\lambda\rho}) N_\rho^{\frac{1}{2}} (-1)^{\sum_{\lambda=\rho+1}^{b^\mu} N_\lambda} \\ (l_\rho^{N_\rho^\mu} \alpha_\rho^\mu S_\rho^\mu L_\rho^\mu \| l_\rho^{N_\rho^i} \alpha_\rho^i S_\rho^i L_\rho^i) \int dr\, F_{ie}(r) \left[-\tfrac{1}{2}\left(\frac{d^2}{dr^2} - \frac{l_\rho(l_\rho+1)}{r^2}\right) + \frac{Z}{r}\right] \\ P_\rho(r) \langle \bar{S}_1 \cdots S_i \tfrac{1}{2} S \,|\, \bar{S}_1 \cdots S_\rho^i \tfrac{1}{2} (S_\rho^\mu) \cdots S \rangle \\ \langle \bar{L}_1 \cdots L_i l_i L \,|\, \bar{L}_1 \cdots L_\rho^i l_\rho (L_\rho^\mu) \cdots L \rangle \delta_{l_i l_\rho}\end{aligned}$$

The configuration of Φ_μ differs from that of $\Psi(\Gamma_i)$ only by an additional electron in the np subshell, hence the only non-zero term in $\sum_\rho$ is $\rho = np$. Here $N_\rho = q + 1$, $\rho = b_\mu$, $S_\rho^\mu = S$, $L_\rho^\mu = L$, $S_\rho^i = S_i$ and $L_\rho^i = L_i$ since all other subshells are closed. The expression for $\langle H_1 \rangle$ therefore reduces to

$$\begin{aligned}\langle H_1 \rangle = (q+1)^{\frac{1}{2}} (p^{q+1} S L \| p^q S_i L_i) \int dr\, F_{ie}(r) (-\tfrac{1}{2}) \\ \left[\frac{d^2}{dr^2} - \frac{2}{r^2} + \frac{2Z}{r}\right] P_{np}(r) \langle \bar{S}_1 \cdots S_i \tfrac{1}{2} S \,|\, \bar{S}_1 \cdots S_i \tfrac{1}{2} S \rangle \\ \langle \bar{L}_1 \cdots L_i l_i L \,|\, \bar{L}_1 \cdots l_i l_i L \rangle \delta_{l_i 1}\end{aligned}$$

There is no recoupling of the angular momenta, hence the recoupling coefficients are both unity and

$$\begin{aligned}\langle H_1 \rangle = (q+1)^{\frac{1}{2}} (p^{q+1} S L \| p^q S_i L_i) \int dr\, F_{ie} \left[-\tfrac{1}{2}\frac{d^2}{dr^2} + \frac{1}{r^2} - \frac{Z}{r}\right] \\ P_{np}(r)\, \delta_{l_i 1}\end{aligned}$$

Also S.M. (60) is

$$\begin{aligned}\left\langle \frac{1}{r} \right\rangle = \sum_{\rho_i \rho_\mu \sigma_\mu} \prod_{\lambda} \delta(N_\lambda^i, N_\lambda^\mu + \delta_{\lambda\rho_i} - \delta_{\lambda\rho_\mu} - \delta_{\lambda\sigma_\mu}) \left[N_{\rho_i} N_{\rho_\mu} (N_{\sigma_\mu} - \delta_{\rho_\mu\sigma_\mu})\right]^{\frac{1}{2}} \\ (-1)^{\Delta\rho} \sum_{\epsilon=0,1} (-1)^\epsilon (1 - \epsilon\, \delta_{\rho_\mu\sigma_\mu}) \sum_{\substack{\bar{\alpha}_{\rho_i} \\ \bar{L}_{\sigma_\mu}}} (l_{\rho_i}^{N_{\rho_i}} \alpha_{\rho_i} S_{\rho_i} L_{\rho_i} \| l_{\rho_i}^{\bar{N}_{\rho_i}} \bar{\alpha}_{\rho_i} \bar{S}_{\rho_i} \bar{L}_{\rho_i}) \\ (l_{\rho_\mu}^{N_{\rho_\mu}} \alpha_{\rho_\mu} S_{\rho_\mu} L_{\rho_\mu} \| l_{\rho_\mu}^{\bar{N}_{\rho_\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu}) (l_{\sigma_\mu}^{N_{\sigma_\mu}} \alpha_{\sigma_\mu} S_{\sigma_\mu} L_{\sigma_\mu} \| l_{\sigma_\mu}^{\bar{N}_{\sigma_\mu}} \bar{\alpha}_{\sigma_\mu} \bar{S}_{\sigma_\mu} \bar{L}_{\sigma_\mu}) \\ \langle S_i \tfrac{1}{2} S_\mu \rangle^\epsilon \sum_t R_t(\rho_i F_{ie} \eta 5) (l_i\, t\, 0 \,|\, l_\eta\, 0) (l_5\, t\, 0 \,|\, l_i\, 0) \\ \langle 0_i 1 0_\mu \rangle_t^\epsilon\end{aligned}$$

Here $\sigma = np$ and $\rho_i = \rho_\mu = \rho$ where ρ runs over all subshells $1s, \ldots np$, $\Delta P = \sum_{\lambda=\rho_{i-1}+1}^{\rho_i} \bar{N}_\lambda - \sum_{\lambda=\rho_{\mu-1}+1}^{\sigma_\mu} \bar{N}_\lambda = 0$ and $\bar{S}_\sigma = S_i$, $\bar{L}_\sigma = L_i$, $S_\sigma^\mu = S$, $L_\sigma^\mu = L$. For $\epsilon = 0$, $\eta = \rho$, $S = np$

$$\langle s_i | s_\mu \rangle = \langle \bar{s}_1 \cdots \bar{s}_\rho \tfrac{1}{2N}(s_\rho) \cdots s_i \tfrac{1}{2N+1} S \,|\, \bar{s}_1 \cdots \bar{s}_\rho \tfrac{1}{2N}(s_\rho) \cdots s_i \tfrac{1}{2N+1} S \rangle = 1$$

$$\langle o_i | o_\mu \rangle = \langle \bar{L}_1 \cdots \bar{L}_\rho [l_\rho \epsilon(l_\rho)] L_\rho \cdots L_i l_i L \,|\, \bar{L}_1 \cdots \bar{L}_\rho l_\rho (L_\rho) \cdots L_i \epsilon l_i (l_\sigma) L \rangle$$

This is exactly the orbital recoupling coefficient that appears in the direct potential, with ℓ_σ replacing ℓ_j and L_σ replacing L_j. For $\epsilon = 1$, $\eta = np$, $S = \rho$

$$\langle s_i | s_\mu \rangle = \langle \bar{s}_1 \cdots \bar{s}_\rho \tfrac{1}{2N}(s_\rho) \cdots s_i \tfrac{1}{2N+1} S \,|\, \bar{s}_1 \cdots \bar{s}_\rho \tfrac{1}{2N+1}(s_\rho) \cdots s_i \tfrac{1}{2N} S \rangle$$

$$\langle o_i | o_\mu \rangle = \langle \bar{L}_1 \cdots \bar{L}_\rho [l_\sigma \epsilon(l_\rho)] L_\rho \cdot L_i l_i L \,|\, \bar{L}_1 \cdots \bar{L}_\rho [\epsilon l_i (l_\rho)] L_\rho \cdot L_i l_\sigma L \rangle$$

These recoupling coefficients are exactly those which appear in the exchange term since the order of coupling is the same in both sets of coefficients. We note that the expression of a recoupling coefficient in terms of Racah coefficients depends only on the order of coupling of the vectors and is therefore independent of the subshells to which the vectors belong. In this example, the vector ℓ_j of the exchange term and the vector ℓ_σ of the L^C term both have the property of being the last vector to be coupled under the prescribed coupling scheme.

Using the expressions derived for the direct and exchange recoupling coefficients we obtain

$$\left\langle \frac{1}{r} \right\rangle = \sum_{\rho \text{ closed}} (q+1)^{\frac{1}{2}} N_\rho{}^i (p^{q+1} LS \| p^q L_i S_i) \left[R_0(\rho F, \rho n_\rho) - \frac{1}{2} \sum_t (2t+1)^{-1} (l_\rho 1 0 0 | t 0)^2 R_t(\rho F_{il} n_\rho \rho) \right] \delta_{li1}$$

$$+ q(q+1)^{\frac{1}{2}} \sum_{L'S' L_2 S_2} (p^{q+1} LS \| p^q L'S')(p^q L'S' \| p^{q-1} L_2 S_2)$$

$$(p^q L_i S_i \| p^{q-1} L_2 S_2) \delta_{S_i S'} q [(2L'+1)(2L_i+1)]^{\frac{1}{2}}$$

$$(-1)^{L_2+L+L'+L_i} \sum_t (2t+1)^{-1} (1100|t0)^2$$

$$W(lL'lL_i, Lt) W(lL'lL_i, L_2 t) R_t(n_\rho F_{il} n_\rho n_\rho) \delta_{li1}$$

If we write $L^C_{il,k} = C^k \int dr\, V_i(r) F_{il}(r)$ then collecting the various terms together gives

$$V_i(r) = (q+1)^{\frac{1}{2}} \delta_{li1} \left\{ (p^{q+1} LS \| p^q L_i S_i) \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{1}{r^2} - \frac{Z}{r} \right] \right.$$

$$P_{n_\rho}(r) + \sum_{\rho \text{ closed}} 2(2l_\rho+1) \left[y_0(\rho\rho, r) P_{n_\rho}(r) - \frac{1}{2} \sum_t \right.$$

$$(2t+1)^{-1} (l_\rho 1 0 0 | t 0)^2 y_t(\rho n_\rho, r) P_\rho(r) \Big]$$

$$+ qq \sum_{L'S'} \delta_{S_i S'} (p^{q+1} LS \| p^q L'S') \left[(2L'+1)(2L_i+1) \right]^{\frac{1}{2}}$$

$$\sum_{L_2 S_2} (-1)^{L_2+L+L'+L_i} (p^q L'S' \| p^{q-1} L_2 S_2)(p^q L_i S_i \| p^{q-1} L_2 S_2)$$

$$\sum_t (2t+1)^{-1} (1100|t0)^2 W(lL'lL_i, Lt)$$

$$\left. W(lL'lL_i, L_2 t) y_t(n_\rho n_\rho, r) P_{n_\rho}(r) \right\}$$

This differs from S.H.B. equation (24) because their 'virtual capture' term $\Phi(p^{q+1}LS\pi)$ is not properly antisymmetric with respect to interchange of the 'additional' electron N+1 with a target electron.

To demonstrate this we take $\Phi(p^{m+1}LS\pi)$ to be of the form

$$\Phi_\mu(p^{m+1}LS\pi) = [\eta(N_\lambda^\mu)]^{-\frac{1}{2}} \sum_q (-1)^{p_{qr}} \Phi_{\mu_q}(q\, p^{m+1}LS\pi)$$

where q runs over only those distributions which assign label N+1 to the outer np subshell. With this restriction the normalisation factor becomes

$$\eta(N_\lambda^\mu) = N! / \prod_\lambda (N_\lambda^i!)$$

where N_λ^i is the number of electrons in subshell λ in the ion configuration $1s^2 2s^2 \ldots np^m$. With this definition of Φ_μ, S.M. equation (54a) gives

$$\begin{aligned}\langle H_1 \rangle = {} & (N+1)^{\frac{1}{2}} [\eta(N_\lambda^i)\eta(N_\lambda^\mu)]^{-\frac{1}{2}} \eta(\bar{N}_\lambda) \\ & (np^{m+1} S_{np} L_{np} \| np^m S_{np}^i L_{np}^i) \int dr\, F_{il}(r) \left(-\tfrac{1}{2}\tfrac{d^2}{dr^2} + \tfrac{l_i}{r^2} - \tfrac{Z}{r}\right) \\ & P_{np}(r) \langle \bar{S}_1 \cdots S_{np}^i \tfrac{1}{2} S \,|\, \bar{S}_1 \cdots S_{np}^i \tfrac{1}{2} S \rangle \\ & \langle \bar{L}_1 \cdots L_{np}^i l_i L \,|\, \bar{L}_1 \cdots L_{np}^i l_{np} L \rangle \delta_{l_i 1}\end{aligned}$$

As before $\eta(\bar{N}_\lambda) = \dfrac{N!}{\prod_\lambda (\bar{N}_\lambda!)} = \dfrac{N!}{\prod_\lambda (N_\lambda^i!)}$ and the normalisation factors reduce to

$$(N+1)^{\frac{1}{2}} \left[\frac{\prod_\lambda (N_\lambda^i!) \prod_\lambda (N_\lambda^i!)}{N!\ N!} \right]^{\frac{1}{2}} \frac{N!}{\prod_\lambda (\bar{N}_\lambda!)} = (N+1)^{\frac{1}{2}}$$

Hence

$$\begin{aligned}\langle H_1 \rangle = {} & (N+1)^{\frac{1}{2}} \delta_{l_i 1} (p^{m+1} LS \| p^m L_i S_i) \int dr\, F_{il}(r) \\ & \left(-\tfrac{1}{2}\tfrac{d^2}{dr^2} + \tfrac{l_i}{r^2} - \tfrac{Z}{r}\right) P_{np}(r)\end{aligned} \qquad (2.44a)$$

Similarly the factor $[N_{\rho i} N_{\rho\mu}(N_{\sigma\mu} - \delta_{\rho\mu\sigma\mu})]^{\frac{1}{2}}$ in S.M. equation (58), which for this case equals $(m+1)^{\frac{1}{2}} N_\rho^i$, is replaced by

$(N+1)^{1/2} N_\rho^i$. Also, since we have restricted label N+1 to the outer np subshell, only the terms corresponding to $\epsilon = 0$ in S.M. (58) will appear. The matrix element in S.M. (58) will be unaltered as we have merely restricted the range values q_μ and may be simplified in exactly the same manner as before to give

$$\left\langle \frac{1}{r} \right\rangle = (N+1)^{\frac{1}{2}} \sum_{\rho \text{ closed}} 2(2l_\rho+1) \left(p^{m+1} LS \| p^m L_i S_i \right) \delta_{l_i 1}$$
$$R_0(\rho F_{i\rho} np) + 9(N+1)^{\frac{1}{2}} m \sum_{L'S'} \delta_{S_i S'}$$
$$\left(p^{m+1} LS \| p^m L'S' \right) \left[(2L'+1)(2L_i+1) \right]^{\frac{1}{2}}$$
$$\sum_{L_2 S_2} (-1)^{L_2+L+L'+L_i} \left(p^m L'S' \| p^{m-1} L_2 S_2 \right)$$
$$\left(p^m L_i S_i \| p^{m-1} L_2 S_2 \right) \sum_t (2t+1)^{-1} (1001|t0)^2$$
$$W(1L'1L_i, Lt) W(1L'1L_i, L_2 t)$$
$$R_t(np F_{i\rho} np\, np) \delta_{l_i 1}$$

(2.44b)

Comparing equations (2.44a) and (2.44b) with S.H.B. equation (24) we see that the use of this incorrect form of $\Phi(p^{m+1} LS\pi)$ will lead to the expression derived by S.H.B. Comparison of S.M. equations (62a), (67) and (72) with S.H.B. equations (25) and (26) shows that a similar discrepancy arises in the terms quadratic in C

If we consider the particular case of the matrix element $\langle \Phi | H_N | \Phi \rangle$ (S.M. equation 72) for $\Phi = \Phi(2p^3, {}^4S^0)$ and properly antisymmetric, we obtain

$$\langle \Phi | H_N | \Phi \rangle = \frac{1}{7} \left[2E(1s\,2s^2 2p^3, {}^3S^o) + 2E(1s\,2s^2 2p^3, {}^5S^o) \right.$$
$$+ 2E(1s^2 2s\,2p^3, {}^3S^o) + 2E(1s^2 2s\,2p^3, {}^5S^o)$$
$$\left. + 3E(1s^2 2s^2 2p^2, {}^3P^e) \right)$$

where $E(1s\,2s^2\,2p^3, {}^3S^0)$ is the energy of the excited target state $1s\,2s^2\,2p^3, {}^3S^0$, etc. These highly excited levels of the target may not be known accurately and as this difficulty will arise for most complex targets, the expression given in equation 2.21 of this thesis is more convenient for numerical calculations. The reduction of the C^2 term for $\Phi(n\rho^{2+1}LS\pi)$ using this expression is very similar to the reduction of the 'C' term described above. For Φ having configuration $1s^2\,2s^2\,2p^{q+1}$ or $1s^2\,2s^2\,2p^6\,3s^2\,3p^{q+1}$, the matrix element of H_1 reduces immediately to

$$\langle H_1 \rangle = \sum_{\lambda=1s}^{n\rho} -\tfrac{1}{2} N_\lambda \int dr\; P_\lambda(r) \left[\frac{d^2}{dr^2} - \frac{l_\lambda(l_\lambda+1)}{r^2} + \frac{2Z}{r} \right] P_\lambda(r)$$

In the expression for $\langle \frac{1}{r} \rangle$ we have $\rho_i = \rho_j$, $\sigma_i = \sigma_j$ and the following terms will appear in the summations over ρ, σ and k.

(1) $\rho = \sigma = 1s \ldots n\rho$ and $k = 0$. All the various Clebsch-Gordan, and recoupling coefficients are unity therefore these terms contribute

$$\frac{1}{2} \sum_{\lambda=1s}^{n\rho} N_\lambda (N_\lambda - 1) R_0(\lambda\lambda, \lambda\lambda)$$

(2) $\rho > \sigma$, $k = 0$, $\epsilon = \epsilon'$. Again all the Clebsch-Gordan and recoupling coefficients are unity (the recoupling coefficients for $\epsilon = \epsilon'$ are the direct type) and the summation over the C.F.P.'s gives unity. Also the contributions from $\epsilon = \epsilon' = 0$ and $\epsilon = \epsilon' = 1$ are equal hence the complete contribution is

$$\sum_{\rho>\sigma} N_\rho N_\sigma R_0(\rho\sigma, \rho\sigma)$$

(3) $\rho > \sigma$, ρ and σ both s subshells, $\epsilon \neq \epsilon'$. For these terms the only allowed value of k is $k = 0$. The recoupling

coefficients are of the exchange type. $\langle S_i | S_j \rangle = \frac{1}{2}$ and all other coefficients are unity. These terms therefore contribute

$$\sum_{\rho > \sigma,\ s\ \text{subshells}} -\tfrac{1}{2} N_\rho N_\sigma R_0(\rho\sigma,\sigma\rho)$$

(4) $\rho > \sigma$ ρ = p subshell, σ = S subshell or vice versa, $\epsilon \neq \epsilon'$ Here k = 1 $\langle S_i | S_j \rangle = \frac{1}{2}$, $\langle L_i | L_j \rangle = \frac{1}{3}$ hence the contribution is

$$\sum_{\substack{\rho = p\ \text{subshell} \\ \sigma = s\ \text{subshell}}} -\frac{1}{6} N_\rho N_\sigma R_1(\rho\sigma,\sigma\rho)$$

(5) $\rho > \sigma$ both p subshells, $\epsilon \neq \epsilon'$. Such a term will only occur for the configurations $1s^2 2s^2 2p^6 3s^2 3p^{q+1}$ hence ρ = 3p, σ = 2p. Since the 2p subshell is closed the recoupling coefficients will be independent of k and as for case 4 $\langle S_i | S_j \rangle = \frac{1}{2}$, $\langle L_i | L_j \rangle = \frac{1}{3}$. The contribution from this term is therefore

$$-\frac{1}{6} N_{2p} N_{3p} \sum_k (1k\,00|10)^2 R_k(2p\,3p\,3p\,2p)$$

(6) $\rho = \sigma$ = np, k = 2 ($\epsilon = \epsilon'$). Substituting the numerical values of the Clebsch-Gordan coefficient and using the expression for the orbital recoupling coefficient that we derived earlier we obtain.

$$\frac{3q(q+1)}{5} \sum_{\bar{L}_i \bar{L}_j \bar{\bar{L}} \bar{S} \bar{\bar{S}}} (2p^{q+1} L S \,||\, 2p^q \bar{L}_i \bar{S})$$
$$(2p^{q+1} L S \,||\, 2p^q \bar{L}_j \bar{S})(2p^q \bar{L}_i \bar{S} \,||\, 2p^{q-1} \bar{\bar{L}} \bar{\bar{S}})$$
$$(2p^q \bar{L}_j \bar{S} \,||\, 2p^{q-1} \bar{\bar{L}} \bar{\bar{S}}) [(2\bar{L}_i + 1)(2\bar{L}_j + 1)]^{\frac{1}{2}}$$
$$W(\bar{\bar{L}} 1 L_i 2, L_j 1) W(L_j 2 L 1, L_i 1) R_2(np\,np\,np\,np)$$

Collecting together the various terms we obtain

$$\langle \Phi | H_N | \Phi \rangle = -\frac{1}{2} \sum_{\lambda=1s}^{np} N_\lambda \int dr\, P_\lambda(r) \left[\frac{d^2}{dr^2} - \frac{l_\lambda(l_\lambda+1)}{r^2} \right.$$

$$\left. + \frac{2Z}{r} \right] P_\lambda(r) + \frac{1}{2} \sum_{\lambda=1s}^{np} N_\lambda (N_\lambda - 1)\, R_0(\lambda\lambda,\lambda\lambda)$$

$$+ \sum_{\rho>\sigma=1s}^{np} N_\rho N_\sigma\, R_0(\rho\sigma\rho\sigma)$$

$$- \sum_{\rho>\sigma,\ s\ \text{subshells}} 2\, R_0(\rho\sigma,\sigma\rho)$$

$$- \sum_{\substack{\rho=p\ \text{subshell} \\ \sigma\neq\rho}} \frac{1}{6} N_\rho N_\sigma \sum_k (l_\sigma\, k\, 0\,0\,|\,1\,1\,0)^2 R_k(\rho\sigma\sigma\rho)$$

$$+ 3q\frac{(q+1)}{5} \sum_{\bar{L}_i \bar{L}_j \bar{\bar{L}} \bar{\bar{S}} \bar{S}} (2p^{q+1} L S \,\|\, 2p^q \bar{L}_i \bar{S})$$

$$(2p^{q+1} L S \,\|\, 2p^q \bar{L}_j \bar{S})(2p^q \bar{L}_i \bar{S} \,\|\, 2p^{q-1} \bar{\bar{L}} \bar{\bar{S}})$$

$$(2p^q \bar{L}_j \bar{S} \,\|\, 2p^{q-1} \bar{\bar{L}} \bar{\bar{S}})(-1)^{\bar{\bar{L}}+L} [(2\bar{L}_i+1)(2\bar{L}_j+1)]^{\frac{1}{2}}$$

$$W(L_i\, 1\, L_j\, 1, \bar{\bar{L}}\, 2)\, W(L_i\, 1\, L_j\, 1, L\, 2)\, R_2(np\, np\, np\, np)$$

SECTION 3: THE PHOTOIONISATION CROSS SECTIONS

In this section we derive expressions for the total and differential photoionisation cross sections of a general atomic system using the Hartree-Fock wave functions discussed in section 2 as our approximate wave functions for the system.

Fano (1961) has shown, using configuration interaction theory, that the autoionising levels of the target atom will manifest themselves as asymmetric peaks in the absorption spectra, and has obtained a parameterisation of the line shapes in terms of quantities directly related to the matrix elements of the energy and electric dipole moments. These results have been recently derived by Shore (1967) from scattering theory. The ability of the eigenfunction expansion method to describe autoionising states, as well as the continuum states of the target, supports our choice of wave functions calculated using this method as final state wave functions.

In this section we shall make the 'relaxed core' approximation. That is, we take our initial state wave function $\Phi(LS\pi)$ to be constructed from the bound state Hartree Fock functions for the unperturbed target atom but make an expansion of our final state wave function Ψ in terms of unperturbed wave functions of the residual ion. As noted earlier such an expansion neglects the effect of the free electron on the ionic field. An alternative approximation, proposed by Bates (1946) is to assume that the radial wave

functions of the final ion state are the same as those of the initial state. This 'unrelaxed core' approximation implies that, if exchange effects are neglected, the ejected electron would move in the same field both before and immediately after ionisation takes place. It also has the advantage of simplifying the expressions for the cross sections as both initial and final wave functions are constructed from the same bound state orbitals. In processes where an electron is ejected from the outermost subshell this approximation has been found to give good results especially at higher electron energies. However Bagus (1965) has shown that this approximation may not be valid for inner shell excitations.

In order to achieve the greatest generality we shall derive expressions for the cross sections assuming a relaxed core. The expressions for the case of an unrelaxed core may be obtained from these directly by substituting the alternative set of Hartree Fock orbitals.

3.1 Total Cross section

We consider an unpolarised beam of photons with energy $h\nu << mc^2$ incident on an atomic system having N+1 electrons and a nuclear charge Z. The method that we use in this section is a generalisation of that used by Henry and Lipsky (1967) to derive expressions for the cross section for ionisation of an electron from the 2p subshell of an atomic system having configuration $1s^2 2s^2 2p^{q+1}$. These authors have calculated photoionisation cross sections for Ne taking into account the possibility of ejection of a 2s electron and have obtained good agreement with experiment. Encouraging results have also been obtained by Conneely, Lipsky and

Smith (1967) for the photoionisation of Si and Ar.

If we first consider the process in which a photon, having propagation vector $\underline{k}$ and polarisation direction $\underset{\sim}{j}$, is absorbed, the Schroedinger equation for the system is, (Heitler § 17)

$$\left[H_{N+1} + \frac{iek}{mc} \sum_{\alpha=1}^{N+1} \underline{A} \cdot \nabla_{N+1} - E \right] \Psi = 0 \qquad (3.0)$$

to first order in $\underline{A}$, where H_{N+1} is the N+1 particle Hamiltonian given in equation (2.1) and $\underline{A}$ is the vector potential of a classical electromagnetic wave having propagation vector $\underline{k}$ and polarisation vector $\underline{j}$. For low energy photons ($k^2 = 0(1)$ryd) $\underline{A}$ is constant to good approximation and for a flux of one photon per cm^2 per sec. $|A|^2 = \frac{2\pi c\hbar}{\nu}$

For low energy photons we may regard $\frac{iek}{mc} A \cdot \nabla$ as a small perturbation on the initial state wave function Φ. If the electron is ejected in channel Γ and the final state wave function is $\widetilde{\Psi}(\Gamma)$, then, to first order the cross section is

$$\Gamma \sigma_E = \frac{2\pi e^2 k^2}{m^2 c \nu} \left| \left\langle \widetilde{\Psi}(\Gamma) \left| \underset{\sim}{j} \cdot \sum_{\alpha=1}^{N+1} \nabla_\alpha \right| \Phi \right\rangle \right|^2 \qquad (3.1)$$

where $\widetilde{\Psi}(\Gamma)$ is the solution of the equation $[H_{N+1} - E]\Psi = 0$, normalised per unit energy range and whose asymptotic form has an outgoing spherical wave in channel Γ and ingoing waves in all channels. (Breit and Bethe 1954, Mott and Massey, Ch. XXI).

As our approximate wave function $\widetilde{\Psi}(\Gamma_j)$ we take

$$\widetilde{\Psi}(\Gamma_j) = \frac{1}{(N+1)^{\frac{1}{2}}} \sum_{p=1}^{N+1} (-1)^{N+1-p} \sum_{\Gamma_i} \psi(\Gamma_i \underline{x} \hat{x}_p) \frac{\widetilde{F}_{ij}(r_p)}{r_p}$$

where

$$\widetilde{F}_{ij} \sim \sqrt{\frac{2}{\pi k_i}} \left(\delta_{ij} e^{i\theta_i} - S^+ e^{-i\theta_i} \right) \qquad (3.2)$$

(for a discussion of the normalisation of $\tilde{F}$ see Landau and Lifshitz § 33).

S^{+}_{ij} is the adjoint of the scattering matrix S_{ij} and all other quantities are defined as in S.M. In terms of the real functions

$$F_{ij}(r) \sim \frac{1}{k_i^{\frac{1}{2}}}\left[\delta_{ij}\sin\theta_i + R_{ij}\cos\theta_i\right]$$

$$\tilde{\Psi}(\Gamma_j) = i\sqrt{\frac{2}{\pi}}\sum_{\Gamma_i}\frac{1}{(1+iR)_{ij}}\Psi_j(\Gamma_i)$$

$$= i\sqrt{\frac{2}{\pi}}\frac{1}{(N+1)^{\frac{1}{2}}}\sum_{p=1}^{N+1}(-1)^{N+1-p}\sum_{\Gamma_i}\frac{1}{(1+iR)_{ij}}\frac{\psi(\Gamma_i\, x\, \hat{r}_p)F_{ij}(r_p)}{r_p} \qquad (3.3)$$

In this section we shall assume that the F_{ij} are chosen to be orthogonal only to the complete subshells of the ion. That is, we take $\Psi(\Gamma_j)$ to be defined as in equation (2.30) rather than the form used by S.M. In the unrelaxed core approximation, the use of continuum functions F_{ij}, which are orthogonal to all the subshells of the ion, has no advantage, rather, the introduction of the "Φ term" would make the expressions for the cross sections considerably more complicated. If these functions are used, we must replace

$$\tilde{\Psi}(\Gamma_j) \text{ by } \tilde{\Psi}(\Gamma_j) + \sum_{\mu} C_j^{\mu}\Phi_{\mu}(L_jS_j\pi_j)$$

in equation (3.1). The additional matrix elements which arise may be evaluated in exactly the same way as those described below.

To obtain the total cross section for the process in which a photon is absorbed and an electron ejected we must sum

over all open channels Γ and average over the initial spin and angular momentum directions of the target atom and over the polarisations of the photon. If we chose our coordinate frame such that the photons travel along the Z axis, $j_z = 0$. Hence

$$\sigma_V = \frac{2\pi e^2\hbar^2}{m^2 c\nu}\,\frac{1}{2(2L+1)(2S+1)}\sum_{\substack{M_L M_S \Gamma \\ \mu=\pm 1}} \left| \left\langle \widetilde{\Psi}(\Gamma) \left| \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu \right| \Phi(LS\Pi) \right\rangle \right|^2 \qquad (3.4a)$$

HqL, Eq. (1)

where

$$\nabla_\alpha^{\pm 1} = \frac{1}{\sqrt{2}}\left(\mp \frac{\partial}{\partial x_\alpha} - i\frac{\partial}{\partial y_\alpha} \right)$$

Applying the commutation relation $[r, H] = \frac{ih}{m} P$ to (3.4a) gives the "dipole length" form of the cross section

$$\sigma_L = \frac{8\pi^3 \nu e^2}{c\omega} \sum_{\substack{M_L M_S \Gamma \\ \mu=\pm 1}} \left| \left\langle \widetilde{\Psi}(\Gamma) \left| \sum_{\alpha=1}^{N+1} r_\alpha^\mu \right| \Phi(LS\Pi) \right\rangle \right|^2 \qquad (3.4b)$$

where $\omega = 2(2L + 1)(2s + 1)$

$$r_\alpha^{\pm 1} = \frac{1}{\sqrt{2}}\left(\mp x_\alpha - i y_\alpha \right)$$

$$= \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} r_\alpha Y_{1,\pm 1}(\hat{r}_\alpha) \qquad r_\alpha = |\underset{\sim}{r}_\alpha|$$

The two expressions, (3.4a) and (3.4b) will only be equivalent if exact wave functions Ψ and Φ are used. In any calculation one must necessarily use approximate wave functions which will give considerably different values to σ_V and σ_L. (We note that the error due to the approximate wave functions will in general be large in comparison with the error due to the approximations made in deriving equations (3.4).) Comparing equations (3.4a) and (3.4b) we see that equation (3.4b) may be expected to give most reliable results for wave functions accurate for large r and that equation (3.4a) may be expected to give better results for wave functions accurate at small r. Chandrasekhar (1945) has made a detailed

WHY?

comparison of the photoionisation cross sections of H^- obtained using the dipole length, velocity and acceleration formulae (the latter expresses the cross section in terms of the matrix elements of $\frac{r}{r^3}$). Using the most accurate wave functions available, he found that the results given by the three formula were almost identical, but for less accurate wave functions the dipole length formula gave the best results. The experience of other workers also suggest that the dipole velocity formula is the most reliable. However it is useful to compare the cross sections given by the dipole length formula with those given by the velocity formula as this will give some measure of the inaccuracy of the wave functions used.

Substituting (3.3) into (3.4a) and (3.4b) gives

$$\sigma_V = \frac{2\pi e^2\hbar^2}{m^2 c\,\nu\omega} \sum_{\substack{M_L M_S \Gamma_K \\ \mu=\pm 1}} \sum_{\Gamma_i \Gamma_j} \langle \Psi_K(\Gamma_i) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \Phi(LS\pi) \rangle \langle \Phi(LS\pi) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^{\mu *} | \Psi_K(\Gamma_j) \rangle \frac{2}{\pi} \frac{1}{(1+iR)_{iK}(1-iR)_{Kj}} \tag{3.5a}$$

$$\sigma_L = \frac{8\pi^3 \nu e^2}{c\omega} \sum_{\substack{M_L M_S \Gamma_K \\ \mu=\pm 1}} \sum_{\Gamma_i \Gamma_j} \langle \Psi_K(\Gamma_i) | \sum_{\alpha=1}^{N+1} r_\alpha^\mu | \Phi(LS\pi) \rangle \langle \Phi(LS\pi) | \sum_{\alpha=1}^{N+1} r_\alpha^{\mu *} | \Psi_K(\Gamma_j) \rangle \frac{2}{\pi} \frac{1}{(1+iR)_{iK}(1-iR)_{Kj}} \tag{3.5b}$$

We assume that the radial functions $F_{ij}(r)$ and the corresponding R matrix have been calculated, which leaves us with the task of simplifying the matrix elements which appear in the expressions for σ

$$\langle \underline{\Psi}_K(\Gamma_i) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \underline{\Phi}(LS\pi) \rangle = \frac{1}{(N+1)^{\frac{1}{2}}} \sum_{p=1}^{N+1} (-1)^{N+1-p} \eta(N_\lambda^i)^{-\frac{1}{2}}$$

$$\sum_{q_i} (-1)^{P_{q_i}} \langle \psi_u(q_i \underline{X} \hat{\underline{x}}_p) \underline{F}_{ik}(r_p) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \underline{\Phi}(LS\pi) \rangle$$

From the symmetry of the operator and antisymmetry of the wave functions, each distribution q_i will contribute equally hence

$$\langle \underline{\Psi}_K(\Gamma_i) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \underline{\Phi}(LS\pi) \rangle = (N+1)^{\frac{1}{2}} [\eta(N_\lambda^i)]^{\frac{1}{2}}$$

$$\langle \psi_u(q_0 \underline{X} \hat{\underline{x}}_{N+1}) \underline{F}_{ik}(r_{N+1}) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \underline{\Phi}(LS\pi) \rangle$$

$$= (N+1)^{\frac{1}{2}} \left[\frac{\eta(N_\lambda^i)}{\eta(N_\lambda^\phi)} \right]^{\frac{1}{2}} \sum_q (-1)^{P_q} \langle \psi_u(q_0 \underline{X} \hat{\underline{x}}_{N+1})$$

$$\underline{F}_{ik}(r_{N+1}) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \phi_u(q\, LS\pi) \rangle \qquad (3.6)$$

where q_0 is the distribution corresponding to normal order and $\eta(N_\lambda^\phi)$ is the number of possible distributions q of the N+1 electrons of the target atom.

Further simplification of the general expression for the cross sections is made difficult by the lack of orthogonality of the ion Hartree Fock functions and atom Hartree Fock functions. However for a particular atomic system one may simplify the cross section formulae using the orthogonality properties of the angular and spin functions. This is demonstrated in section 3.3 where we derive expressions for the photoionisation cross sections for an atomic system having configuration $1s^2 2s^2 2p^{q+1}$.

An expression for the angular integrals of the dipole length formula is given in section (4), viz

$$\langle L_{ik} | Y_{1\mu}(\hat{r}_\alpha) | L_\phi \rangle = \sqrt{\frac{3}{4\pi}} (l_{\rho_i} 1 0 0 | l_{\rho_\phi} 0) (L_\phi | M_\phi \mu | L_k M_k) \langle L_{ik} | L_\phi \rangle$$

(3.9a)

where ρ_i is the subshell containing electron α in $q_o \Gamma_i$ and ρ_ϕ is the subshell containing α in $\Phi(qL_\phi S_\phi \pi_\phi)$. $\langle L_{ik} | L_\phi \rangle$ is an angular momentum recoupling coefficient which, for the case where q_o and q include the same distribution q of spectator electrons $1 \cdots \alpha-1, \alpha+1 \cdots N+1$, equals, (see equation 4.11)

$$\langle \bar{L}_1 \cdots \bar{L}_{\rho_i} [l_{\rho_\phi} 1 (l_{\rho_i})] L_{\rho_i} \cdots L_k | \bar{L}_1 \cdots \bar{L}_{\rho_\phi} l_{\rho_\phi} (L_{\rho_\phi}) \cdots L_\phi 1 L_k \rangle$$

(3.10)

if q_o and q do not include the same distribution of spectators, then, since q_o corresponds to normal order, $\langle L_{ik} | L_\phi \rangle$ may be expressed in the form

$$\langle L_{ik} | L_\phi \rangle = \sum_{\tilde{L}_\phi} \langle L_{ik} | \tilde{L}_\phi \rangle \langle \tilde{L}_\phi | L_\phi \rangle$$

(3.11)

where the $\langle \tilde{L}_\phi | L_\phi \rangle$ are the recoupling coefficients needed to recouple the angular momenta of the spectator electrons from the order of coupling prescribed by q to the normal order of coupling and $\langle L_{ik} | L_\phi \rangle$ is a recoupling coefficient of the form given by (3.10). For example, if q_o assigns electron β to subshell μ and electron γ to subshell σ, and if q differs from q_o only by assigning β to σ and γ to μ then (for $\beta, \gamma \neq \alpha$)

$$\langle \tilde{L}_\phi | L_\phi \rangle = \langle \bar{L}_1 \cdots \bar{L}_\mu l_\mu^\beta (\tilde{L}_\mu) \cdots \bar{L}_\sigma l_\sigma^\gamma (\tilde{L}_\sigma) \cdots L | | \bar{L}_1 \cdots \bar{L}_\mu l_\sigma^\gamma (L_\mu^\phi) \cdots \bar{L}_\sigma l_\mu^\beta (L_\sigma^\phi) \cdots L \rangle \delta_{l_\beta l_\sigma}$$

(3.11a)

and the summation in (3.11) runs over all possible values of the intermediate couplings $\tilde{L}_\mu \cdots \tilde{L}_\sigma$.

The corresponding angular integral which occurs in the dipole velocity formula can be obtained directly from (3.9a) using the Wigner Eckhart theorem and is

$$\langle L_{ik} | \nabla^{\mu}_{\alpha} | L_\phi \rangle = (\ell_{\rho_i} \| \nabla_\alpha \| \ell_{\rho\phi}) (2\ell_{\rho_i}+1)^{-\frac{1}{2}} (L_\phi M_\phi \mu | L_k M_k) \langle L_{ik} | L_\phi \rangle \qquad (3.9b)$$

where

$$(\ell_{\rho_i} \| \nabla \| \ell_{\rho\phi}) = (2\ell_{\rho\phi}+1)^{\frac{1}{2}} (\ell_{\rho_i} 1 0 0 | \ell_{\rho\phi} 0) \left[\frac{d}{dr} + \frac{1}{r} + \frac{\ell_{\rho\phi}(\ell_{\rho\phi}+1) - \ell_i(\ell_i+1)}{2r} \right]$$

(see for example Rotenburg, et. al.)

For a given term in $\sum_\alpha$ we may classify the distributions q according to the subshell, ρ_ϕ, to which they assign the particular label a. For this value of a we may replace $\sum_q$ by $\sum_{\rho\phi} \sum_{\bar{q}_\alpha}$ where ρ_ϕ runs over all the subshells to which a may be assigned, that is, all occupied subshells in Φ, and $\bar{q}_a$ runs over all possible distributions of the labels $1 \cdots a-1, a+1, \cdots N+1$ amongst the occupied subshells with $\bar{N}_\lambda > 0$. (The subshell wave functions are properly antisymmetric and normalised, hence we sum over distributions amongst subshells rather than permutations of the labels $1 \cdots a-1, a+1, \cdots, N+1$). We note that the subshell, ρ_i, containing a in $\psi_\mu(q_0 \Gamma_i \underline{X} \hat{x}_{N+1})$, and the corresponding distribution of spectators, are uniquely defined by q_0. Hence, equation (3.6) may be written in the form

$$\langle \Psi_k(\Gamma_i) | \sum_{\alpha=1}^{N+1} \nabla^{\mu}_{\alpha} | \Phi(L_\phi S_\phi \pi_\phi) \rangle = (L_\phi M_\phi \mu | L_k M_k) \left[\prod_{\lambda=1} (N^i_\lambda !) / \prod_{\lambda=1} (N^\phi_\lambda !) \right]^{\frac{1}{2}} \sum_{\alpha \rho_\phi \bar{q}_\alpha} (-1)^{P_q} (\ell_{\rho_i} 1 0 0 | \ell_{\rho\phi} 0) \prod_{\substack{\beta=1 \\ \beta \neq \alpha}}^{N+1} \left[\delta_{\ell^\beta_{\lambda_i} \ell^\beta_{\lambda_\rho}} \langle P^\beta_{\lambda_i}(r_\beta) | P^\beta_{\lambda_\rho}(r_\beta) \rangle \right] \sum_{\bar{\alpha} i k \bar{L}_\phi} CFP(ik) CFP(\phi) \langle S_i q_0 | S_\phi \rho_\phi \bar{q}_\alpha \rangle \langle L_i q_0 | L_\phi \rho_\phi \bar{q}_\alpha \rangle \langle P_{\rho_i}(r_\alpha) | R^\alpha_V | P_{\rho\phi}(r_\alpha) \rangle \qquad (3.12)$$

where $\bar{q}_\alpha$ denotes the distribution of spectators corresponding to q

ρ_i is the subshell containing electron α in q_o

ρ_ϕ is the subshell containing α in distribution q

λ_i^β is the subshell containing β in q_o

λ_ϕ^β is the subshell containing β in q

We note that for $\beta = N+1$

$$P^\beta_{\lambda_i}(r_\beta) = F_{ik}(r_{N+1})$$

$\langle S_i q_o | S_\phi \rho_\phi \bar{q}_\alpha \rangle$ is a spin recoupling coefficient analogous to (3.11a)

$\langle L_i q_o | L_\phi \rho_\phi \bar{q}_\alpha \rangle$ is an orbital recoupling coefficient of the type given in (3.11)

R_V^α is the operator $\left[\frac{d}{dr_\alpha} + \frac{1}{r_\alpha} + \frac{\ell_{\rho\phi}(\ell_{\rho\phi}+1) - \ell_{\rho_i}(\ell_{\rho_i}+1)}{2r}\right]$

CFP(ik) denotes the fractional parentage expansion necessary to separate from $\psi_k(\Gamma_i)$, the one electron orbitals occupied by electrons whose angular momenta are recoupled in $\langle S_i q_o | S_\phi \rho_\phi \bar{q}_\alpha \rangle$ and $\langle L_i q_o | L_\phi \rho_\phi \bar{q}_\alpha \rangle$. That is, we must separate out electron α and those electrons $\beta = 1 \cdots \alpha+1, \alpha-1, \cdots N+1$ for which $\lambda_i^\beta \neq \lambda_\phi^\beta$, from the remaining spectator electrons. In the example given in equation (3.11a)

$$\sum_{\bar{\alpha}_{ik}\bar{L}_{ik}} CFP(ik) = \sum_{\bar{\alpha}_{\rho_i}\bar{L}_\sigma} (\ell_{\rho_i}^{N_{\rho_i}} \alpha_{\rho_i} S_{\rho_i} L_{\rho_i} \| \ell_{\rho_i}^{\bar{N}_{\rho_i}} \bar{\alpha}_{\rho_i} \bar{S}_{\rho_i} \bar{L}_{\rho_i})$$
$$(\ell_\mu^{N_\mu} \alpha_\mu S_\mu L_\mu \| \ell_\mu^{\bar{N}_\mu} \bar{\alpha}_\mu \bar{S}_\mu \bar{L}_\mu)(\ell_\sigma^{N_\sigma} \alpha_\sigma S_\sigma L_\sigma \| \ell_\sigma^{\bar{N}_\sigma} \bar{\alpha}_\sigma \bar{S}_\sigma \bar{L}_\sigma)$$

From the antisymmetry of the subshell wave functions, we see that each label α, assigned by q_o to the same particular subshell ρ_i, will contribute equally to $\sum_\alpha$. Hence we need only evaluate the matrix element for one value $\alpha_o \in \rho_i$ and replace $\sum_\alpha$ by $\sum_{\rho_i} N_{\rho_i}$

Equation (3.12) becomes

$$\langle \bar{\Psi}_k(\Gamma_i) \mid \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu \mid \bar{\Phi}(L_\phi S_\phi \pi_\phi) \rangle = (L_\phi \mid M_\phi \mu \mid L_\kappa M_\kappa)$$

$$\left[\prod_\lambda (N_\lambda^i!)/\prod_\lambda (N_\lambda^\phi!)\right]^{\frac{1}{2}} \sum_{\rho_i \rho_\phi \bar{q}_{\alpha_0}} N_{\rho_i} (-1)^{\rho_\nu} (l_{\rho_i} 1 \, 0 0 \mid l_{\rho_\phi} 0)$$

$$\prod_{\substack{\beta=1 \\ \beta \neq \alpha}}^{N+1} \delta_{l_{\lambda_i}^\beta l_{\lambda_\phi}^\beta} \langle P_{\lambda_i}^\beta(r_\beta) \mid P_{\lambda_\phi}^\beta(r_\beta) \rangle \sum_{\bar{\alpha}_{ik} \cdots \bar{L}_\phi} CFP(ik) CFP(\phi)$$

$$\langle S_i q_0 \mid S_\phi \rho_\phi \bar{q}_{\alpha_0} \rangle \langle L_i q_0 \mid L_\phi \rho_\phi \bar{q}_{\alpha_0} \rangle$$

$$\langle P_{\rho_i}(r_{\alpha_0}) \mid R_v^{\alpha_0} \mid P_{\rho_\phi}(r_{\alpha_0}) \rangle$$

(3.12a)

where $a_0 = \left(\sum_{\lambda=1}^{\rho_i - 1} N_\lambda^i\right) + 1$ is the label of the first electron that has been assigned to subshell ρ_i by q_0.

We note that, in order that the Clebsch-Gordan coefficient $(l_{\rho_i} 1 \, 0 0 \mid l_{\rho\phi} 0)$ be non-zero, we must have $l_{\rho\phi} = l_{\rho_i} \pm 1$. Hence, the only non-zero terms in $\sum_{\rho\phi}$ will be from these ρ_ϕ whose orbital angular momenta satisfy this condition. The Kronecker delta, $\delta_{l_{\lambda_i}^\beta l_{\lambda_\phi}^\beta}$ implies that the matrix element will be non-zero only if Ψ and Φ contain the same number of spectator s electrons, the same number of spectator p electrons, etc. Similarly the only non-zero contributions to $\sum_{\bar{q}_{\alpha_0}}$ will be from these $\bar{q}_{\alpha_0}$ which assign the spectator s electrons of q_0 to s subshells in Φ, the spectator p electrons to p subshells, etc. Hence we may replace $\sum_{\bar{q}_{\alpha_0}}$ by $\sum_{\bar{q}_\alpha^s \bar{q}_\alpha^p \cdots}$ where $\bar{q}_a^s$ runs over all distributions of the labels, assigned by q_0 to the spectator s electrons, amongst the s orbitals of Φ having $\bar{N}_\lambda > 0$, and $\bar{q}_a^p$, $\bar{q}_a^d$ $\cdots$ denote the corresponding distributions of p, d, $\cdots$ electrons.

If we choose $\Psi(\Gamma)$ to be defined as in S.M. equation 15, we must replace $\Psi(\Gamma)$ by $\Psi(\Gamma) + \sum_\mu C^\mu \Phi_\mu(LS\pi)$ in equations (3.4a) and

(3.4b). Making this substitution we obtain

$$\sigma_V = \frac{2\pi e^2 h^2}{m^2 c \nu \omega} \sum_{M_L M_S \Gamma_K} \Big\{ \Big| \Big\langle \widetilde{\Phi}(\Gamma_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi(LS\pi) \Big\rangle \Big|^2$$
$$+ 2 \mathrm{Re} \sum_{\mu}^{m=\pm 1} C_K^\mu \Big\langle \widetilde{\Phi}(\Gamma_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi(LS\pi) \Big\rangle$$
$$\times \Big\langle \Phi(LS\pi) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi_\mu(L_K S_K \pi_K) \Big\rangle$$
$$+ \sum_{\mu\nu} C_K^\mu C_K^\nu \Big\langle \Phi_\mu(L_K S_K \pi_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi(LS\pi) \Big\rangle$$
$$\times \Big\langle \Phi(LS\pi) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi_\nu(L_K S_K \pi_K) \Big\rangle \Big\}$$

and an analogous expression for σ_L.

The evaluation of the matrix elements $\langle \Phi_\mu | \sum_{\alpha=1}^{N+1} \nabla_\alpha^m | \Phi \rangle$ may be carried out in exactly the same way as the evaluation of the matrix elements described above. We first express the matrix element in terms of unsymmetrised wave functions

$$\Big\langle \Phi_\mu(L_K S_K \pi_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi(LS\pi) \Big\rangle = \eta(N_\lambda^\mu)^{-\frac{1}{2}} \sum_{q_\mu} (-1)^{p_{q_\mu}}$$
$$\Big\langle \phi_{\mu\mu}(q_\mu L_K S_K \pi_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi(LS\pi) \Big\rangle$$

where $\eta(N_\lambda^\mu)$ is the number of distributions q_μ of the N+1 electrons amongst the occupied subshells of Φ_μ. The operator is symmetric and $\Phi(LS\pi)$ is antisymmetric under interchange of any pair of labels, hence

$$\Big\langle \Phi_\mu(L_K S_K \pi_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi(LS\pi) \Big\rangle = \eta(N_\lambda^\mu)^{\frac{1}{2}}$$
$$\Big\langle \phi_{\mu\mu}(q_0 L_K S_K \pi_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi(LS\pi) \Big\rangle$$
$$= \left[\frac{\eta(N_\lambda^\mu)}{\eta(N_\lambda^{\mu'})} \right]^{\frac{1}{2}} \sum_q (-1)^{p_q} \Big\langle \phi_{\mu\mu}(q_0 L_K S_K \pi_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi_\mu(q LS\pi) \Big\rangle$$
$$= \left[\frac{\prod_\lambda (N_\lambda^{\mu'}!)}{\prod_\lambda (N_\lambda^{\phi}!)} \right]^{\frac{1}{2}} \sum_q (-1)^{p_q} \Big\langle \phi_{\mu\mu}(q_0 L_K S_K \pi_K) \Big| \sum_{\alpha=1}^{N+1} \nabla_\alpha^m \Big| \Phi_\mu(q LS\pi) \Big\rangle$$

$\phi_{\mu u}$ is constructed from antisymmetric subshell wave functions in exactly the same way as ψ_u. Here electron N+1 is assigned by q_o to the outermost subshell b_μ of $\phi_{\mu'}$. Comparing the above expression with equation (3.6), we see that this matrix element may be reduced to a form exactly analogous to equation (3.12a) with $P_{\lambda_\mu}^{N+1}(r_{N+1}) = P_{b_\mu}(r_{N+1})$.

The expression for the matrix element

$$\langle \Psi_k(\Gamma_i) \mid \sum_{\alpha=1}^{N+1} r_\alpha^\mu \mid \Phi(LS\pi) \rangle$$

may be obtained directly from (3.12), merely by replacing R_V^a by $R_L^a = r_a$.

We may write (3.12a) in the abbreviated form

$$\langle \Psi_k(\Gamma_i) \mid \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu \mid \Phi(LS\pi) \rangle = (L\,1\,M_L\,\mu \mid L_k M_k) G_{ik}$$

where G_{ik} is independent of the quantum numbers $M_L M_S, \mu$ and M_k. Similarly

$$\langle \Phi(LS\pi) \mid \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu \mid \Psi_k(\Gamma_j) \rangle = (L\,1\,M_L\,\mu \mid L_k M_k)\, G_{jk}^*$$

Hence equation (3.5a) becomes

$$\sigma_V = \frac{2\pi e^2 k^2}{m^2 c \nu \omega} \sum_{M_L M_S \Gamma_k \mu = \pm 1} \sum_{\Gamma_i \Gamma_j} (L\,1\,M_L\,\mu \mid L_k M_k)^2 G_{ik} G_{jk}^* A_{ij}^k$$

$$= \frac{2\pi e^2 k^2}{m^2 c \nu \omega} \sum_{M_L M_S \Gamma_k \mu = \pm 1} \frac{(2L_k+1)}{3} (L_k\, L\, M_k - M_L \mid 1\mu)^2 \sum_{\Gamma_i \Gamma_j} G_{ik} G_{jk}^* A_{ij}^k$$

where $A_{ij}^k = \dfrac{1}{(1+iR)_{ik}(1-iR)_{jk}} \cdot \dfrac{2}{\pi}$

performing the summation over M_k we obtain

$$\sigma_V = \frac{2\pi e^2 k^2}{3 m^2 c \nu} \sum_{M_S \Gamma_k' \mu = \pm 1} (2L_k+1) \sum_{\Gamma_i \Gamma_j} G_{ik} G_{jk}^* A_{ij}^k$$

$$= \frac{2\pi e^2 k^2}{3 m^2 c \nu (2L+1)} \sum_{\Gamma_k' \Gamma_i \Gamma_j} (2L_k+1)\, G_{ik} G_{jk}^* A_{ij}^k$$

(3.13a)

where $\sum_{\Gamma_k}'$ denotes summation over all quantum numbers needed to describe Γ except M_k. Similarly (3.5b) becomes

$$\sigma_L = \frac{8\pi^3 \nu e^2}{3c(2L+1)} \sum_{\Gamma_k' \Gamma_i \Gamma_j} H_{ik} H_{jk}^* A_{ij}^* \qquad (3.13b)$$

where H_{ik} is obtained by replacing R_V^a by R_L^a in G_{ik}.

3.2 Differential Cross Section

Recently experiments have been performed to determine the angular distribution of electrons ejected in the photoionisation of rare gas atoms (Berkowitz and Ehrhardt 1966), Vilesov et al. 1967). Lipsky (1967) has derived an expression for the differential cross section for the ejection of one of the outer p electrons of a rare gas atom, within the framework of the close coupling approximation. It is of interest therefore to extend this result to the photoionisation of a general atomic system.

The differential cross section for the absorption of a photon travelling along the Z axis with energy $h\nu$ resulting in the ejection of an electron with momentum $h\underset{\sim}{k}$ is, in the dipole velocity approximation

$$d\sigma_L(E) = \frac{2\pi e^2 k^2}{m^2 c \nu \omega} \sum_{\substack{M_L M_S \gamma \\ S_k M_k M_{S_k} \mu = \pm 1}} |\langle \widetilde{\Psi}(\underset{\sim}{k}) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \Phi \rangle|^2 d\rho(E) \qquad (3.14)$$

where $d\rho(E)$ is the number of final states $\widetilde{\Psi}$ per unit interval of electron energy with the electron ejected in a direction which lies within a cone of infinitesimal solid angle $d\Omega$ with axis along $\underset{\sim}{k}$. If Ψ is normalised per unit energy range

$$d\rho(E) = \frac{k\, d\Omega}{(2\pi)^3} \qquad \underset{\sim}{k} = k\,\underset{\sim}{\Omega} \qquad \text{(Heitler § 21)} \qquad ?$$

$$\tilde{\Psi}(\underset{\sim}{k}) \sim \psi(\gamma S_K M_{S_K} \underset{\sim}{X} \sigma) k^{-\frac{1}{2}} \left[e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} + f(\underset{\sim}{n}) \frac{e^{-ikr}}{r} \right]$$

$\gamma = \{a_T L_T M_T S_T\}$, a_T denotes the other quantum numbers necessary to specify γ, and the electron spin function $\chi_{\frac{1}{2}m_s}(\sigma)$ is coupled with that of the ion to give total spin $S_k M_{S_k}$.

$\sum_\gamma$ runs over any degenerate states of the ion having $E_\gamma = E - \frac{1}{2}k^2 = E_\phi + h\nu - \frac{1}{2}k^2$. In order to obtain an expression for $d\sigma$ in terms of the channel wave functions $\tilde{\Psi}(\Gamma)$, equation (3.3), we make the partial wave expansion

$$d\sigma_\gamma(E) = \frac{k k^2 e^2}{(2\pi)^2 m^2 c\, v_\gamma} \sum_{\substack{M_L M_S \gamma S_K \\ M_K M_{S_K} \mu = \pm 1}} \left| \sum_{\ell m} \langle \underset{\sim}{n} | \ell m \rangle \right.$$
$$\left. \langle \hat{\Psi}(\ell m) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \Phi \rangle \right|^2 d\Omega \qquad (3.15)$$

$$\langle \underset{\sim}{n} | \ell m \rangle = Y_{\ell m}(\underset{\sim}{n})$$

and $\tilde{\Psi}(\ell m)$ is related to the functions $\tilde{\Psi}(\Gamma)$ by

$$\tilde{\Psi}(\ell m) = \sum_{L_K M_K} (L_T \ell M_T m | L_K M_K) \tilde{\Psi}(\Gamma_K)$$

$$\Gamma_K = \{\alpha_T L_T \ell L_K M_K S_K M_{S_K}\}$$

Also

$$\hat{\Psi}(\Gamma_K) = i\sqrt{\frac{2}{\pi}} \sum_{\Gamma_i} \frac{1}{(1+iR)_{ik}} \Psi_K(\Gamma_j)$$

Hence (3.15) becomes

$$d\sigma_\gamma(E) = \frac{k k^2 e^2}{(2\pi)^2 m^2 c\, v_\gamma} \sum_{\substack{\gamma \ell \ell' \\ S_K L_K L_K'}} \sum_{\substack{M_L M_S M_{S_K} M_K M_K' \\ m, m' \mu = \pm 1}} Y_{\ell m}(\underset{\sim}{n}) Y^*_{\ell' m'}(\underset{\sim}{n})$$
$$(L_T \ell M_T m | L_K M_K)(L_T \ell' M_T m' | L_K' M_K') \sum_{\Gamma_i \Gamma_j}$$
$$\langle \Psi_K(\Gamma_i) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \Phi(LS\Pi) \rangle \langle \Phi(LS\Pi) |$$
$$\sum_{\alpha=1}^{N+1} \nabla_\alpha^{\mu *} | \Psi_{K'}(\Gamma_j) \rangle \frac{2}{\pi} \frac{1}{(1+iR)_{ik}(1-iR)_{jk'}} \qquad (3.16)$$

An expression for the matrix elements is given in equation (3.12), which is of the form

$$\langle \Psi_K(\Gamma_i) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \Psi(LS\pi) \rangle = (L\,1\,M_L\mu \,|\, L_K M_K)\, G_{iK}$$

Hence we may write (3.16) in the form

$$\begin{aligned} d\sigma_R(E) = {} & \frac{k\hbar^2 e^2}{(2\pi)^2 m^2 c\, v\omega} \sum_{\substack{\delta \ell \ell' \\ S_K L_K L_K'}} \sum_{\substack{M_L M_S M_{S_K} \\ M_K M_K' m m' \mu = \pm 1}} Y_{\ell m}(\hat{r})\, Y^*_{\ell' m'}(\hat{r}) \\ & (L_T \ell M_T m \,|\, L_K M_K)(L_T \ell' M_T m' \,|\, L_K' M_K') \\ & (L\,1\,M_L\mu \,|\, L_K M_K)(L\,1\,M_L\mu \,|\, L_K' M_K') \\ & \sum_{r_i r_j} \left(\frac{2}{\pi}\right) \frac{1}{(1+iR)_{iK}(1-iR)_{jK}}\, G_{iK}\, G_{jK}^* \end{aligned} \tag{3.17}$$

We next perform the summations over the azimuthal quantum numbers.

$$\begin{aligned} & \sum_{\substack{M_L M_K M_K' \\ m m' \\ \mu = \pm 1}} Y_{\ell m}(\hat{r})\, Y^*_{\ell' m'}(\hat{r})\, (L_T \ell M_T m \,|\, L_K M_K) \\ & (L_T \ell' M_T m' \,|\, L_K' M_K')(L\,1\,M_L\mu \,|\, L_K M_K)(L\,1\,M_L\mu \,|\, L_K' M_K') \\ = {} & \sum_{\substack{\hat{\ell} \\ M_L M_K M_K' \\ m m' \mu = \pm 1}} \left[\frac{(2\ell+1)(2\ell'+1)}{4\pi(2\hat{\ell}+1)}\right]^{\frac{1}{2}} (\ell \ell' 0 0 \,|\, \hat{\ell} 0)\, Y_{\hat{\ell}\hat{m}}(\hat{r}) \\ & (-1)^{m'} (\ell \ell' m - m' \,|\, \hat{\ell} \hat{m})(L_T \ell M_T m \,|\, L_K M_K) \\ & (L_T \ell' M_T m' \,|\, L_K' M_K')(L\,1\,M_L\mu \,|\, L_K M_K)(L\,1\,M_L\mu \,|\, L_K' M_K') \end{aligned} \tag{3.18}$$

A requirement for the non-vanishing of the Clebsch-Gordan coefficient $(j_1 j_2 m_1 m_2 | jm)$ is that $m_1 + m_2 = m$. Therefore the only non zero contributions to $\sum_{M_K' m'}$ come from $M_k' = M_k$ and $m' = m$ and hence $\hat{m} = m - m' = 0$. The only $Y_{\hat{\ell}\hat{m}}(\hat{r})$ which appear in the final expression for the differential cross section will therefore be those with $\hat{m} = 0$ which is in accordance with the result that the differential

cross section for scattering by a spherically symmetric field is independent of the azimuthal angle ϕ.

If we perform first the summation over m and then the summation over M_k using the relation given by Biedenharn et al. (1952) equation (3.18) reduces to

$$\sum_{\hat{l}\mu=\pm 1} \left[\frac{(2l+1)(2l'+1)}{3\cdot 4\pi}\right]^{\frac{1}{2}} (ll'00|\hat{l}0)\, Y_{\hat{l}0}(\underset{\sim}{n})$$

$$(-1)^{L_T+L} (\hat{l}\,1\,0\mu\,|\,1\mu)(2L_k+1)(2L_k'+1) W(L_k' l' L_k l, L_T \hat{l})$$

$$W(L_k' 1 L_k 1, L\hat{l})$$

$$= \frac{2}{3}\sqrt{\frac{1}{4\pi}}\,(2L_k+1)\,\delta_{L_k L_k'}\,\delta_{ll'}\,Y_{00}(\underset{\sim}{n})$$

$$+ \left[\frac{(2l+1)(2l'+1)}{4\pi}\right]^{\frac{1}{2}} \sqrt{\frac{2}{15}}\,(ll'00|20)(2L_k+1)$$

$$(2L_k'+1)(-1)^{L_T+L} W(L_k' l' L_k l, L_T 2)$$

$$W(L_k' 1 L_k 1, L 2)\, Y_{20}(\underset{\sim}{n})$$

Substituting this expression in equation (3.17) gives

$$d\sigma_R(E) = \frac{k\hbar^2 e^2}{(2\pi)^2 c\, v\, m^2} \left\{ \sum_{\substack{\gamma l \\ M_s L_k}} S_k M_{s_k} \frac{2}{3}\frac{1}{\sqrt{4\pi}}(2L_k+1)\, Y_{00}(\underset{\sim}{n}) \right.$$

$$\sum_{r_i r_j} G_{ik}\, G_{jk}^{*}\, A_{ij}^{k} + \sum_{\substack{\gamma l l' \\ M_s L_k L_k'}} S_k M_{s_k} (2L_k+1)(2L_k'+1)\sqrt{\frac{2}{15}}$$

$$\left[\frac{(2l+1)(2l'+1)}{4\pi}\right]^{\frac{1}{2}} (ll'00|20)(-1)^{L_T+L} W(L_k' l' L_k l, L_T 2)$$

$$W(L_k' 1 L_k 1, L 2)\, Y_{20}(\underset{\sim}{n}) \sum_{r_i r_j} G_{ik}\, G_{jk'} \left(\frac{2}{\pi}\right) \qquad (3.19)$$

$$\cdot \frac{1}{(1+iR)_{ik}(1-iR)_{jk'}}$$

Comparing the first term in (3.19) with the expression for the total cross section σ_V given by equation (3.13a) we see that

$$d\sigma_\Omega(E) = \frac{k}{(2\pi)^3}\sigma_v(E) + \sum_{\Gamma_k'\Gamma_{k'}'} B_{kk'} \sum_{\Gamma_i\Gamma_j} G_{ik} G^*_{jk'} \left(\frac{2}{\pi}\right) (1+iR)^{-1}_{ik} (1-iR)^{-1}_{jk'} Y_{20}(\hat{n}) \qquad (3.20)$$

where

$$B_{kk'} = \frac{k(2S+1)\hbar^2 e^2}{(2\pi)^{\frac{5}{2}} m^2 c \nu\omega} \sqrt{\frac{1}{15}} (2L_k+1)(2L_k'+1)(-1)^{L_T+L} [(2l_k+1)(2l_k'+1)]^{\frac{1}{2}} (l_k l_k' 00|20) W(L_k' l_k' L_k l_k, L_T 2) W(L_k' 1 L_k 1, L 2) \qquad (3.21)$$

Apart from the factor $(2L_k' + 1)$ in the expression for $B_{kk'}$, the expression for the differential cross section given by equation (3.20) and (3.21) is of the same form as that given by Lipsky (1967). The lack of symmetry in Lipsky's expression for $B_{\Gamma\Gamma'}$ suggests that it is incorrect.

3.3. Photoionisation Cross Section for an Atomic System Having Configuration $1s^2 2s^2 2p^q$

As a demonstration of the reduction of the general expression for the total cross section given in section 3.1, we consider the photoionisation of an atomic system having configuration $1s^2 2s^2 2p^q$ and check the simplified expression against that given by Henry and Lipsky (1967).

We first simplify the expression for G_{ik} given by equation (3.12). In this case Φ has configuration $1s^2 2s^2 2p^q$ and $\Psi(\Gamma_i)$ has configuration $1s^2 2s^2 2p^{q-1} k\ell$, hence

$$\left[\frac{\prod_> (N_>^{\Phi}!)}{\prod_> (N_>^{i}!)}\right]^{\frac{1}{2}} = q^{\frac{1}{2}}$$

We next consider each term in $\sum_{\rho_i}$ separately.

For ρ_i = 1s equation (3.12) contains the Clebsch-Gordan coefficient $(\ell_{\rho_i} 1 0 0 | \ell_{\rho_f} 0)$. Hence the only non zero term in $\sum_{\rho_\phi}$ will be ρ_ϕ = 2p. For a_o = 1 the orthogonality of the spherical harmonics implies that the non-vanishing terms in $\sum_{q_{a_o}}$ will be from those $\bar{q}_{a_o}$ which assign labels 2, 3, 4 to either the 1s or 2s subshell and labels 5, $\cdots$ q+3 to the 2p subshell. Label 1 is already assigned to the 2p subshell hence label q+4 is assigned to the only remaining vacancy in one of the S subshells. Again the orthogonality of the spherical harmonics implies that the matrix element will be zero for $\ell_i \neq 0$. There are 6 distributions $\bar{q}_{a_o}$ which satisfy the above requirements. These are characterised by their distribution of the labels 2, 3, 4, q+4 amongst the 1s and 2s subshells

	1s	2s	Pq
q_1	(q+4, 2)	(3, 4)	odd
q_2	(3, 4)	(q+4, 2)	odd
q_3	(q+4, 3)	(2, 4)	even
q_4	(2, 4)	(q+4, 3)	even
q_5	(q+4, 4)	(2. 3)	even
q_6	(2, 3)	(q+4, 4)	even

For q_1

$$\langle S_i q_0 | S_\phi q_1 \rangle = \langle \tfrac{1}{2_1} \tfrac{1}{2_2} (0) S_i \tfrac{1}{2}_{q+4} S_\mu | \tfrac{1}{2}_{q+4} \tfrac{1}{2_2} (0) \bar{S} \tfrac{1}{2_1} S \rangle$$

$$= \left\langle \tfrac{1}{2}_1 \tfrac{1}{2}_2 (0) \tfrac{1}{2}_{q+4}, \tfrac{1}{2} \middle| \tfrac{1}{2}_1, \tfrac{1}{2}_2 \tfrac{1}{2}_{q+4} (0) \tfrac{1}{2} \right\rangle \delta_{s_i \bar{s}_{2\rho}} \delta_{s_\kappa s}$$

$$= W\left(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}, 0\,0\right) \delta_{s_i \bar{s}_{2\rho}} \delta_{s_\kappa s}$$

$$= \tfrac{1}{2} \delta_{s_i \bar{s}_{2\rho}} \delta_{s_\kappa s}$$

$$\langle L_i q_0 | L_\phi q_1 \rangle = \langle \bar{L}_{1s} l'_{2\rho} | (0) L_i l_i^{q+4} L_\kappa |$$
$$| \bar{L}_{1s} l_i^{q+4} (0) \bar{L}_{2\rho} l'_{2\rho} (L) | L_\kappa \rangle$$

$$= \langle l_{2\rho} | (0) L_i L_\kappa | L_i l_{2\rho} (L) | L_\kappa \rangle \delta_{L_i \bar{L}_{2\rho}}$$

(removing redundant zeros)

$$= \langle L_i, l_{2\rho} 1 (0) L_\kappa | L_i l_{2\rho} (L) | L_\kappa \rangle \delta_{L_i \bar{L}_{2\rho}}$$

$$= (2L+1)^{\frac{1}{2}} W(L_i 1 L_\kappa 1, L\,0) \delta_{L_i \bar{L}_{2\rho}}$$

In a similar manner it may be shown that

$$\langle S_i q_0 | S_\phi q \rangle \quad \begin{cases} \tfrac{1}{2} \delta_{s_i \bar{s}_{2\rho}} \delta_{s_\kappa s} & \text{for Pq odd} \\ \tfrac{1}{4} \delta_{s_i \bar{s}_{2\rho}} \delta_{s_\kappa s} & \text{for Pq even} \end{cases}$$

$$\langle L_i q_0 | L_\phi q \rangle = (2L+1)^{\frac{1}{2}} W(L_i 1 L_\kappa 1, L\,0) \delta_{L_i \bar{L}_{2\rho}}$$

for all Pq

The contribution to equation (3.12) from ρ_i = 1s is therefore

$$2(0100|10)^2\delta_{l,0}\langle P_{2p}^{\ i}|P_{2p}^{\ \phi}\rangle^{q-1}\sum_{\bar{L}_{2p}\bar{S}_{2p}}(2p^q LS\|2p^{q-1}\bar{L}_{2p}\bar{S}_{2p})$$

$$(2L+1)^{\frac{1}{2}}W(L_iL_k11,0L)\delta_{\bar{L}_{2p}L_k}\langle P_{1s}^{\ i}|R|P_{2p}^{\ \phi}\rangle\delta_{s_k s}\delta_{s_i\bar{s}_{2p}}$$

$$\Big[-\tfrac{1}{2}\langle F_i|P_{1s}^{\ \phi}\rangle\langle P_{1s}^{\ i}|P_{1s}^{\ \phi}\rangle\langle P_{2s}^{\ i}|P_{2s}^{\ \phi}\rangle^2$$

$$-\tfrac{1}{2}\langle P_{2s}^{\ i}|P_{1s}^{\ \phi}\rangle^2\langle F_i|P_{2s}^{\ \phi}\rangle\langle P_{1s}^{\ i}|P_{2s}^{\ \phi}\rangle$$

$$+\tfrac{1}{2}\langle F_i|P_{1s}^{\ \phi}\rangle\langle P_{2s}^{\ i}|P_{1s}^{\ \phi}\rangle\langle P_{1s}^{\ i}|P_{2s}^{\ \phi}\rangle\langle P_{2s}^{\ i}|P_{2s}^{\ \phi}\rangle$$

$$+\tfrac{1}{2}\langle P_{1s}^{\ i}|P_{1s}^{\ \phi}\rangle\langle P_{2s}^{\ i}|P_{1s}^{\ \phi}\rangle\langle F_i|P_{2s}^{\ \phi}\rangle\langle P_{2s}^{\ i}|P_{2s}^{\ \phi}\rangle\Big]$$

$$= -\sqrt{3}\,(1100|100)\delta_{l,0}\langle P_{2p}^{\ i}|P_{2p}^{\ \phi}\rangle^{q-1}(2L+1)^{\frac{1}{2}}$$

$$(2p^q\ LS\|2p^{q-1}L_iS_i)\delta_{L_iL_k}W(L_iL_k11,0L)\delta_{s_k s}$$

$$\langle P_{1s}^{\ i}|R|P_{2p}^{\ \phi}\rangle(F_i\,2s^i|1s^\phi 2s^\phi)(1s^i\,2s^i|1s^\phi 2s^\phi)$$

where

$$(1s^i 2s^i|1s^\phi 2s^\phi) = \Big[\langle P_{1s}^{\ i}|P_{1s}^{\ \phi}\rangle\langle P_{2s}^{\ i}|P_{2s}^{\ \phi}\rangle - \langle P_{1s}^{\ i}|P_{2s}^{\ \phi}\rangle\langle P_{2s}^{\ i}|P_{1s}^{\ \phi}\rangle\Big]$$

and $(F_i\,2s^i|1s^\phi 2s^\phi)$ is defined similarly. The contribution from

$\rho_i = 2s$ may be found in exactly the same manner.

For $\rho_i = 2p$ in order that the Cleb ch-Gordan coefficient $(l_{\rho_i} 1 0 0 | l_{\rho\phi} 0)$ be non zero we must have $l_{\rho\phi} = 0$ or $l_{\rho\phi} = 2$. There are no occupied d subshells in Φ hence $\rho_\phi = 1s$ or $2s$. However the orthogonality of the spherical harmonics imply that the only non zero contributions to $\sum_{\bar{q}_\alpha}$ come from those $\bar{q}_a$ which assign labels $1\cdots,4$ to the S subshells. Φ contains only 4 occupied S orbitals and therefore the contribution to $\sum_{\rho_i}$ from $\rho_i = 2p$ must be zero.

Finally we must consider a = continuum. As for $\rho_i = 2p$ the non zero contributions to $\sum_{\bar{q}_{\alpha_c}}$ come from those $\bar{q}_{a_c}$ which assign labels $1\cdots4$ to the S subshells. Again we will have 6 such $\bar{q}_{a_c}$, corresponding to the 6 distributions for $\rho_i = 1s$, with P^i_{1s} replacing F_i, and here

$$\langle S_i q_c | S_\phi q \rangle = \begin{cases} \delta_{s_k S}\ \delta_{\bar{s}_{2\rho} s_i} & \text{for } P_q \text{ even} \\ \frac{1}{2}\delta_{s_k S}\ \delta_{\bar{s}_{2\rho} s_i} & \text{for } P_q \text{ odd} \end{cases}$$

$$\langle L_i q_c | L_\phi q \rangle = \langle L_i l_{2\rho} | (l_i) L_k | \bar{L}_{2\rho}\, l_{2\rho} (L) | L_k \rangle$$

$$= [(2l_i+1)(2L+1)]^{\frac{1}{2}} W(L_i | L_k 1, L l_i)\, \delta_{\bar{L}_{2\rho} l_i}$$

The complete contribution from a = continuum is

$$[(2L+1)(2l_i+1)]^{\frac{1}{2}} (l_i 1 0 0 | 1 0)(2p^q LS \| 2p^{q-1} L_i S_i)$$

$$\delta_{s_k S}\, W(L_i | L_k 1, L l_i)(1s^i 2s^i | 1s^\phi 2s^\phi) \langle 2p^i | 2p^\phi \rangle^{q-1}$$

$$(F_i | R | P^\phi_{2\rho})$$

Equation (3.12) therefore reduces to

$$\langle \overline{\Psi}_\kappa(\Gamma_i) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \overline{\Phi}(LS\pi) \rangle = (3q)^{\frac{1}{2}} (L\,1\,M_\mu | L_\kappa M)$$
$$(2L+1)^{\frac{1}{2}} (2p^q\, LS\,\} 2p^{q-1} L_i S_i)\, \delta_{S_\kappa S}\, (11\,00 | l_i 0)$$
$$W(L_i L_\kappa 11, l_i L)(1s^i 2s^i | 1s^\phi 2s^\phi)^2 \langle 2p^i | 2p^\phi \rangle^{q-1}$$
$$\Big[(F_i | R_v | P_{2p}^\phi) - \delta_{l_i 0} \Big\{ \frac{(F_i\, 2s^i | 1s^\phi 2s^\phi)(1s^i | R_v | 2p^\phi)}{(1s^i 2s^i | 1s^\phi 2s^\phi)}$$
$$+ \frac{(1s^i F_i | 1s^\phi 2s^\phi)(2s^i | R_v | 2p^\phi)}{(1s^i 2s^i | 1s^\phi 2s^\phi)} \Big\} \Big] \qquad (3.31)$$
$$\equiv (3q)^{\frac{1}{2}} (L\,1\,M_\mu | L_\kappa M_\kappa)(2L+1)^{\frac{1}{2}}\, g_{ik}\, \delta_{S S_\kappa}$$

$$R_v = \frac{d}{dr} + \frac{2 - l_i(l_i+1)}{2r} \qquad (3.31a)$$

Similarly

$$\langle \overline{\Phi}(LS\pi) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^{\mu *} | \overline{\Psi}_\kappa(\Gamma_j) \rangle = (3q)^{\frac{1}{2}} (L_\kappa\, 1\, M_\kappa - \mu | L M)$$
$$(2L_\kappa+1)^{\frac{1}{2}} (2p^q\, LS\,\} 2p^{q-1} L_j S_j)\, \delta_{S_\kappa S}\, (11\,00 | l_j 0)$$
$$W(L_j L_\kappa 11, l_j L)(1s^\phi 2s^\phi | 1s^j 2s^j)^2 (2p^\phi | 2p^j)^{q-1}$$
$$\Big[(2p^\phi | R_v | F_j) - \delta_{l_j 0} \Big\{ (2p^\phi | R_v | 1s^j)(1s^\phi 2s^\phi | 1s^j 2s^j)$$
$$+ (2p^\phi | R_v | 2s^j)(1s^\phi 2s^\phi | 1s^j F_j) \Big\} (1s^\phi 2s^\phi | 1s^j 2s^j)^{-1} \Big] \qquad (3.32)$$
$$\equiv (3q)^{\frac{1}{2}} (L\,1\,M_\mu | L_\kappa M_\kappa)(2L+1)^{\frac{1}{2}}\, g_{jk}^*\, \delta_{S S_\kappa}$$

Substituting equations (3.31) and (3.32) into equation (3.5a) gives

$$\sigma_v = \frac{2\pi e^2 k^2}{m^2 c v \omega} \sum_{\substack{M_L M_S \Gamma_\kappa \Gamma_i \Gamma_j \\ \mu = \pm 1}} 3q\,(2L+1)\,(L\,1\,M_\mu | L_\kappa M_\kappa)^2\, \delta_{S_\kappa S}\, g_{ik}\, A_{ij}^{\,k}\, g_{jk}^*$$

where

$$A_{ij}^{\,k} = \left(\frac{2}{\pi}\right) \frac{1}{(1+iR)_{ik}\,(1-iR)_{kj}}$$

$$\sigma_v = \frac{2\pi}{c\nu\omega} \sum_{\substack{M_L M_s \Gamma_k \Gamma_i \Gamma_j \\ \mu = \pm 1}} 3q \frac{(2L+1)(2L_k+1)}{3} (L_k L M_k - M_L 1 \mu)^2 \; g_{ik} A_{ij}^{k} g_{jk}^{*}$$

$$= \frac{2\pi}{c\nu} \sum_{\Gamma_k' \Gamma_i \Gamma_j} (2L_k+1) g_{ik} A_{ij}^{k} g_{jk}^{*}$$

(3.33)

The paper of Lipsky and Henry contains the following typographical errors. (I should like to record my thanks to Dr. Lipsky for pointing out these mistakes.)

The definition of the operator $\nabla_i^{m_1}$ appearing in equation (1) should be $\nabla_i^{\pm 1} = \frac{i}{\sqrt{2}} \left(\mp \frac{\partial}{\partial x_i} - i \frac{\partial}{\partial y_i} \right)$

Equation (5) should read

$$\frac{1}{2m} \hbar^2 k_r^2 = E = h\nu - I_r$$

Taking into account these typographical errors we see that the expression for $g_{ik}(E)$ given by equation (3.31) differs from that given by Henry and Lipsky equation (21) only in the definition of R_V (= P_r of Henry and Lipsky). The expression given by Henry and Lipsky (hereafter refered to as H.L.),

$$P_r = \frac{d}{dr} + \left[1 + \frac{(1-l_r)(2l_r+1)}{2r} \right]$$

is dimensionally inconsistent and we therefore conclude that this is incorrect. Lipsky (unpublished notes) gives an alternative definition

$$P_{l'l} = \frac{d}{dr} + \frac{1-(l'-l)(2l+1)}{2r}$$

For the case considered here $l' = l_i$ $l = 1$

$$P_{\Gamma_i} = \frac{d}{dr} + \frac{1-3(l_i-1)}{2r} \qquad (3.31b)$$

This is not the same form as that given in equation (3.31a). However in order for the Clebsch-Gordan coefficients $(1100|l_i 0)$ to be non-zero we must have $l_i = 0$ or 2. It may easily be verified that

for these values of $\ell_i (= \ell_\Gamma)$ equations (3.31a) and (3.31b) reduce to the same expression. If we compare equation (3.33) with H.L. equation (20a) we note the following differences

(1) H.L. defines $A_{ij}^{\ k} = \dfrac{1}{(1-iR)_{ki}(1+iR)_{jk}}$ whereas we define $A_{ij}^{\ k} = \dfrac{2}{\pi} \dfrac{1}{(1+iR)_{ki}(1-iR)_{jk}}$. The factor $\dfrac{2}{\pi}$ arises from the different normalisation assumed for the continuum wave functions (S.M. equation 17, H.L. equation 18). The different definitions of $A_{ij}^{\ k}$ may be traced back to the different definitions of $\Psi_i(\Gamma_i)$, see equation (3.3) and H.L. equation (12). Henry and Lipsky equation (11) yields

$$S_{\Gamma\Gamma'} = \left[\frac{1+iR}{1-iR}\right]_{\Gamma\Gamma'} \qquad S^{+}_{\Gamma\Gamma'} = \left[\frac{1-iR}{1+iR}\right]_{\Gamma\Gamma'}$$

Substituting the expression for $S^{+}_{\Gamma\Gamma'}$ into H.L. equation (3) gives

$$^{\Gamma}\bar{\Psi}_{\ell_\Gamma s_\Gamma} = i \sum_{\Gamma'} (1+iR)^{-1}_{\Gamma\Gamma'} \, {}^{\Gamma'}\bar{\Psi}_{\ell_\Gamma s_\Gamma}$$

where $^{\Gamma'}\bar{\Psi}_{\ell_\Gamma s_\Gamma}$ is defined in H.L. equation (10). This expression is now in agreement with equation (3.3) of this thesis and also with Lipsky (unpublished notes). Hence we conclude that the definition of $A_{ij}^{\ k}$ should be

$$\frac{1}{(i+iR)_{ki}(1-iR)_{jk}} \quad \text{(using the normalisation of H.L.)}$$

(2) The normalisation factor in equation (3.33) is $\dfrac{2\pi q e^2 \hbar^2}{m^2 c \nu}$ whereas the factor in H.L. equation (20a) is

$$\frac{6\pi q e^2 \hbar^2}{m^2 c \nu \omega} = \frac{3\pi q e^2 \hbar^2}{m^2 c \nu (2L+1)(2S+1)}$$

Lipsky evaluates the matrix element

$$P^{\Gamma_\kappa} = \frac{1}{(2L+1)(2S+1)} \sum_{\substack{M_L M_S M_{L_\kappa} M_{S_\kappa} \\ \mu = -1, 0, 1}} |\langle \tilde{\Psi}(\Gamma_\kappa) | \sum_{\alpha=1}^{N+1} \nabla_\alpha^\mu | \Psi(LS\pi) \rangle|^2$$

rather than the expression for the cross section given in equation (3.4a) and obtains the normalisation factor 3q. If we substitute Lipsky's expression into the formula for the cross section and take into account the fact that the summation over μ includes only $\mu = \pm 1$, since we have chosen the direction of propagation of the photons to be along the z axis, we obtain the factor $\frac{2\pi q e^2 \hbar^2}{m^2 c \nu}$ in agreement with equation (3.33) of this thesis.

We therefore conclude that the expression for the dipole velocity approximation to the photoionisation cross section given in equation (3.33) is consistent with the expression derived by Lipsky but differs from that given by Lipsky and Henry as described above. The general expression for the dipole length form of the cross section given in equation (3.4b) also differs from that given by H.L. equation (8) in the definition of the operator. We note, however, that applying the commutation relation $[r, H] = \frac{i\hbar}{m} p$ to (3.4a) yields equation (3.4b) where r_i^μ is the μ^{th} component of $\underset{\sim}{r}_i$. In spherical polar coordinates $r_i^\mu = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} r_i Y_1^\mu(\hat{r}_i)$ [see for example Rose "Elementary Theory of Angular Momentum (Wiley) 15] and hence we conclude that the expression given by H.L. is incorrect.

SECTION 4: EVALUATION OF ANGULAR INTEGRALS

In this section we derive expressions for the angular integrals that occur in the matrix elements of $P_K(\hat{r}_N \cdot \hat{r}_{N+1})$, $\nabla^m(r)$ and $Y_{lm}(r)$, described in sections (2) and (3) respectively. These integrals are expressed in terms of generalised angular momenta recoupling coefficients. A method for the evaluation of these coefficients is described in section (4.2) and a FORTRAN program which uses this method is described in section (4.3).

4.1 Expression of Integrals in Terms of Recoupling Coefficients.

We first find an expression for the matrix element of a two particle operator of the form

$$\mathcal{Y}^{kq}_{k_1 k_2}(\hat{r}_N, \hat{r}_{N+1}) = \left[Y^{k_1}(\hat{r}_N) \times Y^{k_2}(\hat{r}_{N+1}) \right]^{kq}$$

$$= \sum_{q_1 q_2} (k_1 k_2 q_1 q_2 | kq) Y_{k_1 q_1}(\hat{r}_N) Y_{k_2 q_2}(\hat{r}_{N+1}) \qquad (4.1)$$

between n particle angular momentum eigenfunctions of the form

$$|\bar{L}_1 \cdots \bar{L}_{s_i} l_{s_i}^{N}(L_{s_i})\ \bar{L}_{t_i} l_{t_i}^{N+1}(L_{t_i}) \cdots L_i\rangle$$

$$= \sum_{\hat{L}_{s_i} \cdots \hat{L}_{t_i} \cdots m_{s_i} \cdots m_{t_i} m} C^{\hat{L}_{s_i} \cdots \hat{L}_{t_i} \cdots m_{s_i} \cdots m_{t_i} m} |\bar{L}_1 \cdots \bar{L}_{s_i} \cdots \bar{L}_{t_i} \cdots L_i\rangle$$

$$|l_{s_i} m_{s_i}\rangle |l_{t_i} m_{t_i}\rangle$$

(4.2)

where the $C^{\hat{L}_{s_i} \cdots m_{s_i} \cdots m}$ is a product of Racah and Clebsch-Gordan coefficients needed to separate off the two one-particle wave functions from the remaining n-2 particle wave function.

- Fano, Prats and Goldschmidt (1963) have derived an expression for the more general tensorial operator

$$\left[l^{k_1} \times T^{k_2} \right]^{kq}$$

The operators with which we are concerned are constructed from the same irreducible tensorial sets as are the angular momentum eigenfunctions, namely the spherical harmonics. This fact enables us to derive an expression for the matrix elements of the operator (4.1) in a more direct manner.

We first separate the operator into two sums of one particle operators using the method of Fano, Prats and Goldschmidt. We introduce two mock particles labelled 0 and $\bar{0}$ with angular momentum eigenfunctions

$|k_1 q_1, (0)\rangle$, $|k_2 q_2 (\bar{0})\rangle$

where $\langle k_1 q_1'(0) | k_1 q_1(0) \rangle = \delta q_1' q_1$

and $\langle k_1 q_1(0)| = (-1)^{q_1} | k - q(0) \rangle$

with similar relations holding for $| k_2 q_2(\bar{0}) \rangle$

Now

$$\begin{aligned} \mathcal{Y}^{kq}_{k_1 k_2}(\hat{r}_N, \hat{r}_{N+1}) &= \sum_{q_1 q_2} (k_1 k_2 q_1 q_2 | kq) Y_{k_1 q_1}(\hat{r}_N) Y_{k_2 q_2}(\hat{r}_{N+1}) \\ &= \sum_{q_1 q_2} (k_1 k_2 q_1 q_2 | kq) Y_{k_1 q_1}(\hat{r}_N) \sum_{q_1^*} \langle k_1 q_1^*(0) | k_1 q_1(0) \rangle \\ &\quad \times \sum_{q_2^*} \langle k_2 q_2^*(\bar{0}) | k_2 q_2(\bar{0}) \rangle Y_{k_2 q_2}(\hat{r}_{N+1}) \\ &= \left\{ \sum_{q_1^*} Y_{k_1 q_1^*}(\hat{r}_N) \langle k_1 q_1^*(0) | \right\} \left\{ \sum_{q_2^*} Y_{k_2 q_2^*}(\hat{r}_{N+1}) \langle k_2 q_2^*(\bar{0}) | \right\} \\ &\quad \times | k_1 k_2, kq \rangle \end{aligned} \tag{4.3}$$

where

$$| k_1 k_2, kq \rangle = \sum_{q_1 q_2} (k_1 k_2 q_1 q_2 | kq) | k_1 q_1(0) \rangle | k_2 q_2(\bar{0}) \rangle$$

consider

$$\begin{aligned} &\langle \ell_{s_i} m_{s_i} | \sum_{q_1^*} Y_{k_1 q_1^*}(\hat{r}_N) \langle k_1 q_1^*(0) | \\ &= \sum_{q_1^* \ell_i' m_i'} \left[\frac{(2\ell_{s_i}+1)(2k_1+1)}{4\pi(2\ell_i'+1)} \right]^{\frac{1}{2}} (\ell_{s_i} k_1 00 | \ell_i' 0)(\ell_{s_i} k_1 m_{s_i} - q_1^* | \ell_i' m_i') \\ &\qquad \times (-1)^{q_1^*} \langle \ell_{s_i} k_1, \ell_i' m_i' | \langle k_1 q_1^*(0) | \\ &= \sum_{q_1^* \ell_i' m_i'} \left[\frac{2k_1+1}{4\pi} \right]^{\frac{1}{2}} (\ell_{s_i} k_1 00 | \ell_i' 0)(\ell_i' k_1 m_i' q_1^* | \ell_{s_i} m_{s_i})(-1)^{k_1} \langle \ell_i' m_i' | \langle k_1 q_1^* | \\ &= \sum_{\ell_i'} \left[\frac{2k_1+1}{4\pi} \right]^{\frac{1}{2}} (-1)^{k_1} (\ell_{s_i} k 00 | \ell_i' 0) \langle \ell_{s_i} k_1 (\ell_i') k_1, \ell_{s_i} m_{s_i} | \end{aligned} \tag{4.4}$$

We now operate on $\langle \ell_{t_i} m_{t_i} |$ with $\left\{ \sum_{q_2^*} Y_{k_2 q_2^*}(\hat{r}_{N+1}) \langle k_2 q_2^*(\bar{0}) | \right\}$ which gives, in analogy with the above expression

$$\langle \ell_{t_i} m_{t_i} | \sum_{q_2^*} Y_{k_2 q_2^*}(\hat{r}_t) \langle k_2 q_2^*(\bar{0}) |$$

$$= \sum_{l_i''} (-1)^{k_2} \left[\frac{2k_2+1}{4\pi} \right]^{\frac{1}{2}} (\ell_{t_i} k_2 00 | \ell_i'' 0) \langle \ell_{t_i} k_2 (\ell_i'') k_2, \ell_{t_i} m_{t_i} |$$

now the L.H.S. of the matrix element is

$$\langle \bar{L}_1 \cdots \bar{L}_{s_i} \ell_{s_i}^N (L_{s_i}) \cdots \bar{L}_{t_i} \ell_{t_i}^{N+1} (L_{t_i}) \cdots L_i | \sum_{q_1^*} Y_{k_1 q_1^*}(\hat{r}_N) \langle k_1 q_1^* | \sum_{q_2^*} Y_{k_2 q_2^*}(\hat{r}_{N+1}) \langle k_2 q_2^* |$$

$$= \sum_{\hat{L}_{s_i} \cdots \hat{L}_{t_i} \cdots \hat{L}_i m_{s_i} m_{t_i} m} C^{\hat{L}_{s_i} \cdots \hat{L}_{t_i} \cdots \hat{L}_i m_{s_i} m_{t_i} m} \langle \bar{L}_1 \cdots \bar{L}_{s_i} \cdots \bar{L}_{t_i} \cdots L_i | \langle \ell_{s_i} m_{s_i} | \sum_{q_1^*} Y_{k_1 q_1^*}(\hat{r}_N)$$

$$\times \langle k_1 q_1^* | \langle \ell_{t_i} m_{t_i} | \sum_{q_2^*} Y_{k_2 q_2^*}(\hat{r}_{N+1}) \langle k_2 q_2^* |$$

$$= \sum_{\hat{L}_{s_i} \cdots \hat{L}_{t_i} \cdots \hat{L}_i m_{s_i} m_{t_i} m} C^{\hat{L}_{s_i} \cdots \hat{L}_{t_i} \cdots \hat{L}_i m_{s_i} m_{t_i} m} \langle \bar{L}_1 \cdots \bar{L}_{s_i} \cdots \bar{L}_{t_i} \cdots L_i | \sum_{l_i'} (-1)^{k_1} \left[\frac{2k_1+1}{4\pi} \right]^{\frac{1}{2}}$$

$$(\ell_{s_i} k_1 00 | \ell_i' 0) \langle \ell_{s_i} k_1 (\ell_i') k_1 \ell_{s_i} m_{s_i} | \sum_{l_i''} (-1)^{k_2} \left[\frac{2k_2+1}{4\pi} \right]^{\frac{1}{2}} (\ell_{t_i} k_2 00 | \ell_i'' 0)$$

$$\langle \ell_{t_i} k_2 (\ell_i'') k_2 \ell_{t_i} m_{t_i} |$$

$$= \sum_{l_i l_i''} (-1)^{k_1+k_2} \left[\frac{(2k_1+1)(2k_2+1)}{4\pi} \right]^{\frac{1}{2}} (\ell_{s_i} k_1 00 | \ell_i' 0)(\ell_{t_i} k_2 00 | \ell_i'' 0)$$

$$\langle \bar{L}_1 \cdots \bar{L}_{s_i} [\ell_i' k_1 (\ell_{s_i})] L_{s_i} \cdots \bar{L}_{t_i} [\ell_j' k_2 (\ell_{t_i})] L_{t_i} \cdots L_i |$$

Since the Racah and Clebsh Gordan coefficients needed to recouple $\langle \ell_{s_i} k_1 (\ell_i') k_1 \ell_{s_i} m_{s_i} |$ and $\langle \ell_{t_i} k_2 (\ell_i'') k_2 \ell_{t_i} m_{t_i} |$ back into the original wave function are just those specified by the $C^{\hat{L}_{s_i} \cdots \hat{L}_{t_i} \cdots m}$

Therefore the complete matrix element

$$\langle Y^{kq}_{k_1 k_2}(\hat{r}_N, \hat{r}_{N+1}) \rangle = (-1)^{k_1+k_2} \left[\frac{(2k_1+1)(2k_2+1)}{4\pi} \right]^{\frac{1}{2}} (\ell_{s_i} k_1 00 | \ell_{s_j} 0)$$

$$\times (\ell_{t_i} k_2 00 | \ell_{t_j} 0) \langle \bar{L}_1 \cdots \bar{L}_{s_i} [\ell_{s_j} k_1 (\ell_{s_i})] L_{s_i} \cdots \bar{L}_{t_i} [\ell_{t_j} k_2 (\ell_{t_i})] L_{t_i} \cdots L_i M_i |$$

$$\times | \bar{L}_1 \cdots \bar{L}_{s_j} \ell_{s_j} (L_{s_j}) \cdots \bar{L}_{t_j} \ell_{t_j} (L_{t_j}) \cdots L_j M_j \rangle | k_1 k_2 k q \rangle$$

$$= (-1)^{k_1+k_2} \left[\frac{(2k_1+1)(2k_2+1)}{4\pi} \right]^{\frac{1}{2}} (\ell_{s_i} k_1 00 | \ell_{s_j} 0)(\ell_{t_i} k_2 00 | \ell_{t_j} 0)(L_j k M_j q | L_i M_i)$$

$$\langle \bar{L}_1 \cdots \bar{L}_{s_i} [\ell_{s_j} k_1 (\ell_{s_i})] L_{s_i} \cdots \bar{L}_{t_i} [\ell_{t_j} k_2 (\ell_{t_i})] L_{t_i} \cdots L_i |$$

$$| \bar{L}_1 \cdots \bar{L}_{s_j} \ell_{s_j} (L_{s_j}) \cdots \bar{L}_{t_j} \ell_{t_j} (L_{t_j}) \cdots L_j \; k_1 k_2 (k) \; L_i \rangle \qquad (4.7)$$

as the sums over ℓ_i' and ℓ_i'' reduce to a single element from the orthogonality of the one electron wave functions i.e.,

$$\langle \ell_i' m_i' (N) \mid \ell_{s_j} m_{s_j} (N) \rangle = \delta_{\ell_i' \ell_{s_j}} \delta_{m_i' m_{s_j}}$$

and

$$\langle \ell_i'' m_i'' (N+1) \mid \ell_{\epsilon_j} m_{\epsilon_j} (N+1) \rangle = \delta_{\ell_i'' \ell_{\epsilon_j}} \delta_{m_i'' m_{\epsilon_j}}$$

The last term on the R.H.S. of equation (4.7) is the inner product of two different functions constructed from the same set of angular momentum eigenfunctions but coupled together in a different order. It is one of the matrix elements of the transformation from the $\{\bar{L}_1 \cdots \bar{L}_{s_i} \ell_{s_j} k_1 (\tilde{\ell}_{s_i}) (L_{s_i}) \cdots \bar{L}_{\epsilon_i} \ell_{\epsilon_j} k_2 (\tilde{\ell}_{\epsilon_i}) L_{\epsilon_i} \cdots L M_L\}$ representation to the $\{\bar{L}_1 \cdots \bar{L}_{s_j} \ell_{s_j} (\tilde{L}_{s_j}) \cdots \bar{L}_{\epsilon_j} \ell_{\epsilon_j} (\tilde{L}_{\epsilon_j}) \cdots (\tilde{L}_j) k_1 k_2 (\tilde{k}) L_j M_j\}$ representation. $(\tilde{L})$ denotes the set of values of the intermediate coupling which has the particular value L in equation (4.7), (the notation has been modified slightly to distinguish between basic set of angular momenta and the sets of intermediate couplings). These matrix elements are known as angular momentum recoupling coefficients.

If C^k is the vector spherical harmonic with components

$$C^k_q = \sqrt{\frac{4\pi}{2k+1}} \cdot Y_{kq}$$

where the Y_{kq} are normalised such that $Y^*_{kq} = (-1)^q Y_{k-q}$ (and not such that $Y^*_{kq} = (-1)^{k-q} Y_{k-q}$ as used by Fano, Prats and Goldschmidt) then

$$(\ell_{s_i} k_1 00 \mid \ell_{s_j} 0) = (-1)^{k_1} [2\ell_{s_i}+1]^{-\frac{1}{2}} (\ell_{s_i} \| C^{k_1} \| \ell_{s_j})$$

$$= [2\ell_{s_j}+1]^{-\frac{1}{2}} (\ell_{s_j} \| C^{k_1} \| \ell_{s_i})$$

and

$$\left\langle Y^{kq}_{k_1 k_2}(r_N, r_{N+1}) \right\rangle = \frac{1}{4\pi}\left[\frac{(2k_1+1)(2k_2+1)}{(2l_{s_i}+1)(2l_{t_i}+1)}\right]^{\frac{1}{2}} (l_{s_i}\|C^{k_1}\|l_{s_j})(l_{t_i}\|C^{k_2}\|l_{t_j})$$

$$(L_j k M_j q \,|\, L_i M_i)\langle \bar{L}_1 \cdots \bar{L}_{s_i}[l_{s_j} k_1(l_{s_i})]L_{s_i} \cdots \bar{L}_{t_i}[l_{t_j} k_2(l_{t_j})]L_{t_j} \cdots L_i|$$

$$|\bar{L}_1 \cdots \bar{L}_{s_j} l_{s_j}(L_{s_j}) \cdots \bar{L}_{t_j} l_{t_j}(L_{t_j}) \cdots L_j \; k_1 k_2(k) L_i\rangle$$

which is a special case of equation (36) of Fano, Prats and Goldschmidt.

The particular matrix elements that we wish to evaluate are

$$(1)\quad \left\langle P_t(\hat{r}_N \cdot \hat{r}_{N+1}) \right\rangle = \frac{4\pi}{2t+1}\left\langle \sum_m Y_{tm}(\hat{r}_N) Y^*_{tm}(\hat{r}_{N+1}) \right\rangle$$

$$= \frac{4\pi}{2t+1}\left\langle \sum_m (-1)^m Y_{tm}(\hat{r}_N) Y_{t-m}(\hat{r}_{N+1}) \right\rangle$$

$$= \frac{4\pi}{[2t+1]^{\frac{1}{2}}}(-1)^t \left\langle Y^{00}_{tt}(\hat{r}_N, \hat{r}_{N+1}) \right\rangle$$

$$= (-1)^t (2t+1)^{\frac{1}{2}}[(2l_{s_i}+1)(2l_{t_i}+1)]^{-\frac{1}{2}}(l_{s_i}\|C^t\|l_{s_j})$$

$$(l_{t_i}\|C^t\|l_{t_j})(L_j\, 0\, M_j\, 0 \,|\, L_i M_i)$$

$$\langle \bar{L}_1 \cdots \bar{L}_{s_i}[l_{s_j} k(l_{s_i})]L_{s_i} \cdots \bar{L}_{t_i}[l_{t_j} k_2(l_{t_i})]L_{t_i} \cdots L_i|$$

$$|\bar{L}_1 \cdots \bar{L}_{s_j} l_{s_j}(L_{s_j}) \cdots \bar{L}_{t_j} l_{t_j}(L_{t_j}) \cdots L_j \; k_1 k_2(0) L_i\rangle$$

$$= (-1)^t (2t+1)^{\frac{1}{2}}[(2l_{s_i}+1)(2l_{t_i}+1)]^{-\frac{1}{2}}(l_{s_i}\|C^t\|l_{s_j})$$

$$(l_{t_i}\|C^t\|l_{t_j})\,\delta_{L_i L_j}$$

$$\langle \bar{L}_1 \cdots \bar{L}_{s_i}[l_{s_j} k(l_{s_i})]L_{s_i} \cdots \bar{L}_{t_i}[l_{t_j} k_2(l_{t_i})]L_{t_i} \cdots L_i|$$

$$|\bar{L}_1 \cdots \bar{L}_{s_j} l_{s_j}(L_{s_j}) \cdots \bar{L}_{t_j} l_{t_j}(L_{t_j}) \cdots L_j \; k_1 k_2(0) L_i\rangle$$

where $k_1 = k_2 = t$, the labels $k_1 k_2$ being retained to identify particles (0) and $(\bar{0})$.

Now the recoupling coefficient may be expressed in the alternative form

$$\begin{aligned}
&\langle \bar{L}_1 \cdots \bar{L}_{s_i}(\ell_{s_j} k_1(\ell_{s_i}))L_{s_i} \quad \bar{L}_{t_i}[\ell_{t_j} k_2(\ell_{t_i})]L_{t_i} \cdots L_i | \\
&\quad | \bar{L}_1 \quad \bar{L}_{s_i} \cdots \bar{L}_{s_j}\ell_{s_j}(L_{s_j}) \cdots \bar{L}_{t_i} \cdots \bar{L}_{t_j}[k_1 k_2(0)\ell_{t_j}, \ell_{t_j}]L_{t_j} \cdots L_j\rangle \delta_{L_i L_j} \\
&= \langle \bar{L}_1 \cdot \bar{L}_{s_i}(\ell_{s_j} k_1(\ell_{s_i}))L_{s_i} \cdots \bar{L}_{t_i}\ell_{t_i}(L_{t_i}) \cdots L_i | \\
&\quad | \bar{L}_1 \cdots \bar{L}_{s_i} \bar{L}_{s_j}\ell_{s_j}(L_{s_j}) \cdots \bar{L}_{t_i} \cdots \bar{L}_{t_j}[k_1 k_2 \ell_{t_j}(\ell_{t_i}), \ell_{t_j}]L_{t_j} \cdots L_j\rangle \\
&\quad \langle k_1 k_2(0)\ell_{t_j}\ell_{t_j} | k_1, k_2 \ell_{t_j}(\ell_{t_i})\ell_{t_j}\rangle \delta_{L_i L_j} \\
&= \left[\frac{(2\ell_{t_i}+1)}{(2k+1)(2\ell_{t_j}+1)}\right]^{\frac{1}{2}} \langle \bar{L}_1 \cdots \bar{L}_{s_i}[\ell_{s_j} k(\ell_{s_i})]L_{s_i} \quad \bar{L}_{t_i}\ell_{t_i}(L_{t_i}) \cdots L_i | \\
&\quad | \bar{L}_1 \cdots \bar{L}_{s_j}\ell_{s_j}(L_{s_j}) \cdots \bar{L}_{t_j}[k\ell_{t_i}(\ell_{t_j})]L_{t_j} \cdots L_j\rangle \delta_{L_i L_j}
\end{aligned}$$

so that

$$\begin{aligned}
\langle P_t(\hat{r}_N \cdot \hat{r}_{N+1})\rangle &= (-1)^t[(2\ell_{s_i}+1)(2\ell_{t_j}+1)]^{\frac{1}{2}}(\ell_{s_i}\|C^t\|\ell_{s_j}) \\
&\quad (\ell_{t_j}\|C^t\|\ell_{t_i})\delta_{L_i L_j} \\
&\quad \langle \bar{L}_1 \cdots \bar{L}_{s_i}[\ell_{s_j} t(\ell_{s_i})]L_{s_i} \cdots \bar{L}_{t_i}\ell_{t_i}(L_{t_i}) \cdots L_i | \\
&\quad | \bar{L}_1 \cdots \bar{L}_{s_j}\ell_{s_j}(L_{s_j}) \cdots \bar{L}_{t_j}[t\ell_{t_i}(\ell_{t_j})]L_{t_j} \cdots L_j\rangle
\end{aligned}$$

(4.10)

The matrix elements required for the evaluation of the photo-ionisation cross sections are

(2) $$\begin{aligned} \langle Y_{1q}(r)\rangle &= \sqrt{4\pi}\,\langle Y_{0c}(r')\,Y_{1q}(r)\rangle \\ &= \sqrt{4\pi}\,\langle {}^{1q}_{01}\gamma\, r' r\rangle \\ &= \frac{-1}{\sqrt{4\pi}}\left[\frac{3}{(2\ell_{t_i}+1)}\right]^{\frac{1}{2}} (\ell_{t_i}\|C^1\|\ell_{t_j}) \\ &\quad (L_j\,1\,M_j\,q\,|\,L_i M_i) \\ &\quad \langle \bar{L}_1\cdots\bar{L}_{t_i}[\ell_{t_j}\,1\,(\ell_{t_i})]L_{t_i}\cdots L_i\,| \\ &\quad\quad |\bar{L}_1\cdots\bar{L}_{t_j}\ell_{t_j}(L_{t_j})\cdots L_j\,1, L_i\rangle \end{aligned}$$

(4.11)

(3) $\langle \nabla^q(r)\rangle$

Now the components ∇^{-1}, ∇^0, ∇^{+1} (defined in section 3) also form an irreducible tensorial set of degree 1. Hence we may apply the Wigner Eckhart theorem (Fano and Racah, Ch. 14) and use equation (4.11) to obtain

$$\begin{aligned} \langle \nabla^q(r)\rangle &= \sqrt{\frac{4\pi}{3}}\,\frac{(\ell_{t_i}\|\bar{\nabla}\|\ell_{t_j})}{(\ell_{t_i}\|C^1\|\ell_{t_j})}\,\langle Y_{1q}(r)\rangle \\ &= (2\ell_{t_i}+1)^{-\frac{1}{2}}\,(\ell_{t_i}\|\bar{\nabla}\|\ell_{t_j})(L_j\,1\,M_j\,q\,|\,L_i M_i) \\ &\quad \langle \bar{L}_1\cdots\bar{L}_{t_i}[\ell_{t_j}\,1\,(\ell_{t_i})]L_{t_i}\cdots L_i\,|\,\bar{L}_1\cdots\bar{L}_{t_j}\ell_{t_j}(L_{t_j})\cdots L_j\,1, L_i\rangle \end{aligned}$$

where

(4.12)

$$(\ell_{t_i}\|\nabla\|\ell_{t_j}) = (2\ell_{t_i}+1)^{\frac{1}{2}}\,(\ell_{t_i}\,1\,0\,0\,|\,\ell_{t_j}\,0)\left[\frac{d}{dr}+\frac{1}{r}+\frac{\ell_{t_j}(\ell_{t_j}+1)-\ell_{t_i}(\ell_{t_i}+1)}{2r}\right]$$

4.2 Evaluation of the recoupling coefficients.

We recall that in constructing the total wave function, equation (2.14) we first coupled together the angular momenta of electrons in discrete orbitals to give subshell angular momenta $L_\lambda S_\lambda$. We then coupled the subshell angular momenta and the angular momentum of the projectile according to the coupling scheme

$$\{L_1 L_2 (L_2{}^a) L_3 (L_3{}^a) \cdots L_\lambda (L_\lambda{}^a) \cdots L_b (L_b{}^a) \ell, L\} \qquad (4.20)$$

to give total angular momenta LS for the system. $L_\lambda{}^a$ denotes the result of coupling L_λ to $L^a_{\lambda-1}$ which is the resultant of $L_1 \cdots L_{\lambda-1}$. If the set of values of the intermediate couplings L^a is not unique then to each set $\{L^{a_i}\}$ there corresponds a distinct state Γ_i specified by the total quantum numbers $LS\pi$ together with an additional parameter α_i which specifies the set of intermediate couplings. It can easily be shown that the wave functions for a given coupling scheme, corresponding to the different values of α_i form a complete orthonormal set.

Three basic types of recoupling coefficients occur in the analysis of S.M. These are those in which

1) One vector is recoupled, the order of coupling of the others remaining unaltered. For example in the recoupling coefficients in S.M. equation (56) the vectors ℓ_i and $\frac{1}{2}$ are recoupled, the order of coupling of the spectator angular momenta $L_\lambda S_\lambda$ remaining unchanged.

2) Two vectors are recoupled. For example the spin recoupling coefficients of S.M. equations (41), (59) and (62a) where the two recoupled vectors are $\frac{1}{2}_N$ and $\frac{1}{2}_{N+1}$. The spin recoupling coefficient equation (49b) is of type (1) since $\frac{1}{2}_{N+1}$ is coupled to S_b^a on both sides of the coefficient and is not recoupled.

3) Three vectors are recoupled. These arise in the evaluation of the matrix elements of $P_K(\hat{r}_N \cdot \hat{r}_{N+1})$ discussed earlier in this section and occur in S.M. equations (40), (49a), (60a) and (62a).

These multivector recoupling coefficients may be expressed in terms of sums of products of three vector recoupling coefficients or Racah coefficients (Biedenharn 1953),

$$\langle j_1 j_2 (j_{12}) j_3 J \mid j_1, j_2 j_3 (j_{23}) J \rangle = [(2j_{12}+1)(2j_{23}+1)]^{\frac{1}{2}} W(j_1 j_2 J j_3; j_{12} j_{23})$$

We first consider recoupling coefficients of type (1), that is, those of the form

$$\langle \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_i}) \bar{L}_\rho l (L_\rho)(L_\rho^{\alpha_i}) \cdots \bar{L}_\sigma \cdots L \mid \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_j}) \bar{L}_\rho (L_\rho^{\alpha_j}) \cdots \bar{L}_\sigma l (L_\sigma) \cdots L \rangle \tag{4.21}$$

We recall that this is the inner product of the wave functions,

$$|\alpha_i L\rangle = |\bar{L}_1 \cdots (L_{\rho-1}^{\alpha_i}) \bar{L}_\rho l (L_\rho)(L_\rho^{\alpha_i}) \cdots \bar{L}_\sigma \cdots L\rangle \tag{4.22}$$

and

$$|\alpha_j L\rangle = |\bar{L}_1 \cdots (L_{\rho-1}^{\alpha_j}) \bar{L}_\rho (L_\rho^{\alpha_j}) \cdots \bar{L}_\sigma l (L_\sigma) \cdots L\rangle \tag{4.23}$$

We wish to expand $\langle \alpha_i L|$ in the complete set of functions of the form of (4.23)

We first recouple the three vectors $L_{\rho-1}^{\alpha_i}$, $\bar{L}_\rho$, l

from the scheme $\{L_{\rho-1}^{a_i}, L_\rho \ell(L_\rho) L_\rho^{a_i}\}$ to $\{L_{\rho-1}^{a_i} L_\rho (L_\rho) \ell L_\rho^{a_i}\}$
by means of the transformation

$$\langle \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_i}) \bar{L}_\rho \ell(L_\rho)(L_\rho^{\alpha_i}) \cdots L| = \sum_{\tilde{L}_\rho} \langle L_{\rho-1}^{\alpha_i} \bar{L}_\rho \ell(L_\rho) L_\rho^{\alpha_i} | L_{\rho-1}^{\alpha_i} \bar{L}_\rho(\tilde{L}_\rho) \ell L_\rho^{\alpha_i} \rangle \langle \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_i}) \bar{L}_\rho(\tilde{L}) \ell(L_\rho^{\alpha_i}) \cdots L|$$

We then recouple ℓ step by step from $\lambda = \rho$ to $\lambda = \sigma$ by transformations of the form

$$\langle \bar{L}_1 \cdots (\tilde{L}_{\lambda-1}) \ell (L_{\lambda-1}^{\alpha_i}) \bar{L}_\lambda (L_\lambda^{\alpha_i}) \cdots L|$$

$$= \sum_{\tilde{L}_\lambda} \langle \tilde{L}_{\lambda-1} \ell (L_{\lambda-1}^{\alpha_i}) \bar{L}_\lambda L_\lambda^{\alpha_i} | \tilde{L}_{\lambda-1} \bar{L}_\lambda (\tilde{L}_\lambda) \ell L_\lambda^{\alpha_i} \rangle \langle \bar{L}_1 \cdots (\tilde{L}_{\lambda-1}) \bar{L}_\lambda (\tilde{L}_\lambda) \ell L_\lambda^{\alpha_i} \cdots L|$$

to give finally

$$\langle \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_i}) \bar{L}_\rho \ell(L_\rho) \cdots \bar{L}_\sigma \cdots L|$$

$$= \sum_{\tilde{L}_\rho \cdots \tilde{L}_\sigma} \langle L_{\rho-1}^{\alpha_i} \bar{L}_\rho \ell(L_\rho) L_\rho^{\alpha_i} | L_{\rho-1}^{\alpha_i} \bar{L}_\rho(\tilde{L}_\rho) \ell L_\rho^{\alpha_i} \rangle$$

$$\prod_{\lambda=\rho+1}^{\sigma-1} \langle \tilde{L}_{\lambda-1} \ell (L_{\lambda-1}^{\alpha_i}) \bar{L}_\lambda L_\lambda^{\alpha_i} | \tilde{L}_{\lambda-1} \bar{L}_\lambda (\tilde{L}_\lambda) \ell L_\lambda^{\alpha_i} \rangle$$

$$\langle \tilde{L}_{\sigma-1} \ell (L_{\sigma-1}^{\alpha_i}) \bar{L}_\sigma L_\sigma^{\alpha_i} | \tilde{L}_{\sigma-1} \bar{L}_\sigma \ell (\tilde{L}_\sigma) L_\sigma^{\alpha_i} \rangle$$

$$\langle \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_i}) \bar{L}_\rho (\tilde{L}_\rho) \cdots (\tilde{L}_{\sigma-1}) \bar{L}_\sigma \ell(\tilde{L}_\sigma) \cdots L| \quad (4.24)$$

so that

$$\langle \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_i}) \bar{L}_\rho \ell(L_\rho)(L_\rho^{\alpha_i}) \cdots \bar{L}_\sigma \cdots L | \bar{L}_1 \cdots \bar{L}_\rho \cdots (L_{\sigma-1}^{\alpha_j}) \bar{L}_\sigma \ell(L_\sigma)(L_\sigma^{\alpha_j}) \cdots L \rangle$$

$$= \sum_{\tilde{L}_\rho \cdots \tilde{L}_\sigma} \langle L_{\rho-1}^{\alpha_i} \bar{L}_\rho \ell(L_\rho) L_\rho^{\alpha_i} | L_{\rho-1}^{\alpha_i} \bar{L}_\rho(\tilde{L}_\rho) \ell L_\rho^{\alpha_i} \rangle$$

$$\prod_{\lambda=\rho+1}^{\sigma-1} \langle \tilde{L}_{\lambda-1} \ell (L_{\lambda-1}^{\alpha_i}) \bar{L}_\lambda L_\lambda^{\alpha_i} | \tilde{L}_{\lambda-1} \bar{L}_\lambda (\tilde{L}_\lambda) \ell L_\lambda^{\alpha_i} \rangle$$

$$\langle \tilde{L}_{\sigma-1} \ell (L_{\sigma-1}^{\alpha_i}) \bar{L}_\sigma L_\sigma^{\alpha_i} | \tilde{L}_{\sigma-1} \bar{L}_\sigma \ell (\tilde{L}_\sigma) L_\sigma^{\alpha_i} \rangle$$

(4.25)

$$\langle \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_i}) \bar{L}_\rho (\tilde{L}_\rho) \cdots (\tilde{L}_{\sigma-1}) \bar{L}_\sigma \ell(\tilde{L}_\sigma) \cdots L | \bar{L}_1 \cdots (L_{\rho-1}^{\alpha_j}) \bar{L}_\rho (L_\rho^{\alpha_j}) \cdots (L_{\sigma-1}^{\alpha_j}) \bar{L}_\sigma \ell (L_\sigma) \cdots L \rangle$$

from the orthonormality of the functions of the form (4.23) we have that

$$
\begin{aligned}
&\langle \bar{L}_1 \cdots (L^{\alpha_i}_{\rho-1}) \bar{L}_\rho \ell (L_\rho) \cdots \bar{L}_\sigma \cdots L | \bar{L}_1 \cdots L^{\alpha_j}_{\rho-1} \bar{L}_\rho (L^{\alpha_j}_{\rho}) \cdots \bar{L}_\sigma \ell (L_\sigma)(L^{\alpha_j}_{\sigma}) \cdots L \rangle \\
&= \langle L^{\alpha_i}_{\rho-1} \bar{L}_\rho \ell (L_\rho) L^{\alpha_i}_{\rho} | L^{\alpha_i}_{\rho-1} \bar{L}_\rho (L^{\alpha_j}_{\rho}) \ell L^{\alpha_j}_{\rho} \rangle \\
&\quad \prod_{\lambda=\rho+1}^{\sigma-1} \langle L^{\alpha_j}_{\lambda-1} \ell (L^{\alpha_i}_{\lambda-1}) \bar{L}_\lambda L^{\alpha_i}_{\lambda} | L^{\alpha_j}_{\lambda-1} \bar{L}_\lambda (L^{\alpha_j}_{\lambda}) \ell L^{\alpha_j}_{\lambda} \rangle \\
&\quad \langle L^{\alpha_j}_{\sigma-1} \ell (L^{\alpha_i}_{\sigma-1}) \bar{L}_\sigma L^{\alpha_i}_{\sigma} | L^{\alpha_j}_{\sigma-1} \bar{L}_\sigma \ell (L_\sigma) L^{\alpha_j}_{\sigma} \rangle \\
&\quad \delta(L^{\alpha_i}_1 L^{\alpha_j}_1) \cdots \delta(L^{\alpha_i}_{\rho-1} L^{\alpha_j}_{\rho-1}) \delta(L^{\alpha_i}_{\sigma} L^{\alpha_j}_{\sigma}) \cdots \delta(L^{\alpha_i}_{\sigma} L^{\alpha_j}_{\sigma}) \\
&= [(2L_\rho+1)(2L^{\alpha_j}_{\rho}+1)]^{\frac{1}{2}} W(L^{\alpha_i}_{\rho-1} \bar{L}_\rho L^{\alpha_i}_{\rho} \ell, L_\rho L^{\alpha_j}_{\rho}) \\
&\quad \prod_{\lambda=\rho+1}^{\sigma-1} [(2L^{\alpha_i}_{\lambda-1}+1)(2L^{\alpha_j}_{\lambda}+1)]^{\frac{1}{2}} W(L^{\alpha_i}_{\lambda-1} \ell \bar{L}_\lambda L^{\alpha_j}_{\lambda}, L^{\alpha_j}_{\lambda-1} L^{\alpha_i}_{\lambda}) \\
&(-1)^{\ell+\bar{L}_\sigma+L_\sigma} [(2L_\sigma+1)(2L^{\alpha_i}_{\sigma-1}+1)]^{\frac{1}{2}} W(L^{\alpha_j}_{\sigma-1} \ell L^{\alpha_i}_{\sigma} \bar{L}_\sigma L^{\alpha_i}_{\sigma-1} L_\sigma)
\end{aligned}
\qquad (4.26)
$$

This proceedure of step by step recoupling may be summarised as follows

(i) Recouple three (or four) of the vectors which appear in either the l.h.s. or r.h.s. of the coefficient. If these three vectors are denoted by ℓ_1, ℓ_2, ℓ_3 and are coupled in $\langle a_i L_i|$ according to the scheme $\ell_1 \ell_1 (\ell_{12}) \ell_3 \ell$ then we may express the original recoupling coefficient in terms of products of two recoupling coefficients of the form

$$
\begin{aligned}
\langle \alpha_i L_i | \alpha_j L_j \rangle = \sum_{\tilde{\ell}} &\langle \ell_1 \ell_2 (\ell^i_{12}) \ell_3 \ell | \ell_1, \ell_2 \ell_3 (\tilde{\ell}) \ell \rangle \\
&\langle \alpha_i \tilde{\ell} L_i | \alpha_j L_j \rangle
\end{aligned}
\qquad (4.27)
$$

(ii) Check whether the new order of coupling of these three vectors is the same as the order in which they are coupled on the other side of the coefficient. If this order is

the same then we may use the orthonormality properties of the spin or angular momentum eigenfunctions to reduce the summation over intermediate couplings to a single term where $\tilde{\ell}$ takes on the value that this intermediate coupling has in the half of the coefficient not currently being re-coupled, i.e.,

$$\langle \alpha_i L_i | \alpha_j L_j \rangle = \langle \ell_1 \ell_2 (\ell_{12}^{i}) \ell_3 \ell | \ell_1 \ell_2 \ell_3 (\ell_{23}^{j}) \ell \rangle \langle \alpha_i \ell_{23}^{j} L_i | \alpha_j L_j \rangle \qquad (4.28)$$

If the three vectors $\ell_1 \ell_2 \ell_3$ are coupled according to some other scheme in $|\alpha_j L_j\rangle$ then we must retain the summation over ℓ.

(iii) Recouple other sets of 3 (or 4) vectors in the manner described above until the order of coupling of the vectors in the l.h.s. of the coefficient is the same as that of the r.h.s. In the final recoupling the second of the coefficients on the r.h.s. of equation (4.27) will be zero for $\tilde{\ell} \neq \ell^{j}$ and will be unity for $\tilde{\ell} = \ell_j$. We will then have expressed the original recoupling coefficient in terms of a summation over products of three (or four) vector recouplings similar to the first coefficient on the r.h.s. of equation (4.28).

This procedure is similar to that used by Innes and Ufford (1958) to obtain expressions, in terms of Racah and 9-j coefficients, for recoupling coefficients analogous to the two "two vector" recoupling coefficients, with $\sigma_i = \sigma_j = b$, which are discussed below. The problem which now remains, is to find the optimum sequence of recouplings

which bring both sides of the recoupling coefficient into some common order of coupling, that is, the sequence which involves the least number of three or four vector recouplings and the least number of summations over intermediate couplings.

"One vector" recoupling coefficients may always be expressed as a simple product of Racah coefficients by this procedure. In the evaluation of a recoupling coefficient in which more than one vector is recoupled we can always obtain an expression analogous to (4.25). However we may need to make additional intermediate recouplings which do not not appear in the r.h.s. of the coefficient and hence the summation over these intermediate recouplings will remain in our final expression for the complete recoupling coefficient.

The "two vector" recoupling coefficients can be divided into three basic types. If the two vectors to be recoupled are labelled N and N + 1 we define subshell ρ to be the subshell containing electron N and σ to be the subshell containing N + 1. For the purpose of recoupling we may regard the continuum electron as being in a subshell b + 1 where b is the outermost of the discrete orbitals and where

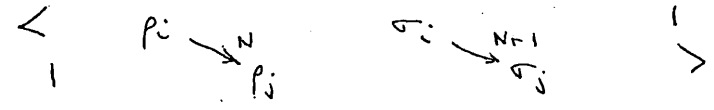
$\bar{L}_{b+1} = \bar{S}_{b+1} = 0$, $L_{b+1} = \ell_i$, $S_{b+1} = \frac{1}{2}$. For example the exchange spin recoupling coefficient is of the form

$$\langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2_N}(S_{\rho_i}) \cdot \bar{S}_{\sigma_i} \tfrac{1}{2_{N+1}}(S_{\sigma_i}) \cdots S_i \,|\, \bar{S}_1 \cdots \bar{S}_{\sigma_j} \tfrac{1}{2_{N+1}}(S_{\sigma_j}) \cdot \bar{S}_{\rho_j} \tfrac{1}{2_N}(S_{\rho_j}) \cdot S_j \rangle$$

(4.27)

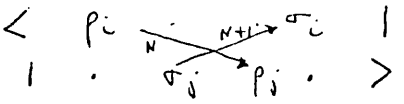
where $\rho_i < \sigma_i$ but $\rho_j > \sigma_j$ (in S.M. equation (41) $\sigma_i = \rho_j$ = continuum) The three types of recoupling coefficients may now be classified according to the relative values of $\rho_i \sigma_i \rho_j \sigma_j$ and are

1) direct: $\max(\rho_i \rho_j) \leq \min(\sigma_i \sigma_j)$. The spin recoupling coefficient of the direct term is a special case of this type. This type of recoupling may occur in S.M. (equations (59) and (62a) depending on the particular configurations considered. Conversely we may also have $\max(\sigma_i \sigma_j) \leq \min(\rho_i \rho_j)$ which may occur in equation (62a). The direct type of recoupling may be represented schematically by



We must recouple N from ρ_i to ρ_j and N+1 from σ_i to σ_j but since these two intervals do not overlap the recoupling may be achieved in two separate steps and the complete recoupling coefficient may be expressed as the product of two "one vector" recoupling coefficients of the form of equation (4.26).

2) exchange: $\min(\rho_i\rho_j) \leq \min(\sigma_i\sigma_j) < \max(\rho_i\rho_j)$ as in equation (4.27) and S.M. equation (41), or conversely, $\min(\sigma_i\sigma_j) \leq \min(\rho_i\rho_j) < \max(\sigma_i\sigma_j)$. Both these cases may occur in equations (59) and (62a). The former case may be represented by



We will have to recouple both N and N+1 through the range σ_j to ρ_j and hence we will have to sum over the intermediate couplings in this range. As an example, the recoupling coefficient (4.27) is

$$\langle S_i | S_j \rangle^E = \langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2_N}(S_{\rho_i}) \cdots \bar{S}_{\sigma_i} \tfrac{1}{2_{N+1}}(S_{\sigma_i}) \cdots S \,|\, \bar{S}_1 \cdots \bar{S}_{\sigma_j} \tfrac{1}{2_{N+1}}(S_{\sigma_j}) \cdots \bar{S}_{\rho_j} \tfrac{1}{2_N}(S_{\rho_j}) \cdots S \rangle$$

and if $\rho_i < \sigma_j < \sigma_i < \rho_j$ we have

$$\begin{aligned}
&\langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2_N}(S_{\rho_i}) \cdots \bar{S}_{\sigma_i} \tfrac{1}{2_{N+1}}(S_{\sigma_i}) \cdots S \,| \\
&= \sum_{\substack{\tilde{S}_{\rho_i} \cdots \tilde{S}_{\rho_j} \\ \sigma_{i-1}}} \langle S^{\alpha_i}_{\rho_i - 1} \bar{S}_{\rho_i} \tfrac{1}{2_N}(S_{\rho_i}) S^{\alpha_i}_{\rho_i} \,|\, S^{\alpha_i}_{\rho_i - 1} \bar{S}_{\rho_i}(\tilde{S}_{\rho_i}) \tfrac{1}{2_N} S^{\alpha_i}_{\rho_i} \rangle \\
&\quad \prod_{\lambda = \rho_i + 1} \langle \tilde{S}_{\lambda-1} \tfrac{1}{2_N}(S^{\alpha_i}_{\lambda-1}) \bar{S}_\lambda S^{\alpha_i}_\lambda \,|\, \tilde{S}_{\lambda-1} \bar{S}_\lambda(\tilde{S}_\lambda) \tfrac{1}{2_N} S^{\alpha_i}_\lambda \rangle \\
&\qquad \langle \tilde{S}_{\sigma_i - 1} \tfrac{1}{2_N}(S^{\alpha_i}_{\sigma_i - 1}) S_{\sigma_i} S^{\alpha_i}_{\sigma_i} \,|\, \tilde{S}_{\sigma_i - 1} S_{\sigma_i}(\tilde{S}_{\sigma_i}) \tfrac{1}{2_N} S^{\alpha_i}_{\sigma_i} \rangle \\
&\qquad \prod_{\lambda = \sigma_i + 1}^{\rho_j - 1} \langle \tilde{S}_{\lambda-1} \tfrac{1}{2_N}(S^{\alpha_i}_{\lambda-1}) \bar{S}_\lambda S^{\alpha_i}_\lambda \,|\, \tilde{S}_{\lambda-1} \bar{S}_\lambda(\tilde{S}_\lambda) \tfrac{1}{2_N} S^{\alpha_i}_\lambda \rangle \\
&\qquad\quad \langle \tilde{S}_{\rho_j - 1} \tfrac{1}{2_N}(S^{\alpha_i}_{\rho_j - 1}) \bar{S}_{\rho_j} S^{\alpha_i}_{\rho_j} \,|\, \tilde{S}_{\rho_j - 1} \bar{S}_{\rho_j} \tfrac{1}{2_N}(\tilde{S}_{\rho_j}) S^{\alpha_i}_{\rho_j} \rangle \\
&\qquad\quad \langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \cdots \bar{S}_{\sigma_i} \tfrac{1}{2_{N+1}}(S_{\sigma_i}) \cdots \bar{S}_{\rho_j} \tfrac{1}{2_N}(\tilde{S}_{\rho_j}) \cdots S \,|
\end{aligned}$$

hence

$$\langle S_i | S_j \rangle^{\Xi} = \langle S^{\alpha_i}_{\rho_{i-1}} \bar{S}_{\rho_i} \tfrac{1}{2N}(S_{\rho_i}) S^{\alpha_i}_{\rho_i} | S^{\alpha_i}_{\rho_{i-1}} \bar{S}_{\rho_i}(S^{\alpha_j}_{\rho_i}) \tfrac{1}{2N} S^{\alpha_i}_{\rho_i} \rangle$$

$$\prod_{\lambda=\rho_i+1}^{\sigma_j+1} \langle S^{\alpha_j}_{\lambda-1} \tfrac{1}{2N}(S^{\alpha_i}_{\lambda-1}) \bar{S}_\lambda S^{\alpha_i}_\lambda | S^{\alpha_j}_{\lambda-1} \bar{S}_\lambda (S^{\alpha_j}_\lambda) \tfrac{1}{2N} S^{\alpha_i}_\lambda \rangle$$

$$\sum_{\tilde{S}_{\sigma_j}} \tilde{S}_{\sigma_{i-1}} \langle S^{\alpha_j}_{\sigma_j-1} \tfrac{1}{2N}(S^{\alpha_i}_{\sigma_j-1}) \bar{S}_{\sigma_j} S^{\alpha_i}_{\sigma_j} | S^{\alpha_j}_{\sigma_j-1} \bar{S}_{\sigma_j}(\tilde{S}_{\sigma_j}) \tfrac{1}{2N} S^{\alpha_i}_{\sigma_j} \rangle$$

$$\prod_{\lambda=\sigma_j+1}^{\sigma_i-1} \langle \tilde{S}_{\lambda-1} \tfrac{1}{2N}(S^{\alpha_i}_{\lambda-1}) \bar{S}_\lambda S^{\alpha_i}_\lambda | \tilde{S}_{\lambda-1} \bar{S}_\lambda (\tilde{S}_\lambda) \tfrac{1}{2N} S^{\alpha_i}_\lambda \rangle$$

$$\langle \tilde{S}_{\sigma_i-1} \tfrac{1}{2N}(S^{\alpha_i}_{\sigma_i-1}) S_{\sigma_i} S^{\alpha_i}_{\sigma_i} | \tilde{S}_{\sigma_i-1} S_{\sigma_i}(S^{\alpha_j}_{\sigma_i}) \tfrac{1}{2N} S^{\alpha_i}_{\sigma_i} \rangle$$

$$\prod_{\lambda=\sigma_i+1}^{\rho_j-1} \langle S^{\alpha_j}_{\lambda-1} \tfrac{1}{2N}(S^{\alpha_i}_{\lambda-1}) \bar{S}_\lambda S^{\alpha_i}_\lambda | S^{\alpha_j}_{\lambda-1} \bar{S}_\lambda (S^{\alpha_j}_\lambda) \tfrac{1}{2N} S^{\alpha_i}_\lambda \rangle$$

$$\langle S^{\alpha_j}_{\rho_j-1} \tfrac{1}{2N}(S^{\alpha_i}_{\rho_j-1}) \bar{S}_{\rho_j} S^{\alpha_i}_{\rho_j} | S^{\alpha_j}_{\rho_j-1} \bar{S}_{\rho_j} \tfrac{1}{2N}(S_{\rho_j}) S^{\alpha_i}_{\rho_j} \rangle$$

$$\langle \bar{S}_1 \cdots \bar{S}_{\rho_i}(S^{\alpha_j}_{\rho_i}) \cdots \bar{S}_{\sigma_j}(\tilde{S}_{\sigma_j}) \cdots \bar{S}_{\sigma_i} \tfrac{1}{2_{N+1}}(S_{\sigma_i}) \cdots \bar{S}_{\rho_j} \tfrac{1}{2N}(S_{\rho_j}) \cdots S |$$

$$| \bar{S}_1 \cdots \bar{S}_{\rho_i}(S^{\alpha_j}_{\rho_i}) \cdots \bar{S}_{\sigma_j} \tfrac{1}{2_{N+1}}(S_{\sigma_j}) \cdots \bar{S}_{\sigma_i}(S^{\alpha_j}_{\sigma_i}) \cdots \bar{S}_{\rho_j} \tfrac{1}{2N}(S_{\rho_j}) \cdots S \rangle$$

In order to complete the recoupling we must recouple $\frac{1}{2}_{N+1}$ from σ_j to σ_i. To do this we expand

$$
\begin{aligned}
&|\overline{S}_1 \cdots \overline{S}_{\rho_i} \cdots \overline{S}_{\sigma_j} \tfrac{1}{2N+1}(S_{\sigma_j}) \cdots \overline{S}_{\sigma_i} \cdots \overline{S}_{\rho_j} \tfrac{1}{2N}(S_{\rho_j}) \cdots S\rangle \\
&= \sum_{\hat{S}_{\sigma_j} \cdots \hat{S}_{\sigma_i}} \langle S^{\alpha_j}_{\sigma_{j-1}} \overline{S}_{\sigma_j} \tfrac{1}{2N+1}(S_{\sigma_j}) S^{\alpha_j}_{\sigma_j} \mid S^{\alpha_j}_{\sigma_{j-1}} \overline{S}_{\sigma_j}(\hat{S}_{\sigma_j}) \tfrac{1}{2N+1} S^{\alpha_j}_{\sigma_j}\rangle \\
&\quad \prod_{\lambda=\sigma_j+1}^{\sigma_i-1} \langle \hat{S}_{\lambda-1} \tfrac{1}{2N+1}(S^{\alpha_j}_{\lambda-1}) \overline{S}_\lambda S^{\alpha_j}_\lambda \mid \hat{S}_{\lambda-1} \overline{S}_\lambda(\hat{S}_\lambda) \tfrac{1}{2N+1} S^{\alpha_j}_\lambda\rangle \\
&\quad \langle \hat{S}_{\sigma_i-1} \tfrac{1}{2N+1}(S^{\alpha_j}_{\sigma_i-1}) \overline{S}_{\sigma_i} S^{\alpha_j}_{\sigma_i} \mid \hat{S}_{\sigma_i-1} \overline{S}_{\sigma_i} \tfrac{1}{2N+1}(\hat{S}_{\sigma_i}) S^{\alpha_j}_{\sigma_i}\rangle \\
&\quad |\overline{S}_1 \cdots \overline{S}_{\rho_i} \cdots \overline{S}_{\sigma_j}(\hat{S}_{\sigma_j}) \cdots \overline{S}_{\sigma_i} \tfrac{1}{2N+1}(\hat{S}_{\sigma_i}) \cdots S_{\rho_j} \cdots S\rangle
\end{aligned}
$$

which gives finally

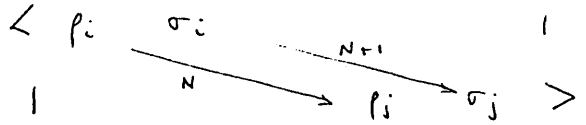
$$
\begin{aligned}
\langle S_i | S_j \rangle^E &= \langle S^{\alpha_i}_{\rho_i-1} \overline{S}_{\rho_i} \tfrac{1}{2N}(S_{\rho_i}) S^{\alpha_i}_{\rho_i} \mid S^{\alpha_i}_{\rho_i-1} \overline{S}_{\rho_i}(S^{\alpha_j}_{\rho_i}) \tfrac{1}{2N} S^{\alpha_i}_{\rho_i}\rangle \\
&\prod_{\lambda=\rho_i+1}^{\sigma_j-1} \langle S^{\alpha_j}_{\lambda-1} \tfrac{1}{2N}(S^{\alpha_i}_{\lambda-1}) \overline{S}_\lambda S^{\alpha_i}_\lambda \mid S^{\alpha_j}_{\lambda-1} \overline{S}_\lambda(S^{\alpha_j}_\lambda) \tfrac{1}{2N+1} S^{\alpha_i}_\lambda\rangle \\
&\sum_{\tilde{S}_{\sigma_j} \cdots \tilde{S}_{\sigma_i-1}} \langle S^{\alpha_j}_{\sigma_j-1} \tfrac{1}{2N}(S^{\alpha_i}_{\sigma_j-1}) \overline{S}_{\sigma_j} S^{\alpha_i}_{\sigma_j} \mid S^{\alpha_j}_{\sigma_j-1} \overline{S}_{\sigma_j}(\tilde{S}_{\sigma_j}) \tfrac{1}{2N} S^{\alpha_i}_{\sigma_j}\rangle \\
&\quad \langle S^{\alpha_j}_{\sigma_j-1} \overline{S}_{\sigma_j} \tfrac{1}{2N+1}(S_{\sigma_j}) S^{\alpha_j}_{\sigma_j} \mid S^{\alpha_j}_{\sigma_j-1} \overline{S}_{\sigma_j}(\tilde{S}_{\sigma_j}) \tfrac{1}{2N+1} S^{\alpha_j}_{\sigma_j}\rangle \\
&\prod_{\lambda=\sigma_j+1}^{\sigma_i-1} \langle \tilde{S}_{\lambda-1} \tfrac{1}{2N}(S^{\alpha_i}_{\lambda-1}) \overline{S}_\lambda S^{\alpha_i}_\lambda \mid \tilde{S}_{\lambda-1} \overline{S}_\lambda(\tilde{S}_\lambda) \tfrac{1}{2N} S^{\alpha_i}_\lambda\rangle \\
&\quad \langle \tilde{S}_{\lambda-1} \tfrac{1}{2N+1}(S^{\alpha_j}_{\lambda-1}) \overline{S}_\lambda S^{\alpha_j}_\lambda \mid \tilde{S}_{\lambda-1} \overline{S}_\lambda(\tilde{S}_\lambda) \tfrac{1}{2N+1} S^{\alpha_j}_\lambda\rangle \\
&\quad \langle \tilde{S}_{\sigma_i-1} \tfrac{1}{2N}(S^{\alpha_i}_{\sigma_i-1}) S_{\sigma_i} S^{\alpha_i}_{\sigma_i} \mid \tilde{S}_{\sigma_i-1} S_{\sigma_i}(S^{\alpha_j}_{\sigma_i}) \tfrac{1}{2N} S^{\alpha_i}_{\sigma_i}\rangle \\
&\quad \langle \tilde{S}_{\sigma_i-1} \tfrac{1}{2N+1}(S^{\alpha_j}_{\sigma_i-1}) \overline{S}_{\sigma_i} S^{\alpha_j}_{\sigma_i} \mid \tilde{S}_{\sigma_i-1} \overline{S}_{\sigma_i} \tfrac{1}{2N+1}(S_{\sigma_i}) S^{\alpha_j}_{\sigma_i}\rangle \\
&\prod_{\lambda=\sigma_i+1}^{\rho_j-1} \langle S^{\alpha_j}_{\lambda-1} \tfrac{1}{2N}(S^{\alpha_i}_{\lambda-1}) \overline{S}_\lambda S^{\alpha_i}_\lambda \mid S^{\alpha_j}_{\lambda-1} \overline{S}_\lambda(S^{\alpha_j}_\lambda) \tfrac{1}{2N} S^{\alpha_i}_\lambda\rangle \\
&\quad \langle S^{\alpha_j}_{\rho_j-1} \tfrac{1}{2N}(S^{\alpha_i}_{\rho_j-1}) \overline{S}_{\rho_j} S^{\alpha_i}_{\rho_j} \mid S^{\alpha_j}_{\rho_j-1} \overline{S}_{\rho_j} \tfrac{1}{2N}(S_{\rho_j}) S^{\alpha_i}_{\rho_j}\rangle
\end{aligned}
$$

which can now be expressed directly in terms of Racah coefficients.

3) translation: $\max(\rho_i\sigma_i) \leq \min(\rho_j\sigma_j)$ or $\max(\rho_j\sigma_j) \leq \min(\rho_i\sigma_i)$. This type of recoupling will only occur in terms linear or quadratic in C., i.e., in equations (59) and (62a) where both interacting electrons may appear in discrete orbitals. For

example the recoupling coefficient in equation (59) for the configurations $1s^2 2s^2 2p^4 3s\, k\ell$ and $1s^2 2s^2 2p^6$ where $\rho_i = 3s$, $\sigma_i = k\ell$ (continuum) and $\rho_j = \sigma_j = 2p$ will be of this form.

Translation recoupling coefficients may be represented by



We must recouple both N and N+1 from σ_i to ρ_j in the former case and from σ_i to σ_j in the latter. This is most easily achieved by coupling the vectors N, N+1 together, recoupling their resultant from σ_i to ρ_j (or σ_i to σ_j) then decoupling them. This gives rise to a single summation, over the possible values of the resultant (N, N+1).

For example the recoupling coefficient

$$\langle \bar{S}_1 \cdots \bar{S}_{\rho_i} \tfrac{1}{2_N}(S_{\rho_i}) \cdots \bar{S}_{\sigma_i} \tfrac{1}{2_{N+1}}(S_{\sigma_i}) \cdots \bar{S}_{\rho_j} \cdots \bar{S}_{\sigma_j} \cdots S \,|$$
$$|\, \bar{S}_1 \cdots \bar{S}_{\rho_i} \cdots \bar{S}_{\sigma_i} \cdots \bar{S}_{\rho_j} \tfrac{1}{2_N}(S_{\rho_j}) \cdots \bar{S}_{\sigma_j} \tfrac{1}{2_{N+1}}(S_{\sigma_j}) \cdots S \rangle$$

$$= \langle S^{\alpha_i}_{\rho_i - 1} \bar{S}_{\rho_i} \tfrac{1}{2_N}(S_{\rho_i}) S^{\alpha_i}_{\rho_i} \,|\, S^{\alpha_i}_{\rho_i - 1} \bar{S}_{\rho_i}(S^{\alpha_j}_{\rho_i}) \tfrac{1}{2_N} S^{\alpha_i}_{\rho_i} \rangle$$
$$\prod_{\lambda = \rho_i + 1}^{\sigma_i - 1} \langle S^{\alpha_j}_{\lambda - 1} \tfrac{1}{2}(S^{\alpha_i}_{\lambda - 1}) \bar{S}_\lambda S^{\alpha_i}_{\lambda} \,|\, S^{\alpha_j}_{\lambda - 1} \bar{S}_\lambda (S^{\alpha_j}_{\lambda}) \tfrac{1}{2} S^{\alpha_i}_{\lambda} \rangle$$
$$\sum_{\widetilde{S}} \langle S^{\alpha_j}_{\sigma_i - 1} \tfrac{1}{2_N}(S^{\alpha_i}_{\sigma_i - 1}) \bar{S}_{\sigma_i} \tfrac{1}{2_{N+1}}(S_{\sigma_i}) S^{\alpha_i}_{\sigma_i} \,|\, S^{\alpha_j}_{\sigma_i - 1} \bar{S}_{\sigma_i}(S^{\alpha_j}_{\sigma_i}) \tfrac{1}{2_N} \tfrac{1}{2_{N+1}}(\widetilde{S}) S^{\alpha_i}_{\sigma_i} \rangle$$
$$\prod_{\lambda = \sigma_i + 1}^{\rho_j - 1} \langle S^{\alpha_j}_{\lambda - 1} \bar{S}(S^{\alpha_i}_{\lambda - 1}) \bar{S}_\lambda S^{\alpha_i}_{\lambda} \,|\, S^{\alpha_j}_{\lambda - 1} \bar{S}_\lambda (S^{\alpha_j}_{\lambda}) \widetilde{S} S^{\alpha_i}_{\lambda} \rangle$$
$$\langle S^{\alpha_j}_{\rho_j - 1} \tfrac{1}{2_N} \tfrac{1}{2_{N+1}}(\widetilde{S}) \bar{S}_{\rho_j} S^{\alpha_i}_{\rho_j} \,|\, S^{\alpha_j}_{\rho_j - 1} \bar{S}_{\rho_j} \tfrac{1}{2_N}(S_{\rho_j}) S^{\alpha_j}_{\rho_j} \tfrac{1}{2_{N+1}} S^{\alpha_i}_{\rho_j} \rangle$$
$$\prod_{\lambda = \rho_j + 1}^{\sigma_j - 1} \langle S^{\alpha_j}_{\lambda - 1} \tfrac{1}{2}(S^{\alpha_i}_{\lambda - 1}) \bar{S}_\lambda S^{\alpha_i}_{\lambda} \,|\, S^{\alpha_j}_{\lambda - 1} \bar{S}_\lambda (S^{\alpha_j}_{\lambda}) \tfrac{1}{2} S^{\alpha_i}_{\lambda} \rangle$$
$$\langle S^{\alpha_j}_{\sigma_j - 1} \tfrac{1}{2}(S^{\alpha_i}_{\sigma_j - 1}) \bar{S}_{\sigma_j} S^{\alpha_i}_{\sigma_j} \,|\, S^{\alpha_j}_{\sigma_j - 1} \bar{S}_{\sigma_j} \tfrac{1}{2}(S_{\sigma_j}) S^{\alpha_i}_{\sigma_j} \rangle$$

The 4-vector recoupling coefficients may be expressed directly in terms of 9-j symbols using the relations

$$\langle j_1\, j_2\, (j_{12})\, j_3\, j_4\, (j_{34})\, J \mid j_1\, j_3\, (j_{13})\, j_2\, j_4\, (j_{24})\, J \rangle$$

$$= [(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)]^{\frac{1}{2}} \times \begin{pmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & J \end{pmatrix}$$

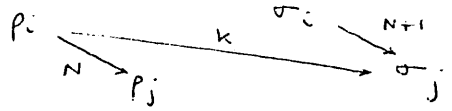
and

$$\langle j_1, j_2\, j_3\, (j_{23})\, j_{123}\, j_4\, J \mid j_1\, j_2\, j_4\, (j_{24})\, j_{124}\, j_3\, J \rangle$$

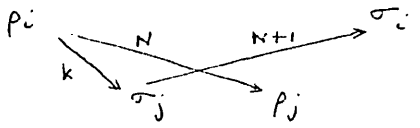
$$= [(2j_{23}+1)(2j_{123}+1)(2j_{24}+1)(2j_{124}+1)]^{\frac{1}{2}} \times \begin{pmatrix} j_1 & j_{23} & j_{123} \\ j_{24} & j_2 & j_4 \\ j_{124} & j_3 & J \end{pmatrix}$$

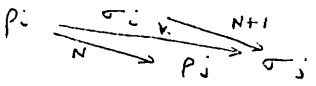
The "three vector" recoupling coefficients have a very similar structure to the two vector coefficients since the third vector k is coupled to ℓ^N on the l.h.s. of the coefficient and to ℓ^{N+1} on the r.h.s. Hence they can be divided into the same three classes as the two vector coefficients and may be represented by

(1) Direct



(2) Exchange



(3) Translation 

The 'one' and 'two' vector recoupling coefficients may therefore be regarded as special cases of the 'three vector' coefficients. However there is one useful property of the 'one' and 'two'vector coefficients which is not shared by the three vector coefficients that occur in the expressions for $\langle i|\frac{1}{r_{N,N+1}}|j\rangle$, namely that $\langle L_i|L_j\rangle = \langle L_j|L_i\rangle$

but $$\langle L_i|L_j\rangle_k \neq \langle L_j|L_i\rangle_k \qquad k \neq 0$$

The asymmetry of the $\langle L_i|L_j\rangle_k$ may be seen in the following way. We have shown that

$$\langle L_i|P_k(\hat{r}_N\cdot\hat{r}_{N+1})|L_j\rangle = (l_{\rho_i} k\,0\,0|l_{\rho_j}0)(l_{\sigma_j} k\,0\,0|l_{\sigma_i}0)\langle L_i|L_j\rangle_k$$

and similarly

$$\langle L_j|P_k(\hat{r}_N\cdot\hat{r}_{N+1})|L_i\rangle = (l_{\rho_j} k\,0\,0|l_{\rho_i}0)(l_{\sigma_i} k\,0\,0|l_{\sigma_j}0)\langle L_j|L_i\rangle_k$$

From the symmetry of the operator

$$\langle L_i|P_k(\hat{r}_N\cdot\hat{r}_{N+1})|L_j\rangle = \langle L_j|P_k(\hat{r}_N\cdot\hat{r}_{N+1})|L_i\rangle$$

hence

$$(\ell_{\rho_i} k\,00|\ell_{\rho_j} 0)(\ell_{\sigma_j} k\,00|\ell_{\sigma_i} 0)\langle L_i|L_j\rangle_k$$
$$= (\ell_{\rho_j} k\,00|\ell_{\rho_i} 0)(\ell_{\sigma_i} k\,00|\ell_{\sigma_j} 0)\langle L_j|L_i\rangle_k$$

and from the symmetry properties of the Clebsch-Gordan coefficients

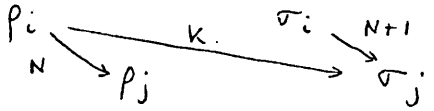
$$[(2\ell_{\rho_i}+1)(2\ell_{\sigma_j}+1)]^{-\frac{1}{2}}\langle L_i|L_j\rangle_k = [(2\ell_{\rho_j}+1)(2\ell_{\sigma_i}+1)]^{-\frac{1}{2}}\langle L_j|L_i\rangle_k$$

This asymmetry implies that, in general, we must couple k to N on the l.h.s. of the coefficient and couple k to N+1 on the r.h.s. However if we choose to evaluate the symmetric quantity $[(2\ell_{\rho_i}+1)(2\ell_{\sigma_j}+1)]^{-\frac{1}{2}}\langle L_i|L_j\rangle_k$ rather than $\langle L_i|L_j\rangle_k$ then we can choose to couple k to either N or N+1 on the l.h.s. (provided we couple it to the other on the r.h.s.).

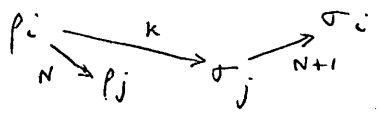
It is clear that any recoupling of vectors, initially coupled according to (4.20) is most easily carried out by successively recoupling the appropriate vectors from left to right. In the above diagrams, the vector ℓ^N is most easily recoupled from ρ_i to ρ_j rather than from ρ_j back to ρ_i, k is most easily recoupled from ρ_i to σ_j, in (1) and (3) ℓ^{N+1} is most easily coupled from σ_i to σ_j, whilst in (2) it is most easily coupled from σ_j to σ_i.

Consider the two cases

(a)



(b)



These are both of the direct type and are the inner product of eigenvectors

$$|\alpha_i L_i\rangle = |\bar{L}_1 \; L^{\alpha_i}_{\rho_{i-1}} \bar{L}_{\rho_i}[\ell^N_{\rho_j} k(\ell_{\rho_i})] L_{\rho_i} \cdots \bar{L}_{\sigma_i} \ell^{N+1}_{\sigma_i}(L_{\sigma_i}) \cdots L\rangle$$

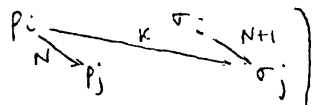
$$|\alpha_j L_j\rangle = |\bar{L}_1 \cdots \bar{L}_{\rho_j} \ell^N_{\rho_j}(L_{\rho_j}) \cdots \bar{L}_{\sigma_j}[k\ell^{N+1}_{\sigma_i}(\ell_{\sigma_j})] L_{\sigma_j} \cdots L\rangle$$

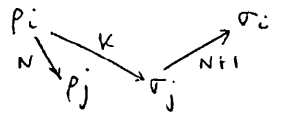
In order to obtain an expression for (a) in terms of Racah (and 9-j) coefficients we first recouple the vectors $L^{a_i}_{\rho_i-1}$, $L_{\rho_i}\ell_{\rho_i}(L_{\rho_i})$ of $\langle a_i L_i|$ to bring them into the same order of coupling as those in $|a_j L_j\rangle$. This step contributes the coefficient $\langle L^{\alpha_i}_{\rho_{i-1}} \bar{L}_{\rho_i} \ell_{\rho_i}(L_{\rho_i}) L^{\alpha_i}_{\rho_i} | L^{\alpha_i}_{\rho_{i-1}} \bar{L}_{\rho_i}(L^{\alpha_j}_{\rho_i}) \ell_{\rho_i} L^{\alpha_i}_{\rho_i}\rangle$ We then recouple ℓ_{ρ_i} step by step from ρ_i to ρ_j. At ρ_j we uncouple $\ell^N_{\rho_j} k(\ell_{\rho_i})$ and couple $\ell^N_{\rho_j}$ to L_{ρ_j} to give L_{ρ_j}. We then proceed to recouple k step by step to σ_i where we couple it to $\ell^{N+1}_{\sigma_i}$ to give ℓ_{σ_j}, and recouple ℓ_{σ_j} from σ_i to σ_j. We will then have brought all the vectors of $\langle a_i L_i|$ into the same order of coupling as in $|a_j L_j\rangle$. In order to express (b) as a product of Racah (and 9-j)coefficients we may proceed in the same manner until we reach the third of the interacting subshells which in this case is σ_j. The vectors adjacent to σ_j in $\langle a_i L_i|$ are now recoupled to $L^{a_j}_{\sigma_j-1} k(L^{a_i}_{\sigma_j-1}) L_{\sigma_j}(L^{a_i}_{\sigma_j}) \ldots$ whereas in $|a_j L_j\rangle$ we have the vectors

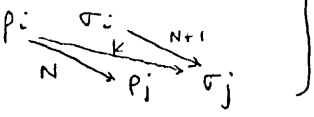
$$\ldots L^{a_j}_{\sigma_j-1}, L_{\sigma_j} k\ell^N_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j}(L^{a_j}_{\sigma_j}) \ldots$$

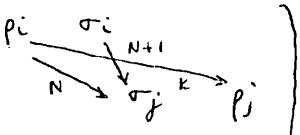
We do not want to recouple ℓ_{σ_i} backwards from σ_i to σ_j and therefore in order to bring the two eigenvectors into the same form we must start to recouple $|a_j L_j\rangle$. Unlike the exchange case there is no need to recouple both $\langle a_i L_i|$ and $|a_j L_j\rangle$. We need only uncouple k and $\ell^N_{\sigma_i}$ then recouple $\ell^N_{\sigma_i}$ from σ_j to σ_i in order to complete the recoupling.

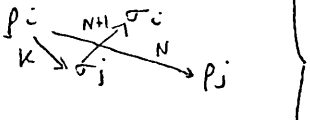
Similarly we will have two types of translation coefficient and two types of exchange coefficient. These six types of recoupling coefficients may be described as follows

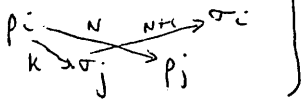
(1) 

(2) 

(3) 

(4) 

(5) 

(6) 

$\left.\begin{array}{l} \\ \\ \\ \\ \\ \\ \end{array}\right\}$ sign $(\rho_i - \sigma_i)$ = sign $(\rho_j - \sigma_j)$

$\left\{\begin{array}{l} \text{subscript of largest} \\ \quad \neq \text{subscript of smallest} \end{array}\right.$

$\left\{\begin{array}{l} \text{subscript of largest} \\ \quad = \text{subscript of smallest} \end{array}\right.$

$\left\{\begin{array}{l} \max(\rho_i\sigma_i) \\ \quad < \min(\rho_j\sigma_j) \end{array}\right.$

$\left\{\begin{array}{l} \text{or } \max(\rho_j\sigma_j) \\ \quad < \min(\rho_i\sigma_i) \end{array}\right.$

$\left.\begin{array}{l} \\ \\ \\ \\ \\ \\ \end{array}\right\}$ sign $(\rho_i - \sigma_i)$ $\neq$ sign $(\rho_j - \sigma_j)$

$\left\{\begin{array}{l} \text{subscript of largest} \\ \quad \neq \text{subscript of smallest} \end{array}\right.$

$\left\{\begin{array}{l} \text{subscript of largest} \\ \quad = \text{subscript of smallest} \end{array}\right.$

The one and two vector recoupling coefficients also fall into these six classifications. We may obtain an expression for a 'two vector' coefficient in terms of Racah coefficients merely by setting $k = 0$ in the expression for the corresponding 3 vector coefficient. We may also obtain an expression for a 'one vector' coefficient by setting $k = 0$ and $\rho_i = \rho_j$.

Explicit expressions for the six basic types of coefficients together with the degenerate cases where some or all of the $\rho_i\rho_j\sigma_i\sigma_j$ are equal, are given below. These expressions are

written in terms of elementary recoupling coefficients which may be expressed directly in terms of either Racah or 9-j coefficients by the use of the following relations

$$\langle j_1 j_2 (j_{12}) j_3 J \mid j_1 j_2 j_3 (j_{23}) J \rangle = [(2j_{12}+1)(2j_{23}+1)]^{\frac{1}{2}} W(j_1 j_2 J j_3, j_{12} j_{23})$$

$$\langle j_1 j_2 (j_{12}) j_3 J \mid j_1 j_3 (j_{13}) j_2 J \rangle = [(2j_{12}+1)(2j_{13}+1)]^{\frac{1}{2}} W(j_{12} j_2 j_3 j_{13}, j_1 J)$$

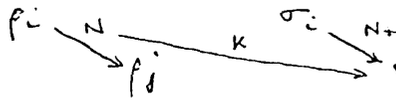
$$\langle j_1 j_2 (j_{12}) j_3 j_4 (j_{34}) J \mid j_1 j_3 (j_{13}) j_2 j_4 (j_{24}) J \rangle = [(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)]^{\frac{1}{2}} \begin{pmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & J \end{pmatrix}$$

$$\langle j_1 j_2 j_3 (j_{23}) j_{123} j_4 J \mid j_1 j_2 j_4 (j_{24}) j_{124} j_3 J \rangle = [(2j_{23}+1)(2j_{123}+1)(2j_{24}+1)(2j_{124}+1)]^{\frac{1}{2}} \begin{pmatrix} j_1 & j_{23} & j_{123} \\ j_{24} & j_2 & j_4 \\ j_{124} & j_3 & J \end{pmatrix}$$

Interchanging the order of coupling of any pair of vectors

$$|j_1 j_2, j m\rangle = (-1)^{j_1+j_2-j} |j_2 j_1, j m\rangle$$

Type (1) Direct



$$\rho_i < \rho_j < \sigma_i < \sigma_j$$

$$\langle \overline{L}_1 \cdots \overline{L}_{\rho_i} \ell_{\rho_j} k(\ell_{\rho_i}) L_{\rho_i} \cdots \overline{L} \cdots \overline{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) \cdots \overline{L}_{\sigma_j} \cdots L \mid$$
$$\mid \overline{L}_1 \cdots \overline{L}_{\rho_i} \cdots \overline{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) \cdots \overline{L}_{\sigma_i} \cdots \overline{L}_{\sigma_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j} \cdots L \rangle$$

$$= \langle L^{\alpha_i}_{\rho_i - 1} \overline{L}_{\rho_i} \ell_{\rho_i}(L_{\rho_i}) L^{\alpha_i}_{\rho_i} \mid L^{\alpha_i}_{\rho_i - 1} \overline{L}_{\rho_i}(L^{\alpha_j}_{\rho_i}) \ell_{\rho_i} L^{\alpha_i}_{\rho_i} \rangle$$

$$\prod_{\lambda = \rho_i + 1}^{\rho_j - 1} \langle L^{\alpha_j}_{\lambda - 1} \ell_{\rho_i}(L^{\alpha_i}_{\lambda - 1}) \overline{L}_\lambda L^{\alpha_i}_\lambda \mid L^{\alpha_j}_{\lambda - 1} \overline{L}_\lambda(L^{\alpha_j}_\lambda) \ell_{\rho_i} L^{\alpha_i}_\lambda \rangle$$

$$\langle L^{\alpha_j}_{\rho_j - 1} \ell_{\rho_j} k(\ell_{\rho_i}) L^{\alpha_i}_{\rho_j - 1}, \overline{L}_{\rho_j} L^{\alpha_i}_{\rho_j} \mid L^{\alpha_j}_{\rho_j - 1} \overline{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) L^{\alpha_j}_{\rho_j} k L^{\alpha_i}_{\rho_j} \rangle$$

$$\prod_{\lambda = \rho_j + 1}^{\sigma_i - 1} \langle L^{\alpha_j}_{\lambda - 1} k(L^{\alpha_i}_{\lambda - 1}) \overline{L}_\lambda L^{\alpha_i}_\lambda \mid L^{\alpha_j}_{\lambda - 1} \overline{L}_\lambda(L^{\alpha_j}_\lambda) k L^{\alpha_i}_\lambda \rangle$$

$$\langle L^{\alpha_j}_{\sigma_i - 1} k(L^{\alpha_i}_{\sigma_i - 1}) \overline{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) L^{\alpha_i}_{\sigma_i} \mid L^{\alpha_j}_{\sigma_i - 1} \overline{L}_{\sigma_i}(L^{\alpha_j}_{\sigma_i}) k \ell_{\sigma_i}(\ell_{\sigma_j}) L^{\alpha_i}_{\sigma_i} \rangle$$

$$\prod_{\lambda = \sigma_i + 1}^{\sigma_j - 1} \langle L^{\alpha_j}_{\lambda - 1} \ell_{\sigma_j}(L^{\alpha_i}_{\lambda - 1}) \overline{L}_\lambda L^{\alpha_i}_\lambda \mid L^{\alpha_j}_{\lambda - 1} \overline{L}_\lambda(L^{\alpha_j}_\lambda) \ell_{\sigma_j} L^{\alpha_i}_\lambda \rangle$$

$$\langle L^{\alpha_j}_{\sigma_j - 1} \ell_{\sigma_j}(L^{\alpha_i}_{\sigma_j - 1}) \overline{L}_{\sigma_j} L^{\alpha_i}_{\sigma_j} \mid L^{\alpha_j}_{\sigma_j - 1} \overline{L}_{\sigma_j} \ell_{\sigma_j}(L_{\sigma_j}) L^{\alpha_i}_{\sigma_j} \rangle$$

(4.30)

Special cases

$$\rho_i = \rho_j = \sigma_i = \sigma_j$$

coefficient reduces to

$$\langle \overline{\overline{L}}_\rho \ell_\rho k(\ell_\rho) \overline{L}^i_\rho \ell'_\rho L_\rho \mid \overline{\overline{L}}_\rho \ell_\rho(\overline{L}^j_\rho) k \ell'_\rho(\ell_\rho) L_\rho \rangle$$

$$\rho_i = \rho_j = \sigma_i < \sigma_j$$

$$< \bar{\bar{L}}_\rho \ell_\rho k(\ell_\rho) \bar{L}^i_\rho \ell'_\rho(L^i_\rho) \cdots \bar{L}_{\sigma_j} \cdots L \mid \bar{\bar{L}}_\rho \ell_\rho(L^j_\rho) \cdots \bar{L}_{\sigma_j} k \ell'_\rho(\ell_{\sigma_j}) L_{\sigma_j} \cdots L >$$

$$= < \bar{\bar{L}}_\rho \ell_\rho k(\ell_\rho) L^i_\rho \mid \bar{\bar{L}}_\rho \ell_\rho(L^j_\rho) k L^i_\rho >$$

$$< L^j_\rho k(L^i_\rho) \ell'_\rho L^i_\rho \mid L^j_\rho k \ell'_\rho(\ell_{\sigma_j}) L^i_\rho >$$

$$< L^{\alpha_i}_{\rho-1} L^j_\rho \ell_{\sigma_j}(L^i_\rho) L^{\alpha_i}_\rho \mid L^{\alpha_i}_{\rho-1} L^j_\rho (L^{\alpha_j}_\rho) \ell_{\sigma_j} L^{\alpha_i}_\rho >$$

$$\overset{\sigma_j - 1}{\underset{\lambda = \rho+1}{\|}} < L^{\alpha_j}_{\lambda-1} \ell_{\sigma_j}(L^{\alpha_i}_{\lambda-1}) \bar{L}_\lambda L^{\alpha_i}_\lambda \mid L^{\alpha_j}_{\lambda-1} \bar{L}_\lambda (L^{\alpha_j}_\lambda) \ell_{\sigma_j} L^{\alpha_i}_\lambda >$$

$$< L^{\alpha_j}_{\sigma_j - 1} \ell_{\sigma_j}(L^{\alpha_i}_{\sigma_j - 1}) \bar{L}_{\sigma_j} L^{\alpha_i}_{\sigma_j} \mid L^{\alpha_j}_{\sigma_j - 1} \bar{L}_{\sigma_j} \ell_{\sigma_j}(L_{\sigma_j}) L^{\alpha_i}_{\sigma_j} >$$

$$\rho_i < \rho_j = \sigma_i = \sigma_j$$

$$< \bar{L}_1 \cdots \bar{L}_{\rho_i} \ell_{\rho_j} k(\ell_{\rho_i}) L_{\rho_i} \cdots \bar{L}_{\sigma_i} \ell_{\sigma_i}(L^i_{\sigma_i}) \cdots L \mid$$

$$\mid \bar{L}_1 \cdots \bar{L}_{\rho_j} \cdots \bar{L}_{\sigma_i} \ell_{\rho_j}(\bar{L}^j_{\sigma_i}) k \ell_{\sigma_i}(\ell_{\sigma_i}) L^j_{\sigma_i} \cdots L >$$

$$= < L^{\alpha_i}_{\rho_i - 1} \bar{L}_{\rho_i} \ell_{\rho_i}(L_{\rho_i}) L^{\alpha_i}_{\rho_i} \mid L^{\alpha_i}_{\rho_i - 1} \bar{L}_{\rho_i}(L^{\alpha_i}_{\rho_i}) \ell_{\rho_i} L^{\alpha_i}_{\rho_i} >$$

$$\overset{\sigma_i - 1}{\underset{\lambda = \rho_i + 1}{\|}} < L^{\alpha_j}_{\lambda-1} \ell_{\rho_i}(L^{\alpha_i}_{\lambda-1}) \bar{L}_\lambda L^{\alpha_i}_\lambda \mid L^{\alpha_j}_{\lambda-1} \bar{L}_\lambda (L^{\alpha_j}_\lambda) \ell_{\rho_i} L^{\alpha_i}_\lambda >$$

$$< L^{\alpha_j}_{\sigma_i - 1} \ell_{\rho_i}(L^{\alpha_i}_{\sigma_i - 1}) L^i_{\sigma_i} L^{\alpha_i}_{\sigma_i - 1} \mid L^{\alpha_j}_{\sigma_i - 1} L^i_{\sigma_i} \ell_{\rho_i}(L^j_{\sigma_i}) L^{\alpha_i}_{\sigma_i - 1} >$$

$$\rho_i = \rho_j < \sigma_i < \sigma_j$$

replace the first three lines of equation (4.30) by

$$< \bar{L}_\rho \ell_\rho k(\ell_\rho) L^i_\rho \mid \bar{L}_\rho \ell_\rho(L^j_\rho) k L^i_\rho >$$

$$< L^{\alpha_i}_{\rho-1} L^j_\rho k(L^i_\rho) L^{\alpha_i}_\rho \mid L^{\alpha_i}_{\rho-1} L^j_\rho (L^{\alpha_j}_\rho) k L^{\alpha_i}_\rho >$$

$$\rho_i < \rho_j < \sigma_i = \sigma_j$$

replace last three lines of (4.30) by

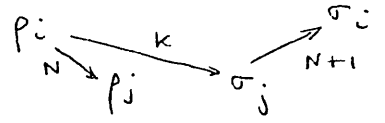
$$< L^{\alpha_j}_{\sigma_{-1}} k\,(L^{\alpha_i}_{\sigma_{-1}})\, L^{i}_{\sigma}\, L^{\alpha_i}_{\sigma} \,|\, L^{\alpha_j}_{\sigma_{-1}}\, L^{i}_{\sigma}\, k\,(L^{j}_{\sigma})\, L^{\alpha_i}_{\sigma} >$$
$$< \bar{L}_{\sigma}\, \ell_{\sigma_i}(L^{i}_{\sigma})\, k\, L^{j}_{\sigma} \,|\, \bar{L}_{\sigma}\, \ell_{\sigma}\, k\,(\ell_{\sigma})\, L^{j}_{\sigma} >$$

$$\rho_i < \rho_j = \sigma_i < \sigma_j$$

replace the third, fourth and fifth lines of (4.30) by

$$\sum_{\tilde{L}} < L^{\alpha_j}_{\rho_{j-1}}\, \ell_{\rho_i}(L^{\alpha_i}_{\rho_{j-1}})\, L_{\sigma_i}\, L^{\alpha_i}_{\rho_j} \,|\, L^{\alpha_j}_{\rho_{j-1}}\, L_{\sigma_i}\, \ell_{\rho_i}(\tilde{L})\, L^{\alpha_i}_{\rho_j} >$$
$$< \bar{L}_{\sigma_i}\, \ell_{\sigma_i}(L_{\sigma_i})\, \ell_{\rho_j}\, k\,(\ell_{\rho_i})\, \tilde{L} \,|\, \bar{L}_{\sigma_i}\, \ell_{\rho_j}(L_{\rho_j})\, \ell_{\sigma_i} k\,(\ell_{\sigma_j})\, \tilde{L} >$$
$$< L^{\alpha_j}_{\rho_{j-1}}\, L_{\rho_j}\, \ell_{\sigma_j}(\tilde{L})\, L^{\alpha_i}_{\rho_j} \,|\, L^{\alpha_j}_{\rho_{j-1}}\, L_{\rho_j}\,(L^{\alpha_j}_{\rho_j})\, \ell_{\sigma_j}\, L^{\alpha_i}_{\rho_j} >$$

Type (2) Direct



$\rho_i < \rho_j < \sigma_j < \sigma_i$

$$< \overline{L}_1 \cdots \overline{L}_{\rho_i} \ell_{\rho_j} k(\ell_{\rho_i}) L_{\rho_i} \cdots \overline{L}_{\rho_j} \cdots \overline{L}_{\sigma_j} \cdots \overline{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) \cdots L \,|$$
$$|\overline{L}_1 \cdots \overline{L}_{\rho_i} \cdots \overline{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) \cdots \overline{L}_{\sigma_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j} \cdots \overline{L}_{\sigma_i} \cdots L >$$

$$= < L^{\alpha_i}_{\rho_i - 1} \overline{L}_{\rho_i} \ell_{\rho_i}(L_{\rho_i}) L^{\alpha_i}_{\rho_i} \,|\, L^{\alpha_i}_{\rho_i - 1} \overline{L}_{\rho_i}(L^{\alpha_j}_{\rho_i}) \ell_{\rho_i} L^{\alpha_i}_{\rho_i} >$$

$$\prod_{\lambda = \rho_i + 1}^{\rho_j - 1} < L^{\alpha_j}_{\lambda - 1} \ell_{\rho_i}(L^{\alpha_i}_{\lambda - 1}) \overline{L}_\lambda L^{\alpha_i}_\lambda \,|\, L^{\alpha_j}_{\lambda - 1} \overline{L}_\lambda (L^{\alpha_j}_\lambda) \ell_{\rho_i} L^{\alpha_i}_\lambda >$$

$$< L^{\alpha_j}_{\rho_j - 1} \ell_{\rho_j} k(\ell_{\rho_i}) L^{\alpha_i}_{\rho_j - 1}, \overline{L}_{\rho_j} L^{\alpha_i}_{\rho_j} \,|\, L^{\alpha_j}_{\rho_j - 1} \overline{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) L^{\alpha_j}_{\rho_j} k L^{\alpha_i}_{\rho_j} >$$

$$\prod_{\lambda = \rho_j + 1}^{\sigma_i - 1} < L^{\alpha_j}_{\lambda - 1} k(L^{\alpha_i}_{\lambda - 1}) \overline{L}_\lambda L^{\alpha_i}_\lambda \,|\, L^{\alpha_j}_{\lambda - 1} \overline{L}_\lambda (L^{\alpha_j}_\lambda) k L^{\alpha_i}_\lambda >$$

$$< L^{\alpha_j}_{\sigma_j - 1} \overline{L}_{\sigma_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j} L^{\alpha_j}_{\sigma_j} \,|\, L^{\alpha_j}_{\sigma_j - 1} k(L^{\alpha_i}_{\sigma_j - 1}) \overline{L}_{\sigma_j}(L^{\alpha_i}_{\sigma_j}) \ell_{\sigma_i} L^{\alpha_j}_{\sigma_i} >$$

$$\prod_{\lambda = \sigma_j + 1}^{\sigma_i - 1} < L^{\alpha_i}_{\lambda - 1} \ell_{\sigma_i}(L^{\alpha_j}_{\lambda - 1}) \overline{L}_\lambda L^{\alpha_j}_\lambda \,|\, L^{\alpha_i}_{\lambda - 1} \overline{L}_\lambda (L^{\alpha_i}_\lambda) \ell_{\sigma_i} L^{\alpha_j}_\lambda >$$

$$< L^{\alpha_i}_{\sigma_i - 1} \ell_{\sigma_i}(L^{\alpha_j}_{\sigma_i - 1}) \overline{L}_{\sigma_i} L^{\alpha_j}_{\sigma_i} \,|\, L^{\alpha_i}_{\sigma_i - 1} \overline{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) L^{\alpha_j}_{\sigma_i} >$$

(4.31)

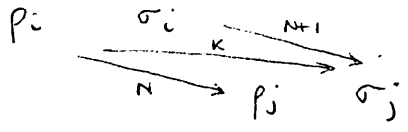
Special Case

$$\rho_i < \rho_j = \sigma_j < \sigma_i$$

replace the third, fourth and fifth lines in (4.31) by

$$\sum_{\widetilde{L}} < L^{\alpha_j}_{\rho_j - 1} \ell_{\rho_i}(L^{\alpha_i}_{\rho_j - 1}) \overline{L}_{\rho_j} L^{\alpha_i}_{\rho_j} \,|\, L^{\alpha_j}_{\rho_j - 1} \overline{L}_{\rho_j} \ell_{\rho_i}(\widetilde{L}) L^{\alpha_i}_{\rho_j} >$$
$$< \overline{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) k \ell_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j} \,|\, \overline{L}_{\rho_j} \ell_{\rho_j} k(\ell_{\rho_i}) \widetilde{L}, \ell_{\sigma_i} L_{\sigma_j} >$$
$$< L^{\alpha_j}_{\rho_j - 1} \widetilde{L} \ell_{\sigma_i}(L_{\sigma_j}) L^{\alpha_j}_{\rho_j} \,|\, L^{\alpha_j}_{\rho_j - 1} \widetilde{L}(L^{\alpha_i}_{\rho_j}) \ell_{\sigma_i} L^{\alpha_i}_{\rho_j} >$$

Type (3) Translation



$\rho_i < \sigma_i < \rho_j < \sigma_j$

$$< \bar{L}_1 \cdots \bar{L}_{\rho_i} \ell_{\rho_j} k(\ell_{\rho_i}) L_{\rho_i} \cdots \bar{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) \cdots \bar{L}_{\rho_j} \cdots \bar{L}_{\sigma_j} \cdots L \,|$$
$$|\bar{L}_1 \cdots \bar{L}_{\rho_i} \cdots \bar{L}_{\sigma_i} \cdots \bar{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) \cdots \bar{L}_{\sigma_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j} \cdots L >$$

$$= < L^{\alpha_i}_{\rho_i - 1} \bar{L}_{\rho_i} \ell_{\rho_i}(L_{\rho_i}) L^{\alpha_i}_{\rho_i} \,|\, L^{\alpha_i}_{\rho_i - 1} \bar{L}_{\rho_i}(L^{\alpha_j}_{\rho_i}) \ell_{\rho_i} L^{\alpha_i}_{\rho_i} >$$

$$\prod_{\lambda = \rho_i + 1}^{\sigma_i - 1} < L^{\alpha_j}_{\lambda - 1} \ell_{\rho_i}(L^{\alpha_i}_{\lambda - 1}) \bar{L}_\lambda L^{\alpha_i}_\lambda \,|\, L^{\alpha_j}_{\lambda - 1} \bar{L}_\lambda (L^{\alpha_j}_\lambda) \ell_{\rho_i} L^{\alpha_i}_\lambda >$$

$$\sum_{\tilde{\ell}} < L^{\alpha_j}_{\sigma_i - 1} \ell_{\rho_i}(L^{\alpha_i}_{\sigma_i - 1}) \bar{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) L^{\alpha_i}_{\sigma_i} \,|\, L^{\alpha_j}_{\sigma_i - 1} \bar{L}_{\sigma_i}(L^{\alpha_j}_{\sigma_i}) \ell_{\rho_i} \ell_{\sigma_i}(\tilde{\ell}) L^{\alpha_i}_{\sigma_i} >$$

$$\prod_{\lambda = \sigma_i + 1}^{\rho_j - 1} < L^{\alpha_j}_{\lambda - 1} \tilde{\ell}(L^{\alpha_i}_{\lambda - 1}) \bar{L}_\lambda L^{\alpha_i}_\lambda \,|\, L^{\alpha_j}_{\lambda - 1} \bar{L}_\lambda (L^{\alpha_j}_\lambda) \tilde{\ell} L^{\alpha_i}_\lambda >$$

$$< \ell_{\rho_j} k(\ell_{\rho_i}) \ell_{\sigma_i} \tilde{\ell} \,|\, \ell_{\rho_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) \tilde{\ell} >$$

$$< L^{\alpha_j}_{\rho_j - 1} \ell_{\rho_j} \ell_{\sigma_j}(\tilde{\ell}) L^{\alpha_i}_{\rho_j - 1} \cdot \bar{L}_{\rho_j} L^{\alpha_i}_{\rho_j} \,|\, L^{\alpha_j}_{\rho_j - 1} \bar{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) L^{\alpha_j}_{\rho_j} \ell_{\sigma_j} L^{\alpha_i}_{\rho_j} >$$

$$\prod_{\lambda = \rho_j + 1}^{\sigma_j - 1} < L^{\alpha_j}_{\lambda - 1} \ell_{\sigma_j}(L^{\alpha_i}_{\lambda - 1}) \bar{L}_\lambda L^{\alpha_i}_\lambda \,|\, L^{\alpha_j}_{\lambda - 1} \bar{L}_\lambda (L^{\alpha_j}_\lambda) \ell_{\sigma_j} L^{\alpha_i}_\lambda >$$

$$< L^{\alpha_j}_{\sigma_j - 1} \ell_{\sigma_j}(L^{\alpha_i}_{\sigma_j - 1}) \bar{L}_{\sigma_j} L^{\alpha_i}_{\sigma_j} \,|\, L^{\alpha_j}_{\sigma_j - 1} \bar{L}_{\sigma_j} \ell_{\sigma_j}(L_{\sigma_j}) L^{\alpha_i}_{\sigma_j} >$$

To obtain an expression for type (4), $\rho_i < \sigma_i < \sigma_j < \rho_j$ merely replace ρ_j by σ_j in the last three lines and in the upper limit of the second product.

Special Cases

$\rho_i = \sigma_i < \rho_j < \sigma_j$ and $\rho_i = \sigma_i < \sigma_j < \rho_j$

replace first three lines by

$$\sum_{\tilde{\ell}} \langle L^{\alpha_i}_{\rho_i - 1} \overline{L}_{\rho_i} \ell_{\rho_i}(\overline{L}_{\sigma_i}) \ell_{\sigma_i} L^{\alpha_i}_{\rho_i} \mid L^{\alpha_i}_{\rho_i - 1} \overline{L}_{\rho_i}(L^{\alpha_j}_{\rho_i}) \ell_{\rho_i} \ell_{\sigma_i}(\tilde{\ell}) L^{\alpha_i}_{\rho_i} \rangle$$

$\rho_i < \sigma_i < \rho_j = \sigma_j$

replace last three lines by

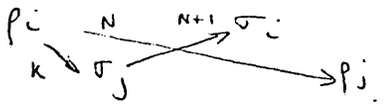
$$\langle L^{\alpha_j}_{\rho_j - 1} \ell_{\rho_j} \ell_{\sigma_j}(\tilde{\ell}) L^{\alpha_i}_{\rho_j - 1} \overline{L}_{\rho_j} L^{\alpha_i}_{\rho_j} \mid L^{\alpha_j}_{\rho_j - 1} \overline{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) \ell_{\sigma_j}(L_{\sigma_j}) L^{\alpha_i}_{0} \rangle$$

$\sigma_i < \rho_i < \rho_j = \sigma_j$

replace last three lines by the above coefficient and the fifth line by

$$\langle \ell_{\sigma_i} \ell_{\rho_j} k(\ell_{\rho_i}) \tilde{\ell} \mid \ell_{\rho_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) \tilde{\ell} \rangle$$
$$= (-1)^{\ell_{\rho_i} + \ell_{\sigma_i} - \tilde{\ell}} \langle \ell_{\rho_j} k(\ell_{\rho_i}) \ell_{\sigma_i} \tilde{\ell} \mid \ell_{\rho_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) \tilde{\ell} \rangle$$

Type (5) Exchange



$\rho_i < \sigma_j < \sigma_i < \rho_j$

$$
\begin{aligned}
&\langle \bar{L}_1 \cdots \bar{L}_{\rho_i} \ell_{\rho_j} k(\ell_{\rho_i}) L_{\rho_i} \cdots \bar{L}_{\sigma_j} \cdots \bar{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) \cdots \bar{L}_{\rho_j} \cdots L \,|\\
&\quad |\bar{L}_1 \cdots \bar{L}_{\rho_i} \cdots \bar{L}_{\sigma_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j} \cdots \bar{L}_{\sigma_i} \cdots \bar{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) \cdots L\rangle\\
&= \langle L^{\alpha_i}_{\rho_i - 1} \bar{L}_{\rho_i} \ell_{\rho_i}(L_{\rho_i}) L^{\alpha_i}_{\rho_i} \,|\, L^{\alpha_i}_{\rho_i - 1} \bar{L}_{\rho_i}(L^{\alpha_j}_{\rho_i}) \ell_{\rho_i} L^{\alpha_i}_{\rho_i}\rangle\\
&\prod_{\lambda = \rho_i + 1}^{\sigma_j - 1} \langle L^{\alpha_j}_{\lambda - 1} \ell_{\rho_i}(L^{\alpha_i}_{\lambda - 1}) \bar{L}_\lambda L^{\alpha_i}_\lambda \,|\, L^{\alpha_j}_{\lambda - 1} \bar{L}_\lambda (L^{\alpha_j}_\lambda) \ell_{\rho_i} L^{\alpha_i}_\lambda\rangle\\
&\sum_{\hat{L}_{\sigma_j} \tilde{L}_{\sigma_j}} \langle L^{\alpha_j}_{\sigma_j - 1} \ell_{\rho_j} k(\ell_{\rho_i}) L^{\alpha_i}_{\sigma_j - 1} \bar{L}_{\sigma_j} L^{\alpha_i}_{\sigma_j} \,|\, L^{\alpha_j}_{\sigma_j - 1} \bar{L}_{\sigma_j} k(\hat{L}_{\sigma_j}) \tilde{L}_{\sigma_j} \ell_{\rho_j} L^{\alpha_i}_{\sigma_j}\rangle\\
&\qquad \langle L^{\alpha_j}_{\sigma_j - 1} \bar{L}_{\sigma_j} k \ell_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j} L^{\alpha_j}_{\sigma_j} \,|\, L^{\alpha_j}_{\sigma_j - 1} \bar{L}_{\sigma_j} k(\hat{L}_{\sigma_j}) \tilde{L}_{\sigma_j} \ell_{\sigma_i} L^{\alpha_j}_{\sigma_j}\rangle\\
&\prod_{\lambda = \sigma_j + 1}^{\sigma_i - 1} \langle \tilde{L}_{\lambda - 1} \ell_{\rho_j}(L^{\alpha_i}_{\lambda - 1}) \bar{L}_\lambda L^{\alpha_i}_\lambda \,|\, \tilde{L}_{\lambda - 1} \bar{L}_\lambda (\tilde{L}_\lambda) \ell_{\rho_j} L^{\alpha_i}_\lambda\rangle\\
&\qquad \langle \tilde{L}_{\lambda - 1} \ell_{\sigma_i}(L^{\alpha_j}_{\lambda - 1}) \bar{L}_\lambda L^{\alpha_j}_\lambda \,|\, \tilde{L}_{\lambda - 1} \bar{L}_\lambda (\tilde{L}_\lambda) \ell_{\sigma_i} L^{\alpha_j}_\lambda\rangle\\
&\qquad \langle \tilde{L}_{\sigma_i - 1} \ell_{\rho_j}(L^{\alpha_i}_{\sigma_i - 1}) L_{\sigma_i} L^{\alpha_i}_{\sigma_i} \,|\, \tilde{L}_{\sigma_i - 1} L_{\sigma_i}(L^{\alpha_j}_{\sigma_i}) \ell_{\rho_j} L^{\alpha_i}_{\sigma_i}\rangle\\
&\qquad \langle \tilde{L}_{\sigma_i - 1} \ell_{\sigma_i}(L^{\alpha_j}_{\sigma_i - 1}) \bar{L}_{\sigma_i} L^{\alpha_j}_{\sigma_i} \,|\, \tilde{L}_{\sigma_i - 1} \bar{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) L^{\alpha_j}_{\sigma_i}\rangle\\
&\prod_{\lambda = \sigma_i + 1}^{\rho_j - 1} \langle L^{\alpha_j}_{\lambda - 1} \ell_{\rho_j}(L^{\alpha_i}_{\lambda - 1}) \bar{L}_\lambda L^{\alpha_i}_\lambda \,|\, L^{\alpha_j}_{\lambda - 1} \bar{L}_\lambda (L^{\alpha_j}_\lambda) \ell_{\rho_j} L^{\alpha_i}_\lambda\rangle\\
&\qquad \langle L^{\alpha_j}_{\rho_j - 1} \ell_{\rho_j}(L^{\alpha_i}_{\rho_j - 1}) \bar{L}_{\rho_j} L^{\alpha_i}_{\rho_j} \,|\, L^{\alpha_j}_{\rho_j - 1} \bar{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) L^{\alpha_i}_{\rho_j}\rangle
\end{aligned}
$$

(4.35)

Special Cases

$$\rho_i = \sigma_j < \sigma_i < \rho_j$$

replace first four lines of (4.35) by

$$\sum_{\widehat{L}_{\rho_i}\widetilde{L}_{\rho_i}\cdots\widetilde{L}_{\sigma_{i-1}}} \langle L^{\alpha_i}_{\rho_{i-1}} \overline{L}_{\rho_i} \ell_{\rho_j} k(\ell_{\rho_i}) L_{\rho_i} L^{\alpha_i}_{\rho_i} \mid L^{\alpha_i}_{\rho_{i-1}} \overline{L}_{\rho_i} k(\widehat{L}_{\rho_i}) \widetilde{L}_{\rho_i} \ell_{\rho_j} L^{\alpha_i}_{\rho_i} \rangle$$
$$\langle L^{\alpha_j}_{\rho_{i-1}} \overline{L}_{\rho_i} k \ell_{\sigma_i}(\ell_{\sigma_j}) L_{\sigma_j} L^{\alpha_j}_{\rho_i} \mid L^{\alpha_i}_{\rho_{i-1}} \overline{L}_{\rho_i} k(\widehat{L}_{\rho_i}) \widetilde{L}_{\rho_i} \ell_{\sigma_i} L^{\alpha_j}_{\rho_i} \rangle$$

$$\rho_i < \sigma_j < \sigma_i = \rho_j$$

replace last four lines of (4.35) by

$$\langle \widetilde{L}_{\sigma_{i-1}} \ell_{\rho_j}(L^{\alpha_i}_{\sigma_{i-1}}) \overline{L}_{\sigma_i} \ell_{\sigma_i}(L_{\sigma_i}) L^{\alpha_i}_{\sigma_i} \mid \widetilde{L}_{\sigma_{i-1}} \ell_{\sigma_i}(L^{\alpha_j}_{\sigma_{i-1}}) \overline{L}_{\sigma_i} \ell_{\rho_j}(L_{\rho_j}) L^{\alpha_i}_{\sigma_i} \rangle$$

$$\rho_i < \sigma_j = \sigma_i < \rho_j$$

$$\langle \overline{L}_1 \cdots \overline{L}_{\rho_i} \ell_{\rho_j} k(\ell_{\rho_i}) L_{\rho_i} \cdots \overline{L}_\sigma \ell_\sigma(L^i_\sigma) \cdots \overline{L}_{\rho_j} \cdots L \mid$$
$$\mid \overline{L}_1 \cdots \overline{L}_{\rho_i} \cdots \overline{L}_\sigma k \ell_\sigma(\ell_\sigma) L^j_\sigma \cdots \overline{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) \cdots L \rangle$$

$$= \langle L^{\alpha_i}_{\rho_{i-1}} \overline{L}_{\rho_i} \ell_{\rho_i}(L_{\rho_i}) L^{\alpha_i}_{\rho_i} \mid L^{\alpha_i}_{\rho_{i-1}} \overline{L}_{\rho_i}(L^{\alpha_j}_{\rho_i}) \ell_{\rho_i} L^{\alpha_i}_{\rho_i} \rangle$$
$$\prod_{\lambda=\rho_i+1}^{\sigma-1} \langle L^{\alpha_j}_{\lambda-1} \ell_{\rho_i}(L^{\alpha_i}_{\lambda-1}) \overline{L}_\lambda L^{\alpha_i}_\lambda \mid L^{\alpha_j}_{\lambda-1} \overline{L}_\lambda(L^{\alpha_j}_\lambda) \ell_{\rho_i} L^{\alpha_i}_\lambda \rangle$$
$$\langle L^{\alpha_i}_{\sigma-1} \ell_{\rho_j} k(\ell_{\rho_i}) L^{\alpha_i}_{\sigma-1} L^i_\sigma L^{\alpha_i}_\sigma \mid L^{\alpha_j}_{\sigma-1} L^i_\sigma k(L^j_\sigma) L^{\alpha_j}_\sigma \ell_{\rho_i} L^{\alpha_i}_\sigma \rangle$$
$$\langle \overline{L}_\sigma \ell_\sigma(L^i_\sigma) k L^j_\sigma \mid \overline{L}_\sigma k \ell_\sigma(\ell_\sigma) L^i_\sigma \rangle$$
$$\prod_{\lambda=\sigma+1}^{\rho_j-1} \langle L^{\alpha_j}_{\lambda-1} \ell_{\rho_j}(L^{\alpha_i}_{\lambda-1}) \overline{L}_\lambda L^{\alpha_i}_\lambda \mid L^{\alpha_j}_{\lambda-1} \overline{L}_\lambda(L^{\alpha_j}_\lambda) \ell_{\rho_j} L^{\alpha_i}_\lambda \rangle$$
$$\langle L^{\alpha_j}_{\rho_j-1} \ell_{\rho_j}(L^{\alpha_i}_{\rho_j-1}) \overline{L}_{\rho_j} L^{\alpha_i}_{\rho_j} \mid L^{\alpha_j}_{\rho_j-1} \overline{L}_{\rho_j} \ell_{\rho_j}(L_{\rho_j}) L^{\alpha_i}_{\rho_j} \rangle$$

An expression for type (6) $\rho_i < \sigma_j < \rho_j < \sigma_i$ may be obtained by replacing the last four lines of (4.35) by

$$\langle \tilde{L}_{\rho_j-1}\, \ell_{\rho_j}(L^{\alpha_i}_{\rho_j-1})\, \bar{L}_{\rho_j} L^{\alpha_i}_{\rho_j} \mid \tilde{L}_{\rho_j-1}\, \bar{L}_{\rho_j}\, \ell_{\rho_j}(L_{\rho_j})\, L^{\alpha_i}_{\rho_j} \rangle$$

$$\langle \tilde{L}_{\rho_j-1}\, \ell_{\sigma_i}(L^{\alpha_j}_{\rho_j-1})\, L_{\rho_j} L^{\alpha_j}_{\rho_j} \mid \tilde{L}_{\rho_j-1}\, L_{\rho_j}(L^{\alpha_i}_{\rho_j})\, \ell_{\sigma_i} L^{\alpha_j}_{\rho_j} \rangle$$

$$\prod_{\lambda=\rho_j+1}^{\sigma_i-1} \langle L^{\alpha_i}_{\lambda-1}\, \ell_{\sigma_i}(L^{\alpha_j}_{\lambda-1})\, \bar{L}_\lambda L^{\alpha_j}_{\lambda} \mid L^{\alpha_i}_{\lambda-1}\, \bar{L}_\lambda(L^{\alpha_i}_{\lambda})\, \ell_{\sigma_i} L^{\alpha_j}_{\lambda} \rangle$$

$$\langle L^{\alpha_i}_{\sigma_i-1}\, \ell_{\sigma_i}(L^{\alpha_j}_{\sigma_i-1})\, \bar{L}_{\sigma_i} L^{\alpha_j}_{\sigma_i} \mid L^{\alpha_i}_{\sigma_i-1}\, \bar{L}_{\sigma_i}\, \ell_{\sigma_i}(L_{\sigma_i})\, L^{\alpha_j}_{\sigma_i} \rangle$$

4.3 Program

A computer program has been written to evaluate the one, two and three vector recoupling coefficients of the type described in section 4.2. The program is written assuming that recoupling coefficients will always occur in pairs of an orbital and a spin coefficient. The classification of the coefficients depends only on the order in which the vectors are coupled and not on their numerical values. Hence both members of a pair of coefficients will belong to the same basic type. The program is therefore written to evaluate a pair of recoupling coefficients and the final value that it returns is a product of the orbital coefficient and the corresponding spin coefficient.

The program is written in FORTRAN and is split into 5 subroutines.

(1) SØRTS: This subroutine examines the input data and classifies the coefficient according to the three basic types described in section 4.2.

(2) RECØPS: Evaluates direct and translation type coefficients.

(3) RECPSX: Evaluates exchange type coefficients.

(4) RACAH: Evaluates Racah coefficients.

(5) FG03B: Evaluates 9-j coefficients.

The versions of RACAH and FG03B used in this program are library routines and will not be described here.

(1) SØRTS: This subroutine may be regarded as the link between the calling program and the recoupling subroutines. For this reason, its form depends on the problem for which recoupling coefficients are needed, whereas subroutines

RECØPS and RECPSX are completely problem-independent. The version of SØRTS described below has been written for the calculation of the recoupling coefficients which arise in the evaluation of the matrix elements of the one electron operator $\langle H_1 \rangle$ and the two electron operator $\left\langle \frac{1}{r_{N,N+1}} \right\rangle$ described in S.M. RECØPS has been written assuming that k is recoupled from the lowest of the 4 interacting subshells to a higher subshell. This may not be true for the required coefficient therefore, instead of returning the values of $\langle L_i | L_j \rangle_k \langle S_i | S_j \rangle$ for the matrix element $\left\langle \frac{1}{r_{N,N+1}} \right\rangle$, SØRTS returns the values of the 'invariant' quantity

$$\left[(2\ell_{p_i}+1)(2\ell_{\sigma_j}+1)\right]^{-\frac{1}{2}} \langle L_i | L_j \rangle_K \langle S_i | S_j \rangle_K$$

(see equation (4.28)

Input data

The program requires the following input, (we use the notation of the preceding sections to describe the various quantities),

I,J - parameters which label the l.h.s. and r.h.s., respectively, of the coefficient.

IRHØ,JRHØ - subshells containing electron N on l.h.s. and r.h.s., respectively. (We label subshells 1,2, 3,···NØRB rather than 1s, 2s, 2p···b.

K - third vector to be recoupled in orbital coefficient.

KFLAG - equals 0 if $\langle L_i | L_j \rangle$ is the angular part of $\langle i | \frac{1}{r_{N,N+1}} | j \rangle$ equals 1 if $\langle L_i | L_j \rangle$ is the angular part of the matrix element $\langle H_1 \rangle$.

NØRB - number of occupied subshells.

NØRB1 = NØRB + 1 - Number of occupied subshells if the continuum is regarded as being the outermost subshell.

ISIG, JSIG - subshells containing electron N+1.

SPI, SPJ, SSI, SSJ - S_{ρ_i}, S_{ρ_j}, S_{σ_i}, S_{σ_j}.

LPI, LPJ, LSI, LSJ - L_{ρ_i}, L_{ρ_j}, L_{σ_i}, L_{σ_j}

LRGL, SPN - total L, S for the system

For each channel I = 1, N and subshell LAM = 1, NØRB

SLAM (LAM, I), LLAM (LAM, I) - S_λ^i, L_λ^i subshell angular momenta

SALPA(LAM, I), LALFA(LAM, I) - $S_\lambda^{a_i}$, $L_\lambda^{a_i}$ intermediate couplings

For each channel I = 1, N

AL2(I) - ℓ_i projectile angular momentum

IWRITE - logical number of output device

IDEBUG (3) - flag for debug prints.

(Note that as we will regard the continuum as an additional subshell the dimensions of SLAM and LLAM must be (NØRB1, N)

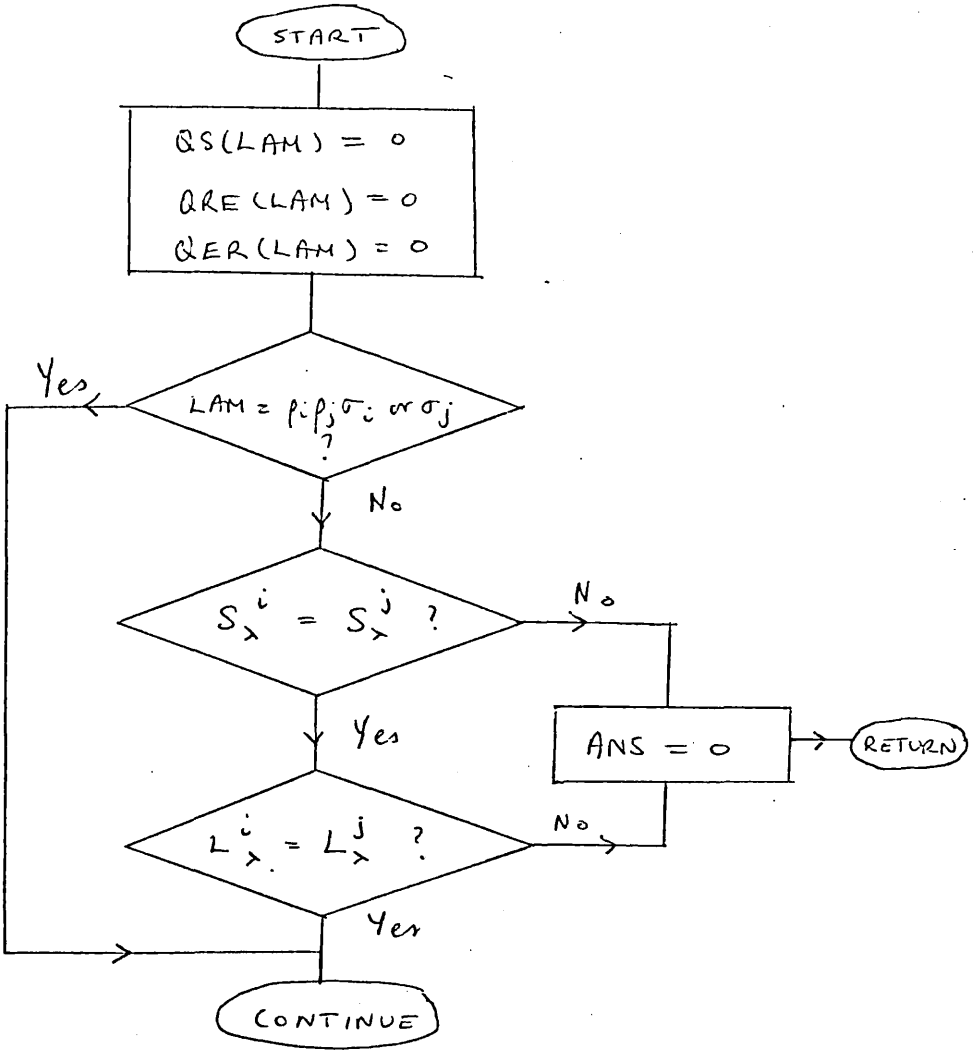
The following local arrays will also be required

QALFA (NØRB1, N) QLAM(NØRB1, N), QL(NØRB1), QS(NØRB1) QRE(NØRB1), QER(NØRB1), Q(4), S(4), L(4), ILAM(4), JEND(NØRB1)

SØRTS performs the following checks and reordering

(1) Checks that the quantum numbers of the spectator subshells are equal.

For each LAM = 1, NØRB1



(2) Sets IMIN = min (IRHØ, ISIG)

IMAX = max (IRHØ, ISIG)

LI1 = $\bar{L}_{IMIN}$

SI1 = $\bar{S}_{IMIN}$

LI2 = $\bar{L}_{IMAX}$

SI2 = $\bar{S}_{IMAX}$

Sets IRS = 1 if IRHØ < ISIG

= 0 if IRHØ = ISIG

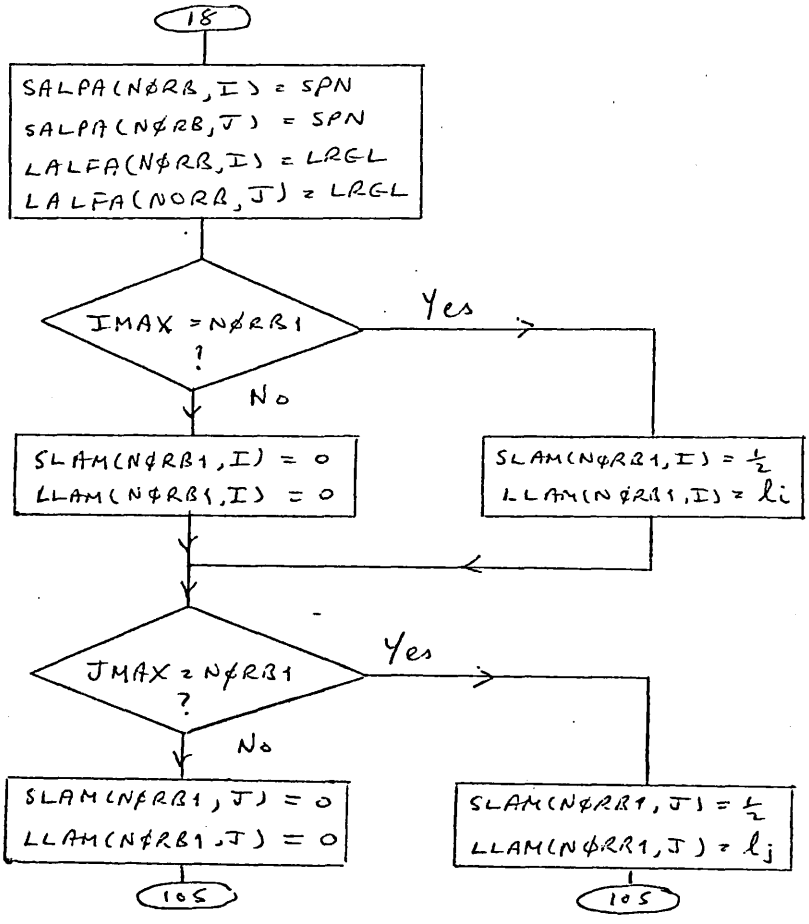
= -1 if IRHØ > ISIG

Defines JMIN, JMAX, LJ1, SJ1, LJ2, SJ2, JRS in similar manner

Sets ANS = 1

MATCH = 0

(3) Defines $S^{a}_{N\emptyset RB}$ $L^{a}_{N\emptyset RB}$ $S_{N\emptyset RB1}$ $L_{N\emptyset RB1}$



(4) Checks the quantum numbers of the spectators in the interacting subshells. Puts $\rho_i \rho_j \sigma_i \sigma_j$ in ascending order and relabels them by defining new arrays

ILAM(4)

L(ILAM) = $\bar{L}_{ILAM}$

S(ILAM) = $\bar{S}_{ILAM}$

When checking the quantum numbers we must consider the following cases

(i) IMIN = JMIN, $\bar{S}_{IMIN} = \bar{S}_{JMIN}$, $\bar{L}_{IMIN} = \bar{L}_{JMIN}$

(ii) IMIN = JMAX, $\bar{S}_{IMIN} = \bar{S}_{JMAX}$, $\bar{L}_{IMIN} = \bar{L}_{JMAX}$

JMIN = IMAX, $\bar{S}_{JMIN} = \bar{S}_{IMAX}$, $\bar{L}_{JMIN} = \bar{L}_{IMAX}$

(iii) IMIN $\neq$ JMIN, JMAX, $\bar{S}_{IMIN} = S^j_{IMIN}$, $\bar{L}_{IMIN} = L^j_{IMIN}$

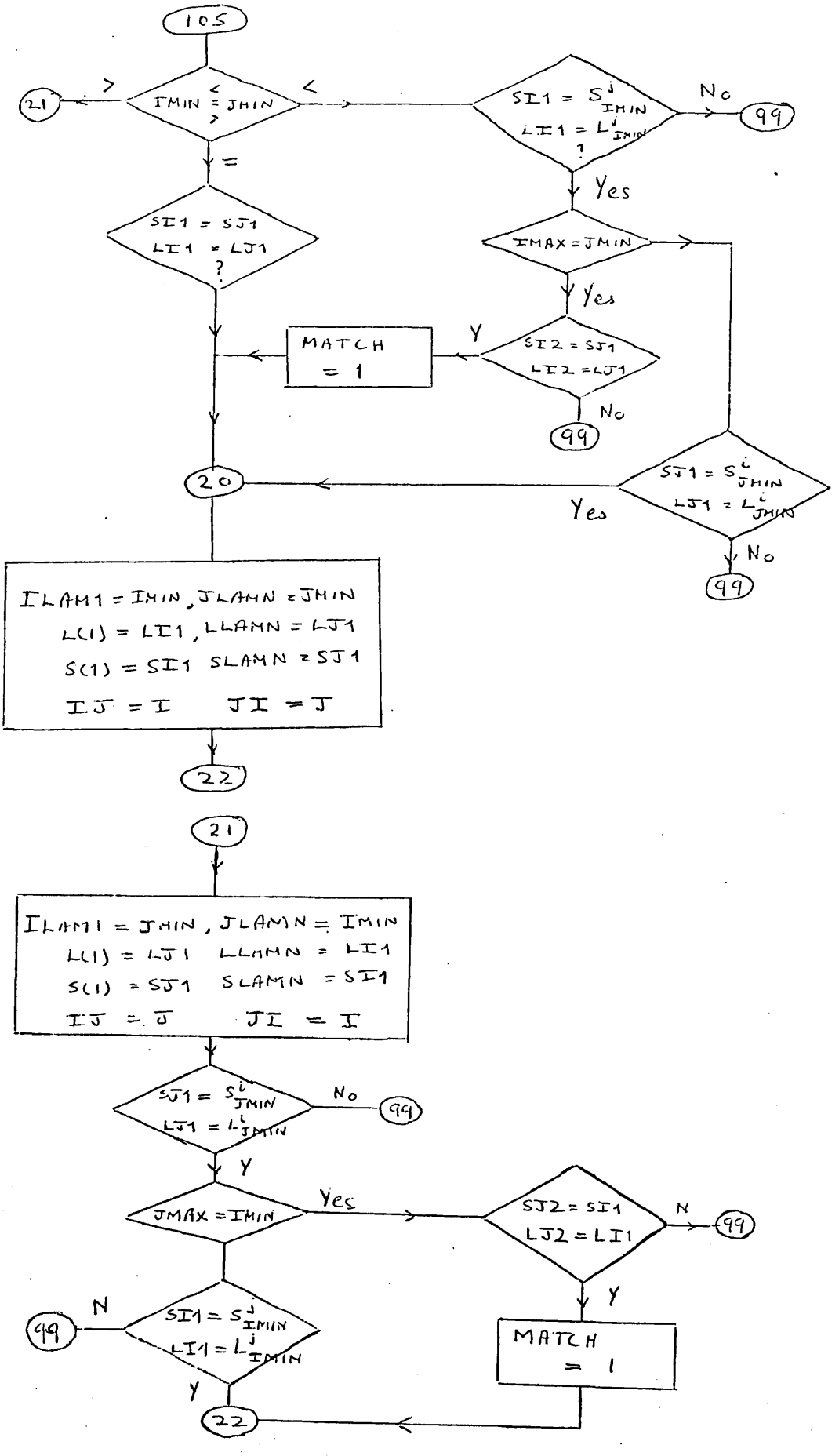
JMIN $\neq$ IMIN, JMAX, $\bar{S}_{JMIN} = S^i_{JMIN}$, $\bar{L}_{JMIN} = L^i_{JMIN}$

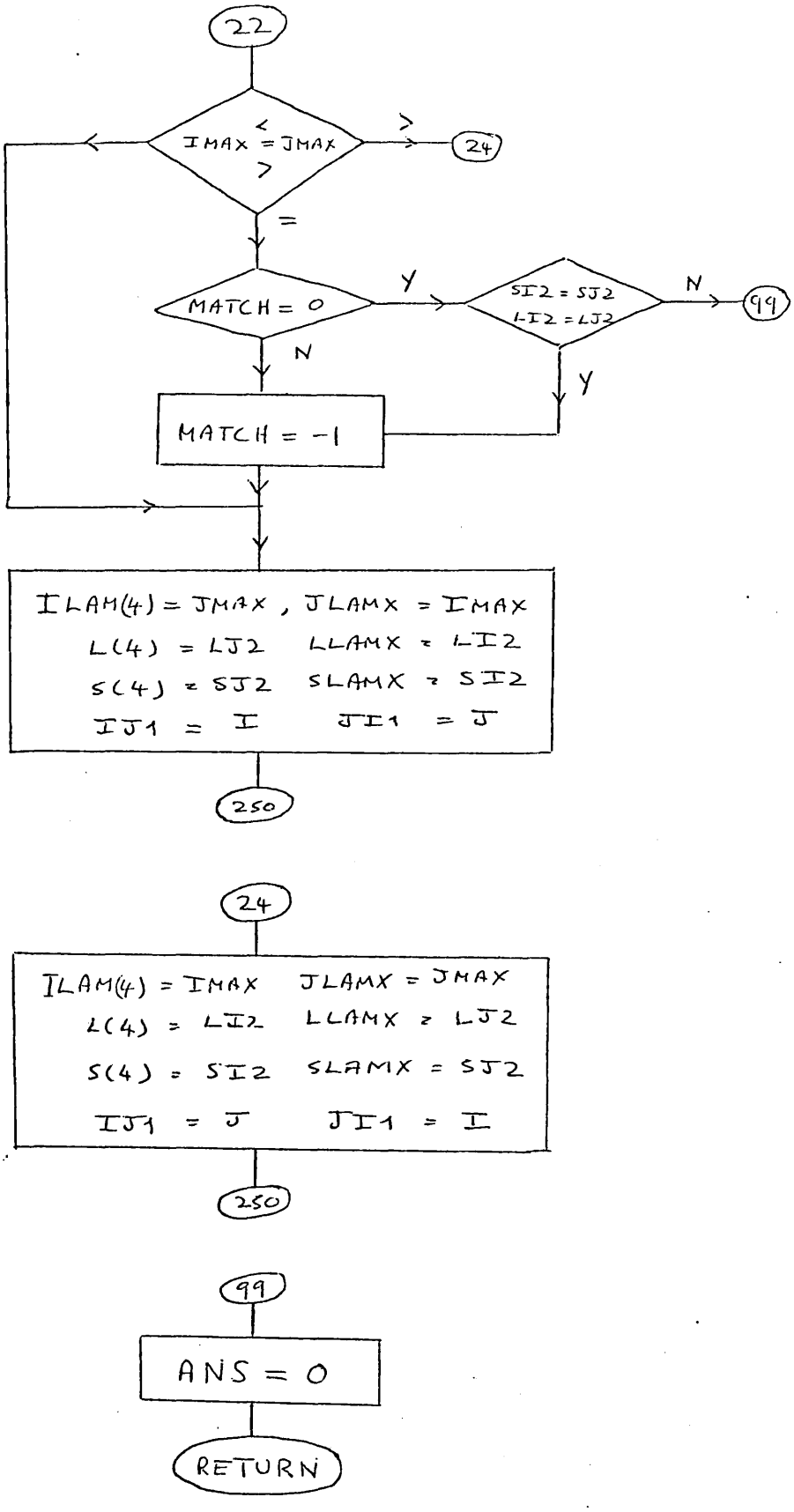
(iv) IMIN = IMAX no check for $\bar{S}_{IMAX}$, $\bar{L}_{IMAX}$

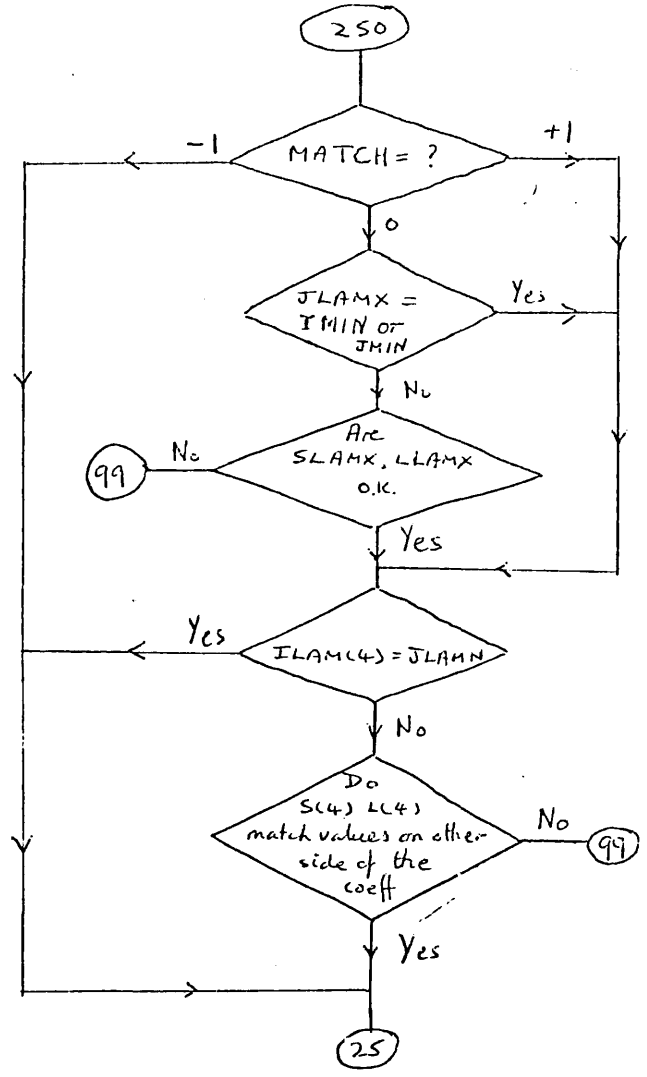
JMIN = JMAX no check for $\bar{S}_{JMAX}$, $\bar{L}_{JMAX}$

(v) IMAX = JMAX $\neq$ IMIN or JMIN $\bar{S}_{IMAX} = \bar{S}_{JMAX}$

$\bar{L}_{IMAX} = \bar{L}_{JMAX}$


105
IMIN ? JMIN
>
21
<
SI1 = S^J_IMIN
LI1 = L^J_IMIN
?
No
99
Yes
=
SI1 = SJ1
LI1 = LJ1
?
IMAX = JMIN
Yes
MATCH = 1
Y
SI2 = SJ1
LI2 = LJ1
No
99
SJ1 = S^I_JMIN
LJ1 = L^I_JMIN
Yes
No
99
20
ILAM1 = IMIN, JLAMN = JMIN
L(1) = LI1, LLAMN = LJ1
S(1) = SI1 SLAMN = SJ1
IJ = I JI = J
22
21
ILAM1 = JMIN, JLAMN = IMIN
L(1) = LJ1 LLAMN = LI1
S(1) = SJ1 SLAMN = SI1
IJ = J JI = I
SJ1 = S^I_JMIN
LJ1 = L^I_JMIN
No
99
Y
JMAX = IMIN
Yes
SJ2 = SI1
LJ2 = LI1
N
99
Y
N
99
SI1 = S^J_IMIN
LI1 = L^J_IMIN
MATCH = 1
Y
22


22
IMAX < = > JMAX
24
=
MATCH = 0
Y
SI2 = SJ2
LI2 = LJ2
N
99
N
Y
MATCH = -1
ILAM(4) = JMAX , JLAMX = IMAX
L(4) = LJ2 LLAMX = LI2
S(4) = SJ2 SLAMX = SI2
IJ1 = I JI1 = J
250
24
ILAM(4) = IMAX JLAMX = JMAX
L(4) = LI2 LLAMX = LJ2
S(4) = SI2 SLAMX = SJ2
IJ1 = J JI1 = I
250
99
ANS = 0
RETURN



We note here that MATCH = -1 $\Rightarrow$ $I_{MAX} = J_{MAX}$

MATCH = +1 $\Rightarrow$ $I_{MIN} = J_{MAX}$

or $J_{MIN} = I_{MAX}$

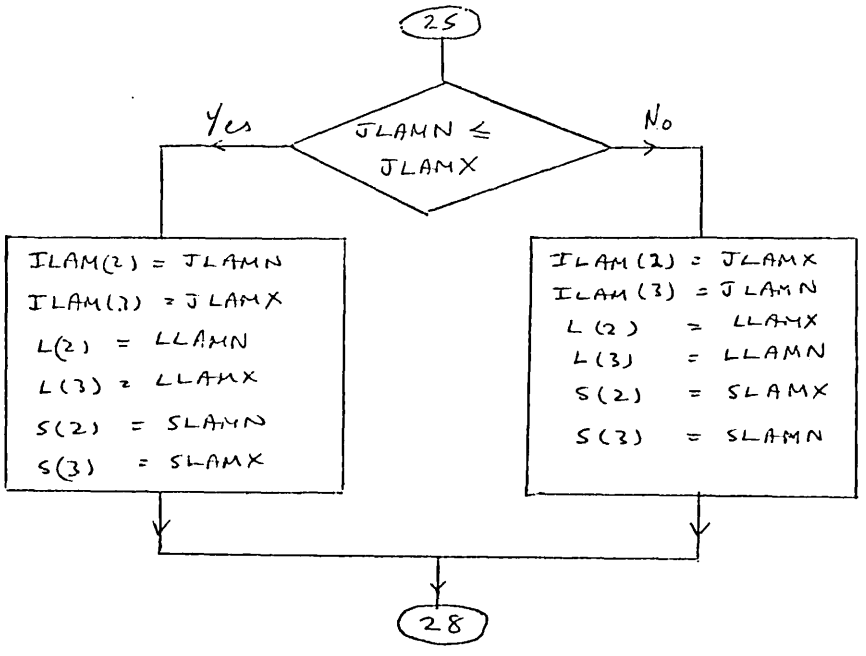
hence MATCH = 0 includes the cases

IMIN = JMIN

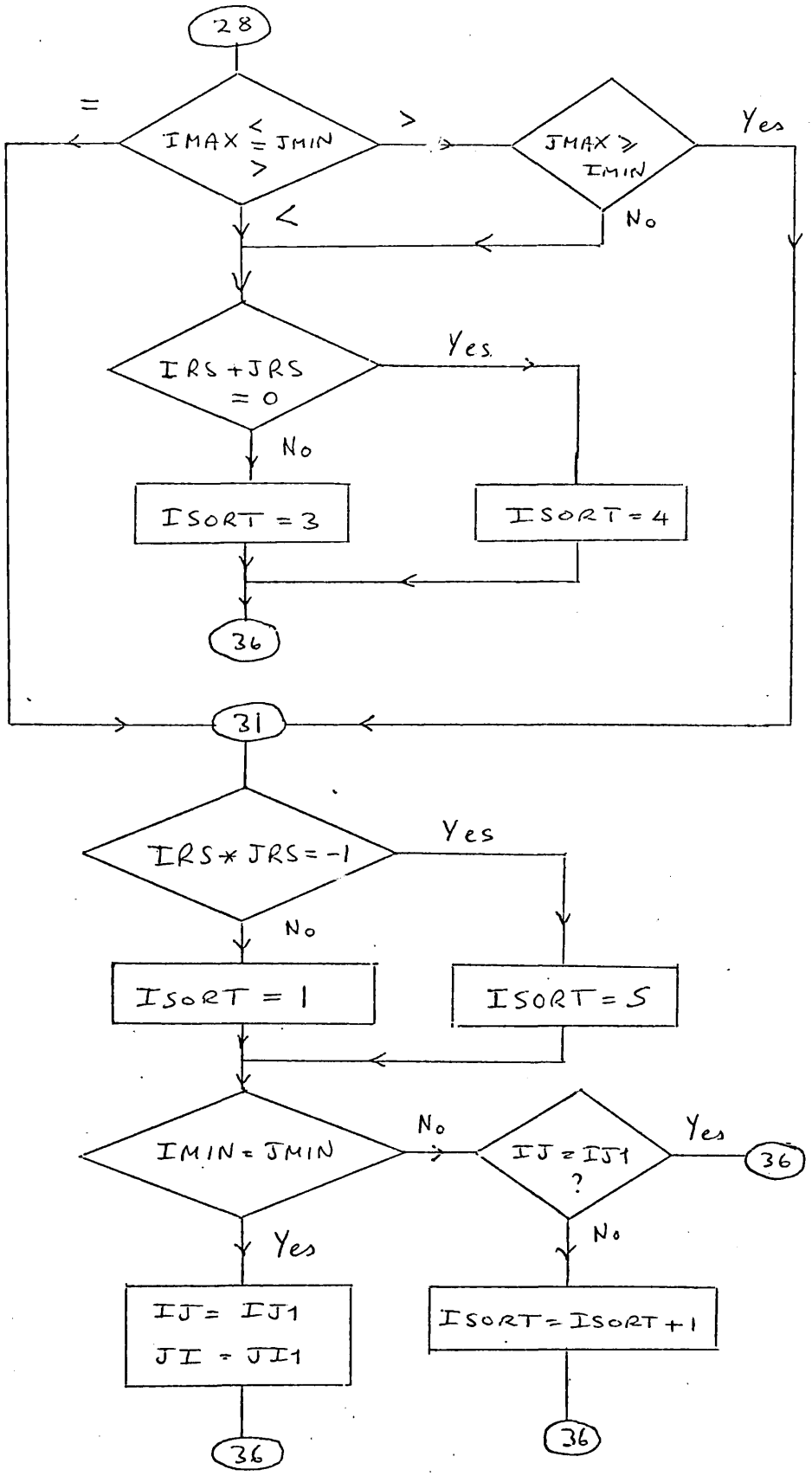
IMIN = IMAX

JMIN = JMAX

and that JLAMN = max (IMIN, JMIN), JLAMX = min (IMAX, JMAX)



(5) Classifies the recoupling coefficient according to the six types discussed in section (4.2) and labelled by ISØRT = 1,···6. Although the spin recoupling coefficients may be obtained by substituting the appropriate values of j together with k = 0 into the expressions for the 3 vector coefficient it is often easier to obtain these more directly. For this reason we reserve ISØRT = 1,···6 for spin recoupling coefficients and set ISØRT(orb) = ISØRT(spin) + 6.


28
IMAX < = > JMIN
=
<
>
JMAX ≥ IMIN
Yes
No
IRS + JRS = 0
Yes
No
ISORT = 3
ISORT = 4
36
31
IRS * JRS = -1
Yes
No
ISORT = 1
ISORT = 5
IMIN = JMIN
No
IJ = IJ1 ?
Yes
36
Yes
No
IJ = IJ1
JI = JI1
ISORT = ISORT + 1
36
36

(6) The program now considers the spin and orbital coefficients separately. The angular momenta of the individual subshells $\lambda <$ ILAM(1) play no part in the recoupling and only their resultant $S^{a}_{ILAM1-1}(L^{a}_{ILAM1-1})$ is required. We define

$$QS(1) = S^{a}_{ILAM1-1} \qquad ILAM1 > 2$$
$$= S_{ILAM1-1} \qquad ILAM1 = 2$$
$$= 0 \qquad ILAM1 = 1$$

$$QRE(1) = S^{\alpha_{IJ}}_{ILAM1} \qquad ILAM1 > 1$$
$$= S^{IJ}_{ILAM1} \qquad ILAM1 = 1$$

$$QER(1) = S^{\alpha_{JI}}_{ILAM1} \qquad ILAM1 > 1$$
$$= S^{JI}_{ILAM1} \qquad ILAM1 = 1$$

We recall that IJ = i, JI = j if ILAM1 = ρ_i or σ_i
IJ = j, JI = i if ILAM1 = ρ_j or σ_j

We next scan through all subshells ILAM1 $< \lambda \leq$ ILAM4 discarding any spectator subshells with $\bar{S}_\lambda = 0$. We store the parameters S_λ^{IJ}, $S_\lambda^{\alpha_{IJ}}$ $S_\lambda^{\alpha_{JI}}$ of the remaining subshells in QS(II), QRE(II) and QER(II) respectively, with the counter II replacing λ. For $\lambda = \rho_i\rho_j\sigma_i$ or σ_j we store JEND(λ) = II(λ) - 1. At λ = ILAM3 we choose to store $S_\lambda^{\alpha_{IJ1}}$ rather than $S_\lambda^{\alpha_{IJ}}$ in QRE, and to store $S_\lambda^{\alpha_{JI1}}$ in QER

(IJ1 = i, JI1 = j if ILAM4 = ρ_j or σ_j
IJ1 = j, JI1 = i if ILAM4 = ρ_i or σ_i)

We have now defined all the quantities needed by RECØPS

and RECPSX. The program now calls RECØPS (which calls RECPSX if necessary) which returns the value of $\langle S_i | S_j \rangle$. We now define QS, QRE, QER etc in terms of the orbital quantum numbers and repeat the process. We note that as the number of non zero $\bar{L}_\lambda$ will not necessarily be the same as the number of non zero $\bar{S}_\lambda$, the process of eliminating redundant couplings in the recoupling coefficient has to be performed separately for $\langle S_i | S_j \rangle$ and $\langle L_i | L_j \rangle$. As mentioned earlier RECØPS assumes that k is initially coupled into ILAM1 and we multiply by the factor $[(2\ell_{ILAM_1}+1)(2\ell_N+1)]^{\frac{1}{2}}$ where

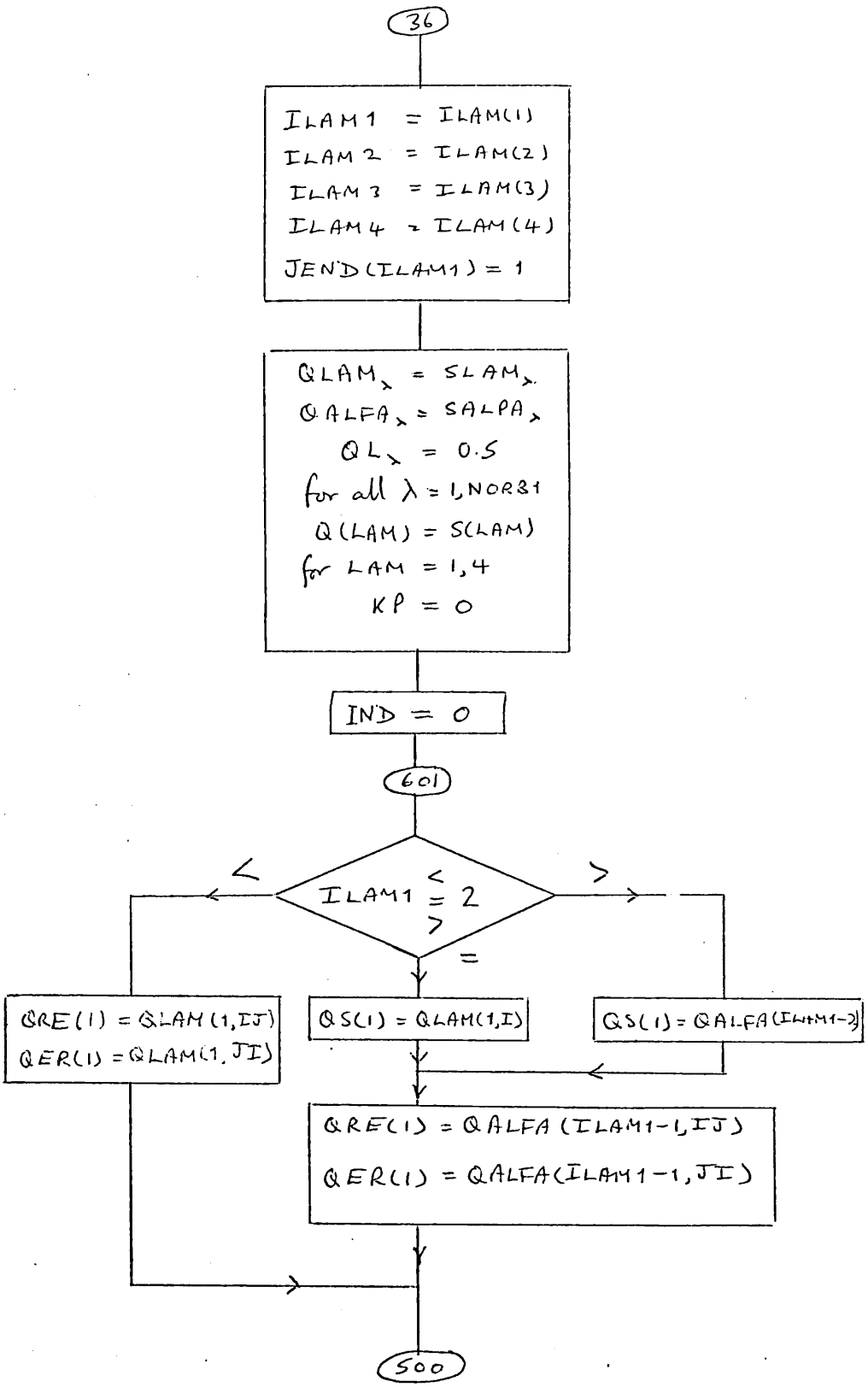
$$\ell_N = \ell_{ILAM4} \quad \text{for} \quad ISØRT = 1,3$$

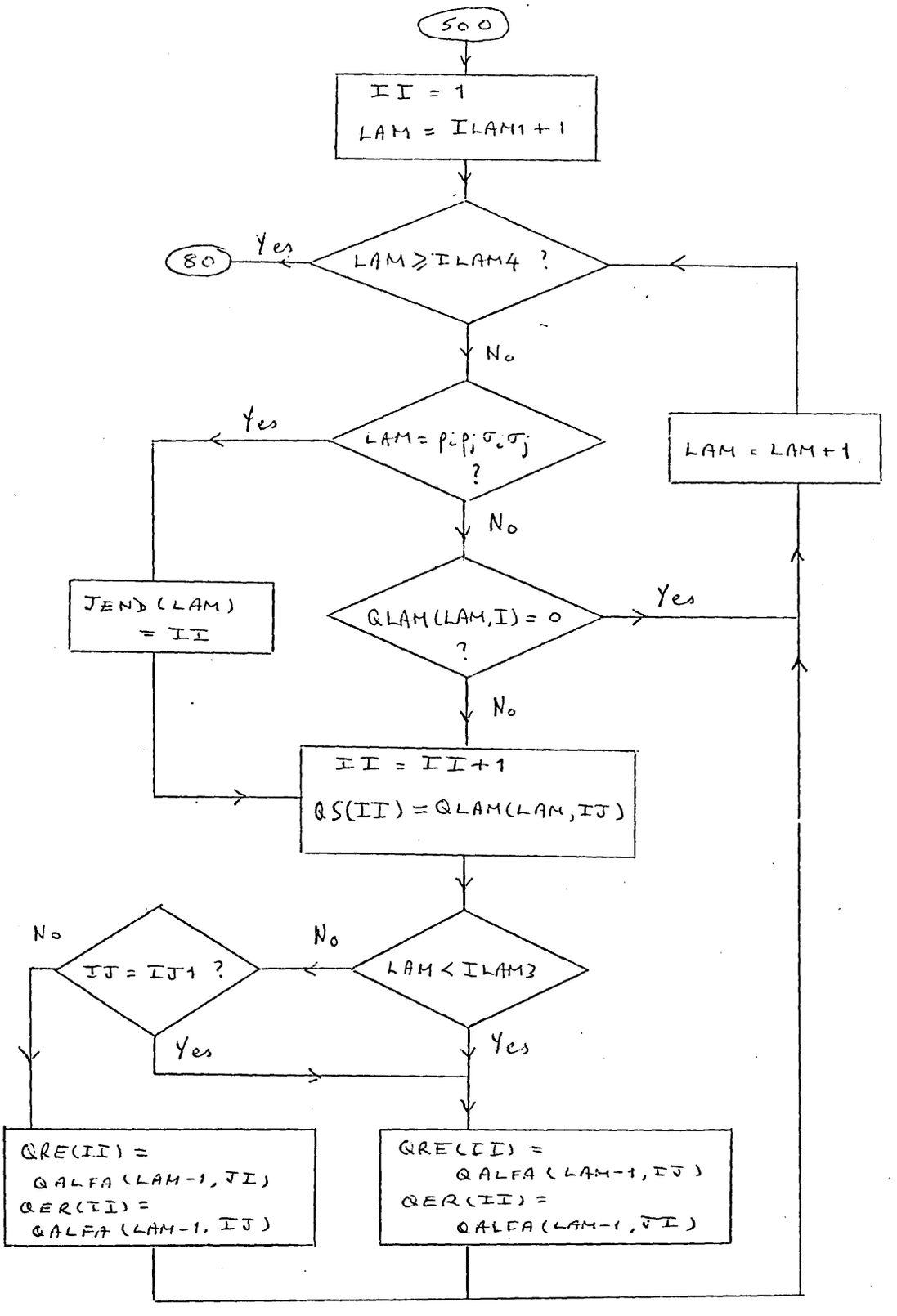
$$= \ell_{ILAM3} \quad ISØRT = 2,4$$

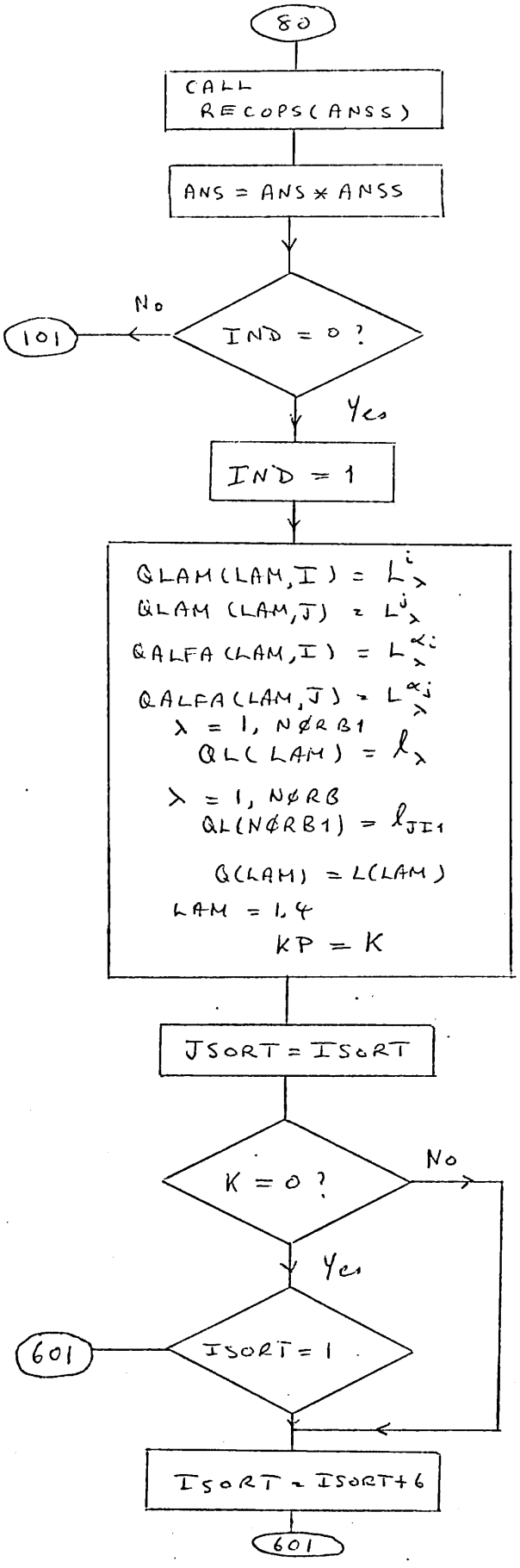
$$= \ell_{ILAM2} \quad ISØRT = 5,6$$

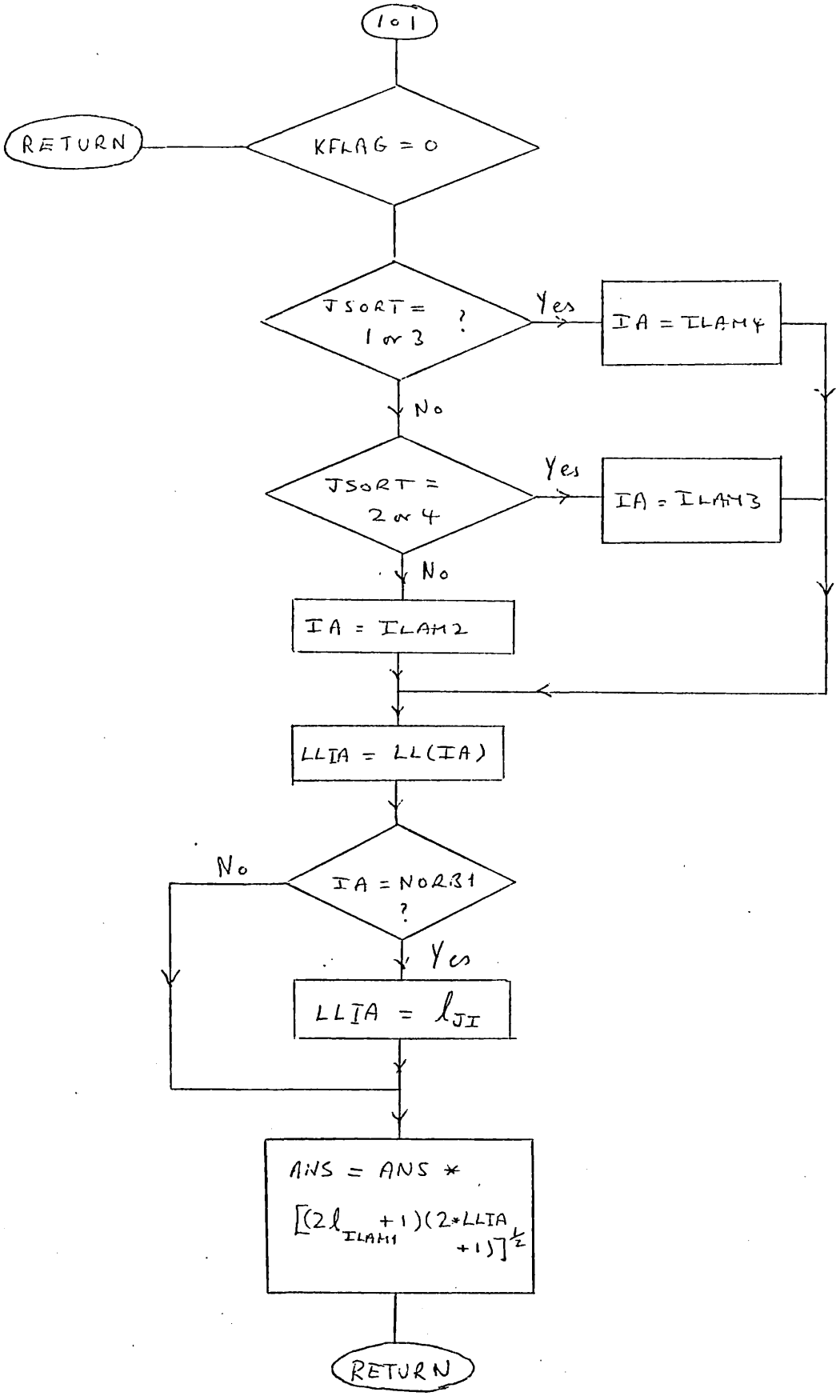
to obtain a quantity independent of the coupling of k. SØRTS therefore returns the value $[(2\ell_{ILAM_1}+1)(2\ell_N+1)]^{\frac{1}{2}} \langle L_i | L_j \rangle_k \langle S_i | S_j \rangle$ for the matrix elements of $\left\langle \frac{1}{r_{N,N+1}} \right\rangle$ and the value of

$\langle L_i | L_j \rangle \langle S_i | S_j \rangle$ for $\langle H_1 \rangle$


36
ILAM1 = ILAM(1)
ILAM2 = ILAM(2)
ILAM3 = ILAM(3)
ILAM4 = ILAM(4)
JEND(ILAM1) = 1
QLAMλ = SLAMλ
QALFAλ = SALPAλ
QLλ = 0.5
for all λ = 1,NORB1
Q(LAM) = S(LAM)
for LAM = 1,4
KP = 0
IND = 0
601
ILAM1 < = > 2
<
=
>
QRE(I) = QLAM(1,IJ)
QER(I) = QLAM(1,JI)
QS(I) = QLAM(1,I)
QS(I) = QALFA(ILAM1-2)
QRE(I) = QALFA(ILAM1-1,IJ)
QER(I) = QALFA(ILAM1-1,JI)
500


500
II = 1
LAM = ILAM1 + 1
80
Yes
LAM ≥ ILAM4 ?
No
Yes
LAM = ρiρj σiσj ?
No
LAM = LAM + 1
JEND(LAM) = II
QLAM(LAM,I) = 0 ?
Yes
No
II = II+1
QS(II) = QLAM(LAM,IJ)
No
IJ = IJ1 ?
No
LAM < ILAM3
Yes
Yes
QRE(II) = QALFA(LAM-1, JI)
QER(II) = QALFA(LAM-1, IJ)
QRE(II) = QALFA(LAM-1, IJ)
QER(II) = QALFA(LAM-1, JI)


80
CALL RECOPS(ANSS)
ANS = ANS * ANSS
No
101
IND = 0 ?
Yes
IND = 1
QLAM(LAM,I) = L^i_λ
QLAM(LAM,J) = L^j_λ
QALFA(LAM,I) = $L^{\alpha i}_\lambda$
QALFA(LAM,J) = $L^{\alpha j}_\lambda$
λ = 1, NØRB1
QL(LAM) = l_λ
λ = 1, NØRB
QL(NØRB1) = l_{JI+1}
Q(LAM) = L(LAM)
LAM = 1,4
KP = K
JSORT = ISORT
No
K = 0 ?
Yes
601
ISORT = 1
ISORT = ISORT+6
601


101
KFLAG = 0
RETURN
JSORT = 1 or 3 ?
Yes
IA = ILAM4
No
JSORT = 2 or 4
Yes
IA = ILAM3
No
IA = ILAM2
LLIA = LL(IA)
IA = NORM1 ?
No
Yes
LLIA = l_{JI}
ANS = ANS * $[(2l_{ILAM1}+1)(2*LLIA+1)]^{\frac{1}{2}}$
RETURN

RECØPS

This subroutine together with RECPSX, RACAH and FG03B performs the actual calculation of the recoupling coefficients. It requires as input the following data.

ISØRT -- label denoting type of coefficient.

ILAM(I) I = 1, 4 -- labels of interacting subshells arranged in ascending order.

IJ = I, JI = J	if ILAM1 = ρ_i or σ_i
IJ = J, JI = I	if ILAM1 = ρ_j or σ_j
IJ1 = J, JI1 = I	if ILAM4 = ρ_i or σ_i
IJ1 = I, IJ1 = J	if ILAM4 = ρ_j or σ_j

JEND(ρ) = number of subshells $\lambda < \rho$ = interacting subshell contributing to recoupling (see SØRTS)

K = value of third vector to be recoupled

IFLAG = $\begin{cases} 0 \text{ if coefficient is part of } \langle i \left| \dfrac{1}{r_{N,N+1}} \right| j \rangle \\ 1 \text{ if coefficient is part of } \langle i | H_1 | j \rangle \end{cases}$

QALFA, QLAM, QS, QRE, QER, Q (≡QL of SØRTS)

QBAR (≡Q of SØRTS) -- quantum numbers appearing in the recoupling coefficient, see SØRTS

The following local arrays are also used,

QMIN(NØRB1), QMAX(NØRB1)

The subroutine uses the expressions for the basic types of recoupling coefficients given in the previous section. We note that if ILAM1 ($\equiv\lambda_1$) $\neq$ILAM2($\equiv\lambda_2$) then the recoupling

$$\langle L^{\alpha_{IJ}}_{\lambda_1-1}\, \bar{L}_{\lambda_1}\, \ell_{\lambda_1}(L^{IJ}_{\lambda_1})\, L^{\alpha_{IJ}}_{\lambda_1} \,|\, L^{\alpha_{IJ}}_{\lambda_1-1}\, \bar{L}_{\lambda_1}(L^{\alpha_{JI}}_{\lambda_1})\, \ell_{\lambda_1} L^{\alpha_{IJ}}_{\lambda_1}\rangle$$

$$\prod_{\lambda=\lambda_1+1}^{\lambda_2-1} \langle L^{\alpha_{JI}}_{\lambda-1}\, \ell_{\lambda_1}(L^{\alpha_{IJ}}_{\lambda-1})\, \bar{L}_{\lambda}\, L^{\alpha_{IJ}}_{\lambda} \,|\, L^{\alpha_{JI}}_{\lambda-1}\, \bar{L}_{\lambda}(L^{\alpha_{JI}}_{\lambda})\, \ell_{\lambda_1} L^{\alpha_{IJ}}_{\lambda}\rangle$$

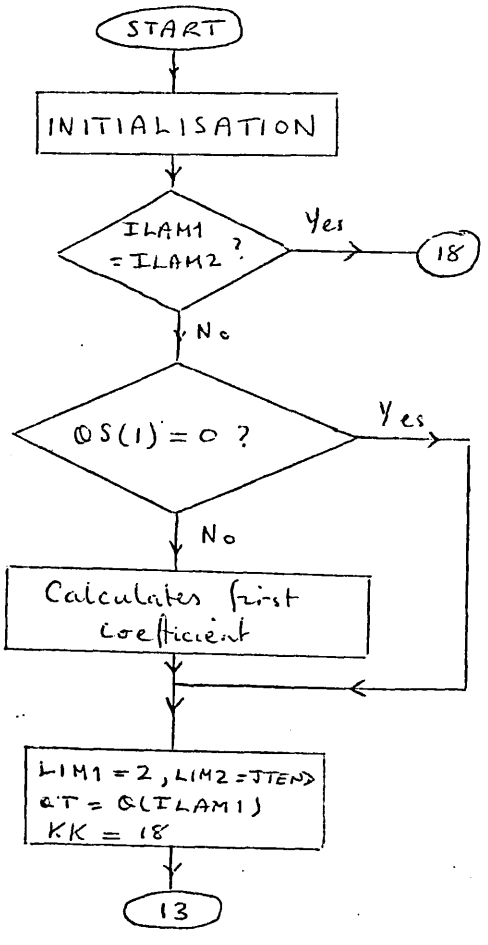
is common to all coefficients. Similarly if ILAM3 ($\equiv\lambda_3$) $\neq$ILAM4($\equiv\lambda_4$) then the recoupling

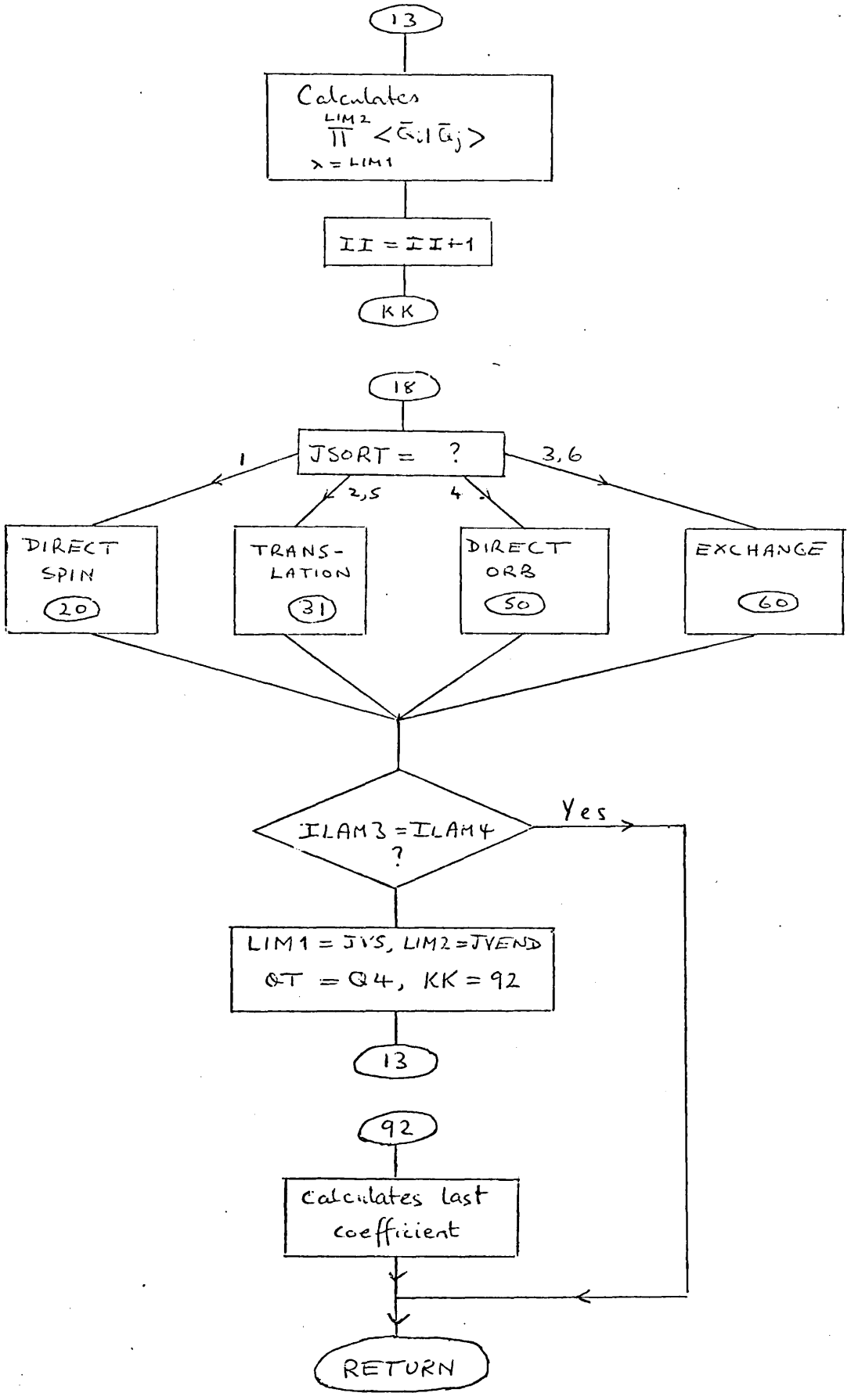
$$\prod_{\lambda=\lambda_3+1}^{\lambda_4-1} \langle L^{\alpha_{JI1}}_{\lambda-1}\, \ell_{\lambda_4}(L^{\alpha_{IJ1}}_{\lambda-1})\, \bar{L}_{\lambda}\, L^{\alpha_{IJ1}}_{\lambda} \,|\, L^{\alpha_{JI1}}_{\lambda-1}\, \bar{L}_{\lambda}(L^{\alpha_{JI1}}_{\lambda})\, \ell_{\lambda_4} L^{\alpha_{IJ1}}_{\lambda}\rangle$$

$$\langle L^{\alpha_{JI1}}_{\lambda_4-1}\, \ell_{\lambda_4}(L^{\alpha_{IJ1}}_{\lambda_4-1})\, \bar{L}_{\lambda_4}\, L^{\alpha_{IJ1}}_{\lambda_4} \,|\, L^{\alpha_{JI1}}_{\lambda_4-1}\, \bar{L}_{\lambda_4}\, \ell_{\lambda_4}(L^{JI1}_{\lambda_4})\, L^{\alpha_{IJ1}}_{\lambda_4}\rangle$$

is common to all types of coefficients.

The subroutine is constructed as follows




13
Calculates
$\prod_{\lambda=LIM1}^{LIM2} \langle \bar{G}_i | \bar{G}_j \rangle$
II = II+1
KK
18
JSORT = ?
1
2,5
4
3,6
DIRECT SPIN
20
TRANS-LATION
31
DIRECT ORB
50
EXCHANGE
60
ILAM3 = ILAM4 ?
Yes
LIM1 = JVS, LIM2 = JVEND
QT = Q4, KK = 92
13
92
Calculates last coefficient
RETURN

The intialisation step includes the following definitions

QK = K

ANS = 1

ANSS = 0

if ILAM3 = NØRB1, Q4 = ℓ_{IJ1} for orbital coefficients

For all other cases Q4 = Q(ILAM3)

JTEND = JEND (ILAM2)

JUS = JTEND + 2

JUEND = JEND (ILAM3)

JVS = JVEND + 2

JVEND = JEND (ILAM4)

JSØRT = 1 for DIRECT SPIN coefficients

2 TRANSLATION SPIN

3 EXCHANGE SPIN

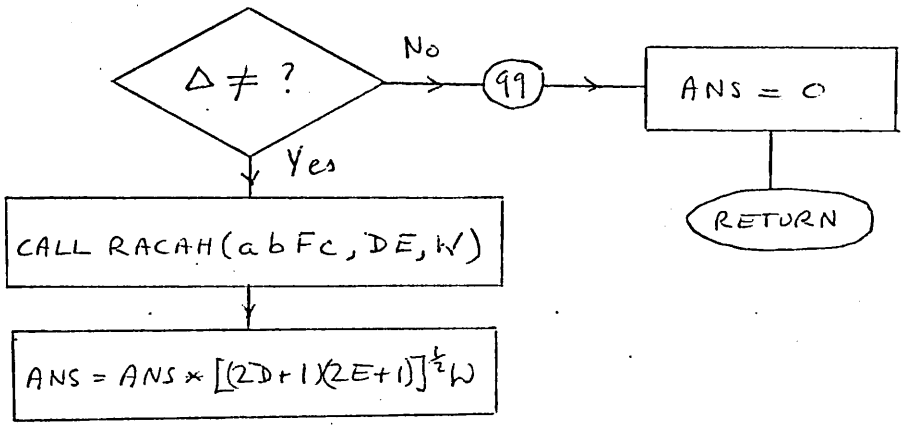
4 DIRECT ØRBITAL

5 TRANS.ØRBITAL

6 EXCHANGE ØRBITAL

The steps "calculate coeff." would consist of the following instructions for the calculation of the coefficient

$$\langle ab(D)cF|a,bc(E)F\rangle = [(2D+1)(2E+1)]^{1/2} W(abFc,DE)$$



where $'\Delta \neq ?'$ is an abbreviation for "are the triangular in-

equalities $\begin{cases} a - b \leq D \leq a + b \\ b - c \leq E \leq b + c \\ D - c \leq F \leq D + c \\ a - E \leq F \leq a + E \end{cases}$ satisfied?"

In practise, we assume that the original intermediate coupling, D, is allowed and we only check that the new intermediate coupling, E, satisfies the triangular inequalities. (RACAH also checks the triangular in equalities therefore this omission is not important).

The direct spin recoupling coefficient is considered separately from the direct orbital coefficient, since the expression for the former in terms of Racah coefficients is considerably less complicated than that for the latter, particularly for the special cases where some or all of the subshells $\rho_i \rho_j \sigma_i \sigma_j$ are equal.

The direct and translation coefficients may be expressed as a product of Racah and 9-j symbols with at most one summation over intermediate couplings. Hence they may be evaluated using a sequence of instructions of the type described above.

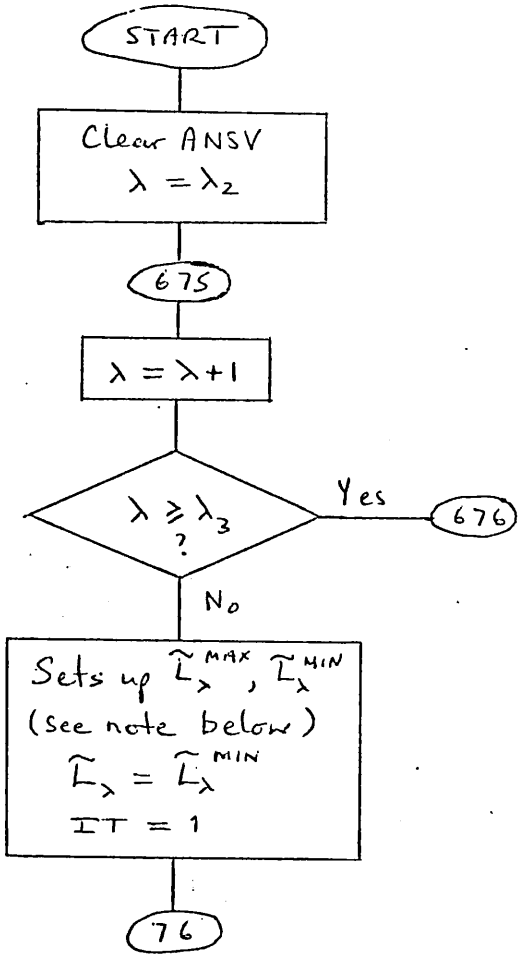
The portion of the exchange coefficient which involves multiple summations over intermediate couplings is evaluated in RECPSX.

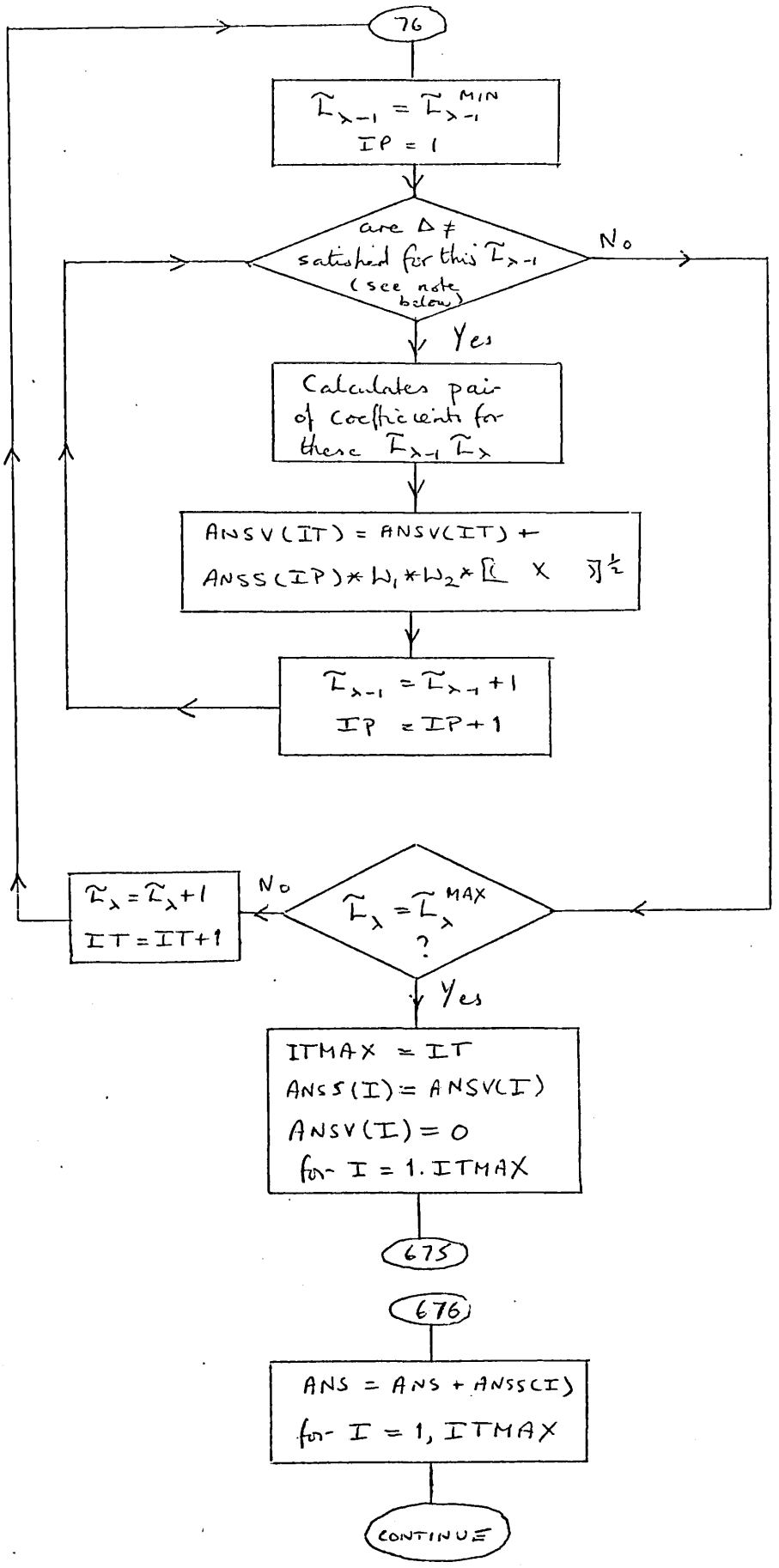
RECPSX

This subroutine is called by RECØPS and evaluates the portion of an exchange type coefficient which involves multiple summations over intermediate couplings. We recall that in general this is a sum of products of coefficients of the form

$$\sum_{\tilde{L}_{\lambda_2}\cdots\tilde{L}_{\lambda_3-1}} \prod_{\lambda=\lambda_2+1}^{\lambda_3-1} \langle \tilde{L}_{\lambda-1}\, l\,(L^{\alpha}_{\lambda-1})\, \bar{L}_{\lambda}\, L^{\alpha}_{\lambda} \,|\, \tilde{L}_{\lambda-1}\, \bar{L}_{\lambda}\,(\tilde{L}_{\lambda})\, l\, L^{\alpha}_{\lambda}\rangle \langle \tilde{L}_{\lambda-1}\, l'\,(L^{\alpha'}_{\lambda-1})\, \bar{L}_{\lambda}\, L^{\alpha'}_{\lambda} \,|\, \tilde{L}_{\lambda-1}\, \bar{L}_{\lambda}\,(\tilde{L}_{\lambda})\, l'\, L^{\alpha'}_{\lambda}\rangle$$

The maximum and minimum values of $\tilde{L}_{\lambda_2}$ and $(\tilde{L}_{\lambda_3})$ will be determined by the triangular inequalities satisfied by the arguments of the coefficients which precede (and follow) the above sum of products. These triangular inequalities will depend on the particular type of recoupling coefficient being considered. Assuming that $\tilde{L}_{\lambda_2}^{\text{MIN}}$ and $\tilde{L}_{\lambda_2}^{\text{MAX}}$ have been determined, and that ANSS(IP) denotes the value of the preceeding product of recoupling coefficients for each possible value of $\tilde{L}_{\lambda_2}$, labelled by IP, we evaluate the sum of products of coefficients in the following manner.




76
$\tilde{L}_{\lambda-1} = \tilde{L}_{\lambda-1}^{MIN}$
IP = 1
are Δ ≠ satisfied for this $\tilde{L}_{\lambda-1}$ (see note below)
No
Yes
Calculates pair of coefficients for these $\tilde{L}_{\lambda-1}$ $\tilde{L}_{\lambda}$
ANSV(IT) = ANSV(IT) +
ANSS(IP) * W1 * W2 * [X] ½
$\tilde{L}_{\lambda-1} = \tilde{L}_{\lambda-1} + 1$
IP = IP + 1
$\tilde{L}_{\lambda} = \tilde{L}_{\lambda} + 1$
IT = IT + 1
No
$\tilde{L}_{\lambda} = \tilde{L}_{\lambda}^{MAX}$?
Yes
ITMAX = IT
ANSS(I) = ANSV(I)
ANSV(I) = 0
for I = 1. ITMAX
675
676
ANS = ANS + ANSS(I)
for I = 1, ITMAX
CONTINUE

Note: $\tilde{L}_\lambda^{MAX}$, $\tilde{L}_\lambda^{MIN}$ are determined from the triangular inequalities

$$|\ell - L_\lambda^{a}| \leq \tilde{L}_\lambda \leq \ell + L_\lambda^{a}$$

$$|\ell - L_\lambda^{a'}| \leq \tilde{L}_\lambda \leq \ell' + L_\lambda^{a'}$$

after choosing a particular value of $\tilde{L}_{\lambda-1}$ we check the other inequality

$$|\tilde{L}_\lambda - \tilde{L}_\lambda| \leq \tilde{L}_{\lambda-1} \leq \bar{L}_\lambda + \tilde{L}_\lambda$$

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Scattering of Electrons by Atomic Systems*

KENNETH SMITH AND LESLEY A. MORGAN
Department of Physics, University of Nebraska, Lincoln, Nebraska
(Received 20 March 1967)

The theory of the scattering of electrons by atoms or ions with any number of incomplete subshells is developed within the Hartree-Fock, or close-coupling, approximation. Allowance is made for the target system to be excited to any electronic configuration constructed from discrete orbitals. The one-electron orbitals of the discrete subshells are assumed known; the scattering (continuum) functions are given as the solutions of coupled integrodifferential equations with prescribed boundary conditions. The form of these equations is such that the continuum functions are orthogonal to all the discrete orbitals. The potential terms appearing in the equations are written in terms of the generalized angular momentum recoupling coefficients. A technique for calculating these coefficients on a computer, which is a complicated algebraic problem, is presented in an Appendix. A computer code for calculating the various elastic, inelastic, and photoionization cross sections has been written and is currently being tested.

1. INTRODUCTION

THE scattering of electrons by many electron systems has been studied by Seaton[1] and by Vainstein and Sobel'man.[2] Seaton showed that the only consistent means of obtaining antisymmetric wave functions in approximate solutions is to make the expansion explicitly antisymmetric. He then analyzed in detail the configuration $nl^q kl$. In this case, the antisymmetrized wave function for a system of $(N+1)$ electrons initially in the state Γ' is

$$\psi(\Gamma',\mathbf{x}_1\cdots\mathbf{x}_{N+1})=(N+1)^{-1/2}\sum_{p=1}^{N+1}(-1)^{N+1-p}\times\sum_{\Gamma}\Phi(\gamma l_p LS\mathbf{X}\hat{r}_p\sigma_p)\frac{F_{\Gamma\Gamma'}(r_p)}{r_p},\quad(1)$$

where $\mathbf{X}=\mathbf{x}_1\cdots\mathbf{x}_N$, with $\mathbf{x}_i$ denoting the space ($\mathbf{r}$) and spin (σ) coordinates of electron i. The quantity γ denotes all the quantum numbers of the N-electron target, while l_p represents the orbital and spin angular momentum of the projectile; L and S are the total quantum numbers.

Vainstein and Sobel'man considered the case of two groups of equivalent electrons.

Calculations of the cross sections for the collision of electrons with many electron atoms have been performed by numerous authors in a variety of different approximations, e.g., Bauer and Browne.[3] Extensive calculations are currently under study by Peterkop and Karule,[4] Krueger and Czyzak,[5] and Smith, Henry, and Burke.[6,7] All these calculations involve only a single incomplete subshell in the target atom, and only a single-electron configuration in the expansion over Γ in Eq. (1).

Recent developments in the calculation of matrix elements of one and two electron operators between wave functions describing configurations with several incomplete subshells (see Shore[8] and Fano[9]) have indicated the method for formulating the general electron-atom problem. In the present paper, the notation of Fano is used to take into account the actual or virtual excitation of any number of atomic terms.

The need for developing the formalism presented in this paper is due to the failure of single-configuration theories to predict the low-energy cross sections for electron-atom scattering (see Smith *et al.*[7]) to provide a close-coupling framework for discussing auto-ionization[10] and photo-ionization[11] since the close-coupling approximation has proved so successful for simple systems,[12] and to provide a theory which will allow the calculation of inelastic cross sections involving a change in the electron configuration.

In Sec. (2), the form of the trial wave function to be substututed into the variational principle is discussed. In Sec. (3), the techniques for evaluating the various matrix elements are presented. Finally, in Sec. (4), the radial equations for the continuum functions are derived.

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2. TRIAL WAVE FUNCTION

An unsymmetrized wave function of an N electron atomic system is (see Fano[9])

$$\psi_u(q\gamma_T\mathbf{X})=[\prod_\lambda (q_\lambda|nl_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda\})]^{\gamma_T}, \quad (2)$$

where γ_T denotes the complete set of quantum numbers which specify the target T. The wave function for each subshell λ, of principal quantum number n and orbital l, with resultant quantum numbers α_λ S_λ L_λ, is antisymmetrized and their angular momenta are compounded to give α S L for the target. The unsymmetrized wave function for an $(N+1)$ electron system can be expanded using the functions of Eq. (2) as a basis:

$$\psi_u(q\mathbf{X}\mathbf{x}_{N+1})=\sum_{\gamma_T}\psi_u(q\gamma_T\mathbf{X})\bar{F}_{\gamma_T}(\mathbf{x}_{N+1}), \quad (3)$$

where we shall assume the sum to include several distinct configurations, and the coefficients $\bar{F}$ can be expanded also in two steps:

$$\bar{F}_{\gamma_T}(\mathbf{x}_{N+1})=\sum_{m_s}\chi_{m_s}^{1/2}(\sigma_{N+1})\mathfrak{F}_{\gamma_T m_s}(\mathbf{r}_{N+1})$$

and

$$\mathfrak{F}_{\gamma_T m_s}(\mathbf{r}_{N+1})=\sum_{l_T m_T} f_{\gamma_T m_s l_T m_T}(r_{N+1})Y_{l_T m_T}(\hat{r}_{N+1})r_{N+1}^{-1},$$

where l_T is the orbital angular momentum of the projectile relative to the target.

Combining the above results we obtain

$$\psi_u(q\mathbf{X}\mathbf{x}_{N+1})=\sum_{\gamma_T l_T L M_L S M_S}[\psi_u(q\gamma_T\mathbf{X})\times(N+1|k_T l_T\tfrac{1}{2}\})]^\Gamma \times\frac{\bar{F}_\Gamma(r_{N+1})}{r_{N+1}}, \quad (4)$$

where Γ denotes the complete set of quantum numbers $(\gamma_T \tfrac{1}{2} l_T L M_L S M_S)$ and where the $\times$ denotes the vector coupling of the N-electron function and the single-electron spin-angle function $(N+1|k_T l_T \tfrac{1}{2}\})$, and

$$\bar{F}_\Gamma(r_{N+1})=\sum_{m_s m_T}(L_T l_T M_{L_T} m_T|LM_L) \times(S_T\tfrac{1}{2}M_{S_T}m_s|SM_S)f_{\gamma_T m_s l_T m_T}(r_{N+1}), \quad (5)$$

where $L_T M_{L_T} S_T M_{S_T}$ are the total orbital and spin quantum numbers of the target T and their z components.

The unsymmetrized wave function of Eq. (4) will be written

$$\psi_u(q\mathbf{X}\mathbf{x}_{N+1})=\sum_\Gamma\psi_u(q\Gamma,\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\bar{F}_\Gamma(r_{N+1})r_{N+1}^{-1}. \quad (6)$$

Asymptotically, the radial functions are superpositions of ingoing and outgoing waves

$$\bar{F}_\Gamma\sim A_\Gamma e^{-i\theta_\Gamma}-B_\Gamma e^{i\theta_\Gamma};$$

$$\theta_\Gamma=k_\Gamma r-\tfrac{1}{2}l_\Gamma\pi+\left(\frac{Z-N}{k}\right)\ln 2k_\Gamma r+\sigma_{l_\Gamma},$$

where the S matrix is defined by

$$B_\Gamma\equiv\sum_{\Gamma'}S_{\Gamma\Gamma'}A_{\Gamma'},$$

where the sum Γ' is taken over the incident channels.

Therefore a new radial function F can be defined by

$$\bar{F}_\Gamma\equiv\sum_{\Gamma'}F_{\Gamma\Gamma'}(r)\sim\sum_{\Gamma'}A_{\Gamma'}[\delta_{\Gamma\Gamma'}e^{-i\theta_\Gamma}-S_{\Gamma\Gamma'}e^{i\theta_\Gamma}]. \quad (7)$$

In terms of these new radial functions F, Eq. (6) is therefore

$$\psi_u(q\mathbf{X}\mathbf{x}_{N+1})=\sum_{\Gamma\Gamma'}\psi_u(q\Gamma,\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\times F_{\Gamma\Gamma'}(r_{N+1})r_{N+1}^{-1}, \quad (8)$$

which is the total, unsymmetrized, wave function for the entire system (projectile+target).

For the system $(p+T)$ initially in the quantum state Γ', the wave function is

$$\psi_u(q\Gamma'\mathbf{X}\mathbf{x}_{N+1})\equiv\sum_\Gamma\psi_u(q\Gamma\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\times F_{\Gamma\Gamma'}(r_{N+1})r_{N+1}^{-1}. \quad (9)$$

The wave function for the target system will be constructed from Hartree-Fock orbitals, $P_{nl}(r)$, which, strictly speaking will depend upon Γ. In this paper we shall ignore this dependence. We can expect this assumption to be valid for inner closed-shell orbitals. Its validity for incomplete outer subshells will be tested by running the computer code with the different sets of P_{nl} and observing the variation of the cross sections. If this variation is substantial, then the problem will have to be reformulated including the Γ dependence in P_{nl}; this will result in considerable complication of the algebra and many more radial equations to be solved.

In order to have a properly antisymmetrized wave function, we antisymmetrize the target function, Eq. (2), as proposed by Fano[9]:

$$\psi(\gamma_T\mathbf{X})=\mathfrak{N}(N_\lambda)^{-1/2}\sum_q(-1)^{P_q}\psi_u(q,\gamma_T\mathbf{X}), \quad (10)$$

and then antisymmetrize with respect to the projectile as in (1) to give a total antisymmetric function

$$\psi(\Gamma',\mathbf{x}_1\cdots\mathbf{x}_{N+1})=(N+1)^{-1/2}\times\sum_{p=1}^{N+1}(-1)^{N+1-p}\sum_\Gamma\psi(\Gamma\mathbf{X}\hat{r}_p\sigma_p)F_{\Gamma\Gamma'}(r_p)r_p^{-1}, \quad (11)$$

instead of the unsymmetrized form given in Eq. (9),

where

$$\psi(\Gamma\mathbf{X}\hat{r}_p\sigma_p)=\mathfrak{A}(N_\lambda)^{-1/2}\sum_q(-1)^{P_q}\psi_u(q\Gamma\mathbf{X}\hat{r}_p\sigma_p)$$

$$=\mathfrak{A}(N_\lambda)^{-1/2}\sum_q(-1)^{P_q}[\prod_\lambda(q_\lambda|nl_\lambda^{N_\lambda}\alpha_\lambda L_\lambda S_\lambda\}]^{\gamma_T}\times(p|k_T l_T\tfrac{1}{2}\}]^\Gamma. \quad (12)$$

Here we assign even parity to the normal order of labels 1, 2, 3, $\cdots$, $p-1$, $p+1$, $\cdots$, N, $N+1$ and a parity P_q to any q according to the number of permutations by which it differs from normal.

The continuum functions $F_{\Gamma\Gamma'}(r_p)$ will be determined from a variational principle, subject to the constraint

$$\int_0^\infty dr\, F_{\Gamma\Gamma'}(r)P_{nl_\lambda}(r)=0. \quad (13)$$

This orthogonalization of F with respect to the discrete orbitals can be interpreted as preventing the projectile from being captured into any incomplete subshell included in the eigenfunction expansion, Eq. (3). Because of the assumed form of the Hamiltonian, each set of $LS\pi$ of the $(N+1)$ electron system is decoupled from the other sets. Consequently to allow for electron capture we must include in our trial function, $(N+1)$ electron wave functions in which there is an extra electron in one of the incomplete subshells included in the eigenfunction expansion, i.e., functions of the form

$$\Phi_\mu(LS\pi,\mathbf{x}_1\cdots\mathbf{x}_{N+1})=\mathfrak{A}(N_\lambda{}^\mu)^{-1/2}\times\sum_{q_\mu}(-1)^{P_q}\phi_u(q_\mu LS\pi\mathbf{x}_1\cdots\mathbf{x}_{N+1}), \quad (14)$$

where μ runs over all the incomplete subshells included in the eigenfunction expansion which can contribute to the $LS\pi$, $\sum_\lambda N_\lambda{}^\mu=\mathrm{N}+1$, and ϕ_u is an unsymmetrized wave function of the form given in Eq. (2).

The trial function ψ_t is taken to be a linear superposition of functions (11) and (14), viz.,

$$\psi_t(\Gamma_i\mathbf{x}_1\cdots\mathbf{x}_{N+1})=\psi(\Gamma_i,\mathbf{x}_1\cdots\mathbf{x}_{N+1})+\sum_\mu C_\mu{}^{\Gamma_i}\mathfrak{A}(N_\lambda{}^\mu)^{-1/2}\times\sum_{q_\mu}(-1)^{P_q}\phi_u(q_\mu LS\pi,\mathbf{x}_1\cdots\mathbf{x}_{N+1}), \quad (15)$$

where the coefficients $C_\mu{}^\Gamma$ are completely arbitrary.

In Secs. (3.2) and (3.3), it will be necessary to separate out the interacting electron in the subshell ρ from its equivalent electrons. This is accomplished using coefficients of fractional parentage [see Fano's Eqs. (24) and (25)].

3. VARIATIONAL PRINCIPLE

We consider

$$\delta[L_{kl}-\tfrac{1}{2}K_{kl}]=0, \quad (16)$$

where the elements of the real and symmetric reactance matrix K_{kl} are defined in terms of the asymptotic form of F in the open channels

$$F_{\Gamma_k\Gamma_l}\sim k_k^{-1/2}[\delta_{kl}\sin\theta_k+K_{kl}\cos\theta_k], \quad (17)$$

and

$$L_{kl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi_t(\Gamma_k,\mathbf{x}_1\cdots\mathbf{x}_{N+1})\times[H_N+H_1(\mathbf{x}_{N+1})+\sum_{\alpha=1}^{N}r_{N+1,\alpha}{}^{-1}-E]\times\psi_t(\Gamma_l,\mathbf{x}_1\cdots\mathbf{x}_{N+1}), \quad (18)$$

where the variations in the continuum functions are such that

$$\delta F_{kl}\sim k_k^{-1/2}\delta K_{kl}\cos\theta_k, \quad (19)$$

subject to the constraint of Eq. (13), and the variations $\delta C_\mu{}^\Gamma$ are arbitrary. Substituting Eq. (15) into (18) gives three types of terms; first, terms independent of C but quadratic in F; second, terms linear in both C and F; third, terms quadratic in C, but independent of F. The first two types of terms will lead to the Hartree-Fock equations for F when we consider $F\rightarrow F+\delta F$. These equations will contain factors linear in C. When variations $C\rightarrow C+\delta C$ are taken in (16), the last two terms give an expression for the C's which will be substituted into the Hartree-Fock equations.

Making the substitution for the first ψ_t in Eq. (18)

$$L_{kl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\times[(N+1)^{-1/2}\sum_{p=1}^{N+1}(-1)^{N+1-p}\sum_{\Gamma_i}\psi(\Gamma_i\mathbf{X}\hat{r}_p\sigma_p)\times F_{ik}(r_p)r_p{}^{-1}+\sum_\mu C_\mu{}^{\Gamma_k}\Phi_\mu(L_kS_k\pi_k,\mathbf{x}_1\cdots\mathbf{x}_{N+1})]\times[H-E]\psi_t(\Gamma_l\mathbf{x}_1\cdots\mathbf{x}_{N+1}).$$

Since H is symmetric under interchange of any pair of electrons and $\psi_t(\Gamma_l)$ is antisymmetric, then

$$L_{kl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\{(N+1)^{1/2}\times\sum_{\Gamma_i}\psi(\Gamma_i\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})F_{ik}(r_{N+1})r_{N+1}{}^{-1}+\sum_\mu C_\mu{}^{\Gamma_k}\Phi_\mu(L_kS_k\pi_k\mathbf{x}_1\cdots\mathbf{x}_{N+1})\}\times[H-E]\psi_t(\Gamma_l\mathbf{x}_1\cdots\mathbf{x}_{N+1}). \quad (20)$$

A. C-Independent Terms

The C-independent terms are

$$L_{ik,jl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}(N+1)^{1/2}\psi(\Gamma_i\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\times F_{ik}(r_{N+1})r_{N+1}{}^{-1}[H-E](N+1)^{-1/2}\times\sum_{p=1}^{N+1}(-1)^{N+1-p}\psi(\Gamma_j\mathbf{X}\hat{r}_p\sigma_p)F_{lj}(r_p)r_p{}^{-1}, \quad (21)$$

which can be separated into so-called direct and exchange terms by writing $\sum_p$ in the form

$$\psi(\Gamma_j X\hat{r}_{N+1}\sigma_{N+1})F_{jl}(r_{N+1}) + \sum_{p=1}^{N}(-1)^{N+1-p}\psi(\Gamma_j X\hat{r}_p\sigma_p)F_{lj}(r_p).$$

The fact that ψ is antisymmetric under interchange of any pair of labels in the target function can be used to give Eq. (21) in the form

$$L_{ik,jl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i X\hat{r}_{N+1}\sigma_{N+1})\frac{F_{ik}(r_{N+1})}{r_{N+1}} \times[H-E]\psi(\Gamma_j X\hat{r}_{N+1}\sigma_{N+1})\frac{F_{jl}(r_{N+1})}{r_{N+1}} -N\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i X\hat{r}_{N+1}\sigma_{N+1}) \times\frac{F_{ik}(r_{N+1})}{r_{N+1}}[H-E]\psi(\Gamma_j X\hat{r}_N\sigma_N)\frac{F_{jl}(r_N)}{r_N}, \quad (22)$$

where the first term is the direct term and the second is the exchange term.

1. Exchange Terms

The matrix element of the N electron Hamiltonian, H_N, will include an overlap integral

$$\int d\mathbf{x}_{N+1}F_{ik}(\mathbf{x}_{N+1})R_{nl}(\mathbf{x}_{N+1})=0, \quad (23)$$

and so will the E term. Furthermore, the term $H_1(x_{N+1})$ will contain

$$\int d\mathbf{x}_N R_{nl}(\mathbf{x}_N)F_{jl}(\mathbf{x}_N)=0. \quad (24)$$

Consequently, the second term in Eq. (22) reduces to

$$L_{ik,jl}{}^E=-N\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i X\hat{x}_{N+1}) \times\frac{F_{ik}(r_{N+1})}{r_{N+1}}\frac{1}{r_{N+1,N}}\psi(\Gamma_j X\hat{x}_N)\frac{F_{jl}(r_N)}{r_N}, \quad (25)$$

where $r_{N+1,N}=|\mathbf{r}_{N+1}-\mathbf{r}_N|$, since the other terms in $\sum_\alpha$ will contain (24). Substituting Eq. (12) into (25) gives

$$L_{ik,jl}{}^E=-N[\mathfrak{N}(N_\lambda{}^i)\mathfrak{N}(N_\lambda{}^j)]^{-1/2}\sum_{q_iq_j}(-1)^{P_{q^i}+P_{q^j}} \times\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}(r_Nr_{N+1})^{-1}\psi_u(q_i\Gamma_i X\hat{x}_{N+1}) \times F_{ik}(r_{N+1})\frac{1}{r_{N,N+1}}\psi_u(q_j\Gamma_j X\hat{x}_N)F_{jl}(r_N), \quad (26)$$

where the distributions q_i, q_j are such that electrons labeled $N+1$, N, respectively, are in the continuum; in other words, neither F_{ik} nor F_{jl} will contain "spectator" electrons. "Spectator" electrons are those with labels other than N and $N+1$, the labels of the two-electron operator. Consequently, in Eq. (26) only one interacting electron can appear in the discrete subshells. If the configuration of the electrons in γ_i differ by two electron jumps from the configuration in γ_j, then the matrix element vanishes, because there will be a factor

$$\int d\mathbf{x}R_{nl_i}(\mathbf{x})R_{nl_j}(\mathbf{x})=0 \quad \text{for} \quad (nl)_i\neq(nl)_j, \quad (27)$$

provided discrete one-electron orbitals are used which are orthogonal to one another whether the subshell is complete or incomplete. If the configuration of electrons differ by one electron jump, e.g., $1s^22s^22p^6$ compared with $1s^22s2p^6nl$, then the interacting electron will be assigned to a $2s$ orbital in the former configuration and to nl in the latter, and the configuration of the spectator electrons among the subshells is determined uniquely. If $\{N_\lambda{}^i\}$ and $\{N_\lambda{}^j\}$ are identical, then the second of the interacting electrons will be found in the same subshell in Γ_i and Γ_j and can be assigned to each of the subshells in turn; that is to say, there are as many configurations of spectator electrons as there are subshells with $N_\lambda{}^i=N_\lambda{}^j\neq0$. We note that the matrix element will vanish unless it is diagonal in the quantum numbers of the spectator electrons.

Symbolically, the exchange terms of Eq. (20) can be written as

$$L_{kl}{}^E=\sum_{\Gamma_i\Gamma_j}L_{ik,jl}{}^E=\sum_{\Gamma_i\Gamma_j}\sum_{\bar{C}}\prod_{\lambda=1a}^{\max(b_i,b_j)}\delta(N_\lambda{}^i,N_\lambda{}^j+\delta_{\lambda\rho_i}-\delta_{\lambda\rho_j}) \times\bar{L}_{ik,jl}{}^E, \quad (28)$$

where $\sum_C$ denotes the sum over possible configurations of spectator electrons. The interacting electron with label N is assigned to $R_{nl(\rho_i)}$ in $\psi(\Gamma_i)$, while the interacting electron with label $N+1$ is assigned to $R_{nl(\rho_j)}$ in $\psi(\Gamma_j)$. If more than one configuration is included in $\sum_\Gamma$ of Eq. (11) then the double sum over Γ_i and Γ_j in Eq. (28) will include terms with $N_\lambda{}^i\neq N_\lambda{}^j$ so that the δ will specify nonzero elements in this sum and designate the subshells which contain the interacting electrons. If $\rho_i\neq\rho_j$, then only a single configuration of spectator electrons is possible. If $\rho_i=\rho_j$, as in the formulations of Seaton and coworkers[5] and Smith, Henry, and Burke, then there will be as many terms in the sum over $\bar{C}$ as there are subshells with $N_\lambda{}^i=N_\lambda{}^j\neq0$.

For the remainder of this subsection we shall consider a particular configuration of spectator electrons; quantities with a bar over them refer to spectator electrons. Both the distributions q_i and q_j include a distribution $\bar{q}_i=\bar{q}_j=\bar{q}$ in order to give nonvanishing

contributions to Eq. (26). The number of different distributions of spectator electrons will be

$$\mathfrak{N}(\bar{N}_\lambda)=(N-1)!/\prod_\lambda(\bar{N}_\lambda!),\quad \sum_\lambda \bar{N}_\lambda=N-1, \quad (29)$$

and their contributions to $\sum_{q_i q_j}$ will be identical. The distributions in the interacting subshells are uniquely specified

$$q_{\rho_i}=\{\bar{q}_{\rho_i},N\} \quad \text{and} \quad q_{\rho_j}=\{\bar{q}_{\rho_j},N+1\}.$$

Now $P_{\bar{q}}$ takes all the spectators to normal order and in $\psi(\Gamma_i)$ label N will be in subshell $\lambda=\rho_i$; consequently, further

$$\sum_{\lambda=\rho_i+1}^{b_i}\bar{N}_\lambda$$

permutations will be required to put the labels of the atomic electrons in normal order, where b_i is the outermost subshell containing an electron in Γ_i. Hence

$$P_{q_i}=P_{\bar{q}}+\sum_{\lambda=\rho_i+1}^{b_i}\bar{N}_\lambda,$$

and similarly for P_{q_j} (since in the exchange term, "normal" order for the atomic electrons is $1\cdots N-1$, $N+1$, the label N being in the continuum). Therefore

$$P_{q_i}+P_{q_j}=\sum_{\lambda=\rho_i+1}^{b_i}\bar{N}_\lambda+\sum_{\lambda=\rho_j+1}^{b_j}\bar{N}_\lambda\equiv\Delta P_{ij}. \quad (30)$$

We can now write, from (26) and (28)–(30), that

$$\bar{L}_{ik,jl}{}^E=-N\mathfrak{N}(\bar{N}_\lambda)[\mathfrak{N}(N_\lambda{}^i)\mathfrak{N}(N_\lambda{}^j)]^{-1/2}\times(-1)^{\Delta P_{ij}}\langle r_{N,N+1}{}^{-1}\rangle, \quad (31)$$

where the outside factor becomes

$$[N_{\rho_i}N_{\rho_j}]^{1/2}. \quad (32)$$

The matrix element in Eq. (31) vanishes unless the representations are diagonal in the quantum numbers of the spectator electrons. For those subshells which just contain spectators

$$\{nl_\lambda{}^{N_\lambda{}^i}\alpha_\lambda{}^i S_\lambda{}^i L_\lambda{}^i|q_\lambda{}^i\}=\{nl_\lambda{}^{\bar{N}_\lambda}\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda|\bar{q}_\lambda\}, \quad (33a)$$

and for those same subshells

$$(q_\lambda{}^j|nl_\lambda{}^{N_\lambda{}^j}\alpha_\lambda{}^j S_\lambda{}^j L_\lambda{}^j\}=(\bar{q}_\lambda|nl_\lambda{}^{\bar{N}_\lambda}\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda\}, \quad (33b)$$

while for the subshells ρ_i and ρ_j, containing the interacting electrons N and $N+1$ respectively, we separate out the interacting electron from the N equivalent particles in the subshell using coefficients of fractional parentage

$$\{nl_\rho{}^{N_\rho}\alpha_\rho S_\rho L_\rho|q_\rho)=\sum_{\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho}(l_\rho{}^{N_\rho}\alpha_\rho S_\rho L_\rho\{|l_\rho{}^{\bar{N}_\rho}\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho l_\rho)\times[\{nl_\rho{}^{\bar{N}_\rho}\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho|\bar{q}_\rho)\times\{nl_\rho|N)]^{S_\rho L_\rho}, \quad (34)$$

where the first factor in the sum is a coefficient of fractional parentage (see Racah[13]). A similar separation is carried out for the ρ_j subshell.

Substituting the above results into Eq. (31) we obtain

$$\bar{L}_{ik,jl}{}^E=[N_{\rho_i}N_{\rho_j}]^{1/2}(-1)^{\Delta P_{ij}+1}\sum_{\bar{\alpha}_i\cdots\bar{L}_j}(l_{\rho_i}{}^{N_{\rho_i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}{}^{\bar{N}_{\rho_i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}l_{\rho_i})\times(l_{\rho_j}{}^{\bar{N}_{\rho_j}}\bar{\alpha}_{\rho_j}\bar{S}_{\rho_j}\bar{L}_{\rho_j}l_{\rho_j}|\}l_{\rho_j}{}^{N_{\rho_j}}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j})\langle\psi_{u\rho_i}(\Gamma_i)F_{ik}|\frac{1}{r_{N+1,N}}|\psi_{u\rho_j}(\Gamma_j)F_{jl}\rangle, \quad (35)$$

where $\psi_{u\rho_i}$ is defined by Fano to be

$$\psi_{u\rho_i}(\Gamma_i)=([\prod_{\lambda\neq\rho_i}\{nl_\lambda{}^{\bar{N}_\lambda}\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda|\bar{q}_\lambda)\times[\{nl_{\rho_i}{}^{\bar{N}_{\rho_i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}|\bar{q}_{\rho_i})\times\{nl_{\rho_i}|N)]^{S_{\rho_i}L_{\rho_i}}]^{\gamma_i}\times\{l_ik_i|N+1)\}^{\Gamma_i}, \quad (36)$$

where we recall $\{l_ik_i|N+1)$ is the spin-angle function associated with the projectile orbital F_{ik}.

In LS coupling, spin and orbital variables are tied together in the matrix element only by the connection between antisymmetrization and addition of angular momenta within each subshell. Writing

$$\mathcal{S}_i=\{\bar{S}_1\cdots\bar{S}_{\rho_i-1}(\bar{S}_{\rho_i\frac{1}{2}}(N))S_{\rho_i}\cdots\bar{S}_{b_i\frac{1}{2}}(N+1),\alpha_iS_i|, \quad (37a)$$

and

$$\Theta_i=\{\bar{L}_1\cdots\bar{L}_{\rho_i-1}(\bar{L}_{\rho_i}l_{\rho_i}(N))L_{\rho_i}\cdots\bar{L}_{b_i}l_i(N+1),\alpha_iL_i|, \quad (37b)$$

we obtain

$$\bar{L}_{ik,jl}{}^E=[N_{\rho_i}N_{\rho_j}]^{1/2}(-1)^{\Delta P_{ij}+1}\sum_{\bar{\alpha}_i\cdots\bar{L}_j}(l_{\rho_i}{}^{N_{\rho_i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}{}^{\bar{N}_{\rho_i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}l_{\rho_i})\times(l_{\rho_j}{}^{\bar{N}_{\rho_j}}\bar{\alpha}_{\rho_j}\bar{S}_{\rho_j}\bar{L}_{\rho_j}l_{\rho_j}|\}l_{\rho_j}{}^{N_{\rho_j}}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j})\langle\mathcal{S}_i|\mathcal{S}_j)\rangle\langle\Theta_iF_{ik}|\frac{1}{r_{N,N+1}}|\Theta_jF_{jl}\rangle. \quad (38)$$

[13] G. Racah, Phys. Rev. 63, 367 (1943).

The spin recoupling coefficient $\langle S_i|S_j\rangle$ will depend upon the problem under consideration. For example, for a target atom with configuration $1s^2 2s^2 2p^q$ when no electron jumps are permitted, the sum over $\bar{C}$ in Eq. (28) will contain three terms, one of them having the factor

$$\langle(\bar{S}_{2p\frac{1}{2}}(N))S_{2p}{}^i,\tfrac{1}{2}(N+1);S_i|(\bar{S}_{2p\frac{1}{2}}(N+1))S_{2p}{}^j,\tfrac{1}{2}(N);S_j\rangle=\delta_{S_iS_j}[(2S_{2p}{}^i+1)(2S_{2p}{}^j+1)]^{1/2}W(S_{2p}{}^i\tfrac{1}{2}\tfrac{1}{2}S_{2p}{}^j;\bar{S}_{2p}S_i). \quad (39)$$

Upon expanding $r_{N,N+1}^{-1}$ in terms of Legendre polynomials $P_t(\hat{r}_N\cdot\hat{r}_{N+1})$ the radial integrals reduce to Slater integrals and the matrix element is

$$\begin{aligned}\langle\Theta_iF_{ik}|\frac{1}{r_{N,N+1}}|\Theta_jF_{jl}\rangle&=\sum R_t(nl_{\rho_i}F_{ik},F_{jl}nl_{\rho_j})\langle\bar{L}_1\cdots(\bar{L}_{\rho_i}l_{\rho_i}(N))L_{\rho_i}\cdots\bar{L}_{b_i}l_i(N+1),L_i|\\&\qquad\times P_t(\hat{r}_N\cdot\hat{r}_{N+1})|\bar{L}_1\cdots(\bar{L}_{\rho_j}l_{\rho_j}(N+1))L_{\rho_j}\cdots\bar{L}_{b_j}l_j(N),L_j\rangle\\&=\sum_t R_t(nl_{\rho_i}F_{ik},F_{jl}nl_{\rho_j})(l_{\rho_i}\|C^t\|l_j)(l_{\rho_j}\|C^t\|l_i)[(2l_{\rho_i}+1)(2l_{\rho_j}+1)]^{-1/2}\\&\qquad\times\langle\bar{L}_1\cdots[\bar{L}_{\rho_i}(l_jt)l_{\rho_i}]L_{\rho_i}\cdots\bar{L}_{b_i}l_i,L_i|\bar{L}_1\cdots[\bar{L}_{\rho_j}(ll_i)l_{\rho_j}]L_{\rho_j}\cdots\bar{L}_{b_j}l_j,L_j\rangle, \quad (40)\end{aligned}$$

using the method of Fano, Prats, and Goldschmidt[14] and where the orbital recoupling coefficient can be calculated in the same way as in the spin coefficient (see Appendix). Combining Eqs. (28), (38), and (40), we obtain

$$\begin{aligned}L_{kl}{}^E=\sum_{\Gamma_i\Gamma_j}\Big[\prod_\lambda\delta(N_\lambda{}^i,N_\lambda{}^j+\delta_{\lambda\rho_i}-\delta_{\lambda\rho_j})\Big]\sum_{\bar{C}}[N_{\rho_i}N_{\rho_j}]^{1/2}(-1)^{\Delta P_{ij}+1}[(2l_{\rho_i}+1)(2l_{\rho_j}+1)]^{-1/2}\\\times\sum_{\bar{\alpha}_i\cdots\bar{L}_j}(l_{\rho_i}{}^{N_{\rho^i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}{}^{\bar{N}_{\rho^i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}l_{\rho_i})(l_{\rho_j}{}^{\bar{N}_{\rho^j}}\bar{\alpha}_{\rho_j}\bar{S}_{\rho_j}\bar{L}_{\rho_j}l_{\rho_j}|\}l_{\rho_j}{}^{N_{\rho^j}}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j})\\\times\langle S_i|S_j\rangle^E\sum_t R_t(nl_{\rho_i}F_{ik},F_{jl}nl_{\rho_j})(l_{\rho_i}\|C^t\|l_j)(l_{\rho_j}\|C^t\|l_i)\langle0_i|0_j\rangle^E, \quad (41)\end{aligned}$$

where the final factor in Eq. (41) denotes the exchange orbital recoupling coefficient as written out in Eq. (40).

2. Direct Terms

These terms are given by the first term in Eq. (22)

$$L_{ik,jl}{}^D=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i\mathbf{X}\hat{x}_{N+1})\frac{F_{ik}(r_{N+1})}{r_{N+1}}[H-E]\psi(\Gamma_j\mathbf{X}\hat{x}_{N+1})\frac{F_{jl}(r_{N+1})}{r_{N+1}}, \quad (42)$$

where ψ is defined in Eq. (12). It will be assumed (as in Smith *et al.*[6]) that

$$\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_N\psi(\gamma_i\mathbf{X})[H_N-\mathcal{E}]\psi(\gamma_j\mathbf{X})=0. \quad (43)$$

Any calculation on $N>1$ target systems must use approximate wave functions, i.e., functions which are the eigenfunctions of an N-electron Hamiltonian $H_N(\text{approx})\neq H_N(\text{exact})$. Consequently, (43) introduces an inconsistency which should lead to a small error if accurate atomic orbitals are used. Because of this assumption, the H_N term in Eq. (42) is

$$\int dr_{N+1}F_{ik}(r_{N+1})\mathcal{E}_i\delta_{ij}F_{jl}(r_{N+1}). \quad (44)$$

Due to the orthonormality of $\psi(\gamma_i\mathbf{X})$ the H_1 term is

$$\delta_{ij}\int dr_{N+1}F_{ik}(r_{N+1})\left[-\frac{1}{2}\left(\frac{d^2}{dr_{N+1}{}^2}-\frac{l_i(l_i+1)}{r_{N+1}{}^2}+\frac{2Z}{r_{N+1}}\right)\right]F_{jl}(r_{N+1}), \quad (45)$$

which leaves us with the evaluation of

$$\int d\hat{x}_{N+1}\int d\mathbf{x}_1\cdots d\mathbf{x}_N\psi(\Gamma_i\mathbf{X}\hat{x}_{N+1})\sum_{\alpha=1}^{N}\frac{1}{r_{N+1,\alpha}}\psi(\Gamma_j\mathbf{X}\hat{x}_{N+1})\equiv V_{ij}(r_{N+1}). \quad (46)$$

[14] U. Fano, F. Prats, and Z. Goldschmidt, Phys. Rev. 129, 2634 (1963).

As for exchange terms, the matrix element will be nonzero only for zero or one-electron jumps, i.e.,

$$V_{ij}(r)=\sum_{C}\prod_{\lambda=1s}^{\max(b_i,b_j)}\delta(N_\lambda^i,N_\lambda^j+\delta_{\lambda\rho_i}-\delta_{\lambda\rho_j})\qquad V_{ij}^D(r)\,, \tag{47}$$

with

$$V_{ij}^D(r)=[N_{\rho_i}N_{\rho_j}]^{1/2}(-1)^{\Delta P ij}\sum_{\bar{\alpha}_i\cdots L_j}(l_{\rho_i}^{N_\rho^i}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}^{\bar{N}_\rho^i}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}l_{\rho_i})$$
$$\times(l_{\rho_j}^{\bar{N}_\rho^j}\bar{\alpha}_{\rho_j}\bar{S}_{\rho_j}\bar{L}_{\rho_j}l_{\rho_j}|\}l_{\rho_j}^{N_\rho^j}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j})\langle\mathcal{S}_i|\mathcal{S}_j\rangle^D[(2l_{\rho_i}+1)(2l_j+1)]^{-1/2}$$
$$\times\sum_t y_t(nl_{\rho_i}nl_{\rho_j}r)(l_{\rho_i}\|C^t\|l_{\rho_j})(l_j\|C^t\|l_i)\langle 0_i|0_j\rangle^D\,, \tag{48}$$

where the direct orbital recoupling coefficient is defined by

$$\langle 0_i|0_j\rangle^D=\langle\bar{L}_1\cdots[\bar{L}_{\rho_i}(l_{\rho_j}l)l_{\rho_i}]L_{\rho_i}\cdots\bar{L}_{b_i}l_i,\alpha_iL_i|\bar{L}_1\cdots(\bar{L}_{\rho_j}l_{\rho_j})L_{\rho_j}\cdots\bar{L}_{b_j}(ll_i)l_j,\alpha_jL_j\rangle\,, \tag{49a}$$

and the direct spin recoupling coefficient is defined to be

$$\langle\mathcal{S}_i|\mathcal{S}_j\rangle^D=\langle\bar{S}_1\cdots(\bar{S}_{\rho_i}\tfrac{1}{2}(N)S_{\rho_i}\cdots\bar{S}_{b_i}\tfrac{1}{2}(N+1),\alpha_iS_i|\bar{S}_1\cdots(\bar{S}_{\rho_j}\tfrac{1}{2}(N))S_{\rho_j}\cdots\bar{S}_{b_j}\tfrac{1}{2}(N+1),\alpha_jS_j\rangle. \tag{49b}$$

Collecting the various factors of the direct terms together gives

$$L_{ik,jl}^D=\int dr_{N+1}F_{ik}(r_{N+1})\left[\delta_{ij}\left(-\frac{1}{2}\left\{\frac{d^2}{dr_{N+1}^2}-\frac{l_i(l_i+1)}{r_{N+1}^2}+\frac{2Z}{r_{N+1}}\right\}+\mathcal{E}_i-E\right)+V_{ij}(r_{N+1})\right]F_{ij}(r_{N+1})\,. \tag{50}$$

B. Terms Linear in C

From Eqs. (15) and (20) we see that the two terms linear in C are

$$L_{ik,jl}^C=\int\cdots\int dx_1\cdots dx_{N+1}(N+1)^{1/2}\Big\{\psi(\Gamma_iX\hat{x}_{N+1})\frac{F_{ik}(r_{N+1})}{r_{N+1}}[H-E]\sum_\nu C_\nu^l\Phi_\nu(L_lS_l\pi_l)$$
$$+\sum_\mu C_\mu^k\Phi_\mu(L_kS_k\pi_k)[H-E]\psi(\Gamma_jX\hat{x}_{N+1})\frac{F_{jl}(r_{N+1})}{r_{N+1}}\Big\}\,. \tag{51}$$

The full term can be written

$$L_{kl}^C=\sum_i(L_{ik,l}^C+L_{k,il}^C)\,, \tag{52}$$

where the two terms on the right are defined in Eq. (51). The matrix elements of (H_N-E) vanish because they contain a factor like the l.h.s. of Eq. (23). From Green's theorem and the boundary conditions of the discrete one-electron orbitals Eq. (52) can be written in the form

$$L_{kl}^C=\sum_i(L_{ik,l}^C+L_{il,k}^C)\,, \tag{53}$$

where the two terms have the same structure, viz.,

$$L_{il,k}^C=(N+1)^{1/2}\sum_\mu C_\mu^k\int\cdots\int dx_1\cdots dx_{N+1}\psi(\Gamma_iX\hat{x}_{N+1})\frac{F_{il}(r_{N+1})}{r_{N+1}}\left[H_1(N+1)+\frac{N}{r_{N+1,N}}\right]\Phi_\mu(L_kS_k\pi_kx_1\cdots x_{N+1})\,. \tag{54}$$

We note that the configurations of $\psi(\Gamma_i)$ and $\Phi_\mu(L_kS_k\pi_k)$ necessarily differ by one electron jump, hence for a nonzero matrix element we must have an interacting electron in the "extra" orbital of Φ_μ. For the one-electron operator this implies that we must have the label $N+1$ in the extra orbital. To calculate the matrix element we must separate off $R_\rho(r_{N+1})$, the radial function of the only interacting electron, from Φ_μ using coefficients of fractional parentage; for the two-electron operator a further two fractional parentage coefficients are introduced, one each from ψ and Φ_μ. We have the matrix element

$$\langle H_1\rangle=(N+1)^{1/2}\sum_{\rho}\prod_\lambda\delta(N_\lambda^i,N_\lambda^\mu-\delta_{\lambda\rho})[\mathfrak{N}(N_\lambda^i)\mathfrak{N}(N_\lambda^\mu)]^{-1/2}\sum_{q^iq^\mu}(-1)^{P_{q^i}+P_{q^\mu}}\int\int\cdots\int dx_1\cdots dx_{N+1}$$
$$\times(l_\rho^{N_\rho}\alpha_\rho^\mu L_\rho^\mu S_\rho^\mu|\}l_\rho^{N_\rho^i}\alpha_\rho^iL_\rho^iS_\rho^il_\rho)\psi_u(q_i\Gamma_i)\frac{F_{il}(r_{N+1})}{r_{N+1}}H_1(N+1)\phi_{u\rho}(q_\mu L_kS_k\pi_k)\frac{R_\rho(r_{N+1})}{r_{N+1}}\,, \tag{54a}$$

where

$$\mathfrak{N}(N_\lambda{}^\mu)=\frac{(N+1)!}{\prod_\lambda (N_\lambda{}^\mu!)}, \tag{55}$$

and ψ_u and $\phi_{u\rho}$ do not include the radial functions of the electron with label $(N+1)$. Here, $N_\lambda{}^\mu$ denotes the number of electrons in the discrete subshell λ, with an extra electron in subshell $\lambda=\mu$ (compared with the configuration of the parent state γ.) For a properly antisymmetrized $(N+1)$ electron wave function we must allow for the label $(N+1)$ to be in any of the subshells for which $N_\lambda{}^\mu\neq 0$. The number of alternative configurations of electrons which are spectators for the interaction $H_1(N+1)$ is

$$\mathfrak{N}(\bar{N}_\lambda)=\frac{N!}{\prod_\lambda (\bar{N}_\lambda!)}.$$

Equation (54a) becomes

$$\langle H_1\rangle=\sum_\Gamma \prod_\lambda \delta(N_\lambda{}^i,N_\lambda{}^\mu-\delta_{\lambda\rho})N_\rho{}^{1/2}(-1)^{\Sigma_\lambda-\rho+1^{b^\mu}\,N_\lambda}\ (l_\rho{}^{N_\rho{}^\mu}\alpha_\rho{}^\mu S_\rho{}^\mu L_\rho{}^\mu|\}l_\rho{}^{N_\rho{}^i}\alpha_\rho{}^i S_\rho{}^i L_\rho{}^i l_\rho)$$
$$\times\int dr F_{il}\left\{-\frac{1}{2}\left(\frac{d^2}{dr^2}-\frac{l_\rho(l_\rho+1)}{r^2}+\frac{2Z}{r}\right)\right\}P_{nl_\rho}(r)$$
$$\times\langle S_\rho{}^i\cdots S_b{}^i\tfrac{1}{2},S_i|(S_\rho{}^i\tfrac{1}{2})S_\rho{}^\mu\cdots S_b{}^\mu,S_k\rangle\langle L_\rho{}^i\cdots L_b{}^i l_i,L_i|(L_\rho{}^i l_\rho)L_\rho{}^\mu\cdots L_b{}^\mu,L_k\rangle. \tag{56}$$

We note that $\langle L_\rho{}^i\cdots L_b{}^i l_i,L_i|(L_\rho{}^i l_\rho)L_\rho{}^\mu\cdots L_b{}^\mu,L_k\rangle$ will be nonzero only for $l_i=l_\rho$ since it contains

$$\int d\hat{x}_{N+1}Y_{l_i m}{}^*(\hat{x}_{N+1})\ Y_{l_\rho m}(\hat{x}_{N+1}).$$

This is equivalent to saying that the incident electron can only be captured into the incomplete subshell ρ if its orbital angular momentum equals that of the subshell. In general $\rho\neq\mu$ since the 'extra' orbital μ of Φ_μ may be matched by one in Γ_i. For example, if the target atom in state γ_i has configuration $1s^2 2s^2 2p^4$ and Φ_μ has configuration $1s^2 2s^2 2p^5(=1s^2 2s 2p^6+2s)$ then $\mu=2s$ but $\rho=2p$.

For the two-electron operator in Eq. (54) let ρ_μ and σ_μ be the subshells containing the interacting electrons. For a nonzero matrix element we must have identical distributions $\bar{q}$ of spectator electrons and for each $\bar{q}$ there are in general two possible distributions of interacting electrons labeled by $\epsilon=0$, 1. Viz., for $\lambda\neq\rho_\mu$ or σ_μ, $q_\lambda{}^\epsilon=\bar{q}_\lambda$, $\epsilon=0$ or 1, and for $\lambda=\rho_\mu$ or σ_μ either $\rho_\mu\neq\sigma_\mu$, $q_{\rho_\mu}{}^\epsilon=\{\bar{q}_{\rho_\mu}, N+\epsilon\}$ and $q_{\sigma_\mu}{}^\epsilon=\{\bar{q}_{\sigma_\mu}N+1-\epsilon\}$ or

$$\rho_\mu=\sigma_\mu,\ q_{\rho_\mu}{}^\epsilon=\{\bar{q}_{\rho_\mu}N,\ N+1\},\ \epsilon=0\quad\text{or}\quad 1. \tag{57}$$

Substituting Eqs. (12) and (14) into Eq. (54) and using Eq. (57) we get for a function f of q_i and q_μ, that

$$\sum_{q_i q_\mu} f(q_i q_\mu)\rightarrow\mathfrak{N}(\bar{N}_\lambda)\sum_{\epsilon=0,1}(1-\epsilon\delta_{\rho_\mu\sigma_\mu})g(\epsilon\rho_i\rho_\mu\sigma_\mu).$$

Defining ΔP to be the number of permutations to take the N electron of ρ_i, and the interacting electrons of ρ_μ and σ_μ, out to normal order, the matrix element of the two-electron operator is

$$\left\langle\frac{1}{r_{N,N+1}}\right\rangle=\sum_{\bar{C}}^{\max(b_i b_\mu)}\prod_{\lambda=1s}\delta(N_\lambda{}^i,N_\lambda{}^\mu+\delta_{\lambda\rho_i}-\delta_{\lambda\rho_\mu}-\delta_{\lambda\sigma_\mu})\quad[N_{\rho_i}N_{\rho_\mu}(N_{\sigma_\mu}-\delta_{\rho_\mu\sigma_\mu})]^{1/2}(-1)^{\Delta P}\sum_\epsilon(-1)^\epsilon(1-\epsilon\delta_{\rho_\mu\sigma_\mu})$$
$$\times\left\langle\psi_u(q_i\Gamma_i)F_{il}\left|\frac{1}{r_{N,N+1}}\right|\phi_u(q_\mu{}^\epsilon L_k S_k\pi_k)\right\rangle, \tag{58}$$

where

$$\Delta P=\sum_{\lambda=\rho i+1}^{b_i}\bar{N}_\lambda-\sum_{\lambda=\rho_\mu+1}^{\sigma_\mu}\bar{N}_\lambda.$$

We recall there is only one term in $\sum\bar{c}$ if $\psi(\Gamma_i)$ and ϕ_u differ by two electron jumps, but "b" terms when they differ by only one electron jump, and the matrix element vanishes unless it is diagonal in the quantum numbers of the

spectator electrons. The matrix element on the r.h.s. of Eq. (58) can be expanded out into the form

$$\sum_{\bar{\alpha}_{\rho i}\cdots\bar{L}_{\sigma\mu}} (l_{\rho i}{}^{N\rho^i}\alpha_{\rho i}S_{\rho i}L_{\rho i}\{|l_{\rho i}{}^{\bar{N}\rho^i}\bar{\alpha}_{\rho i}\bar{S}_{\rho i}\bar{L}_{\rho i}l_{\rho i})(l_{\rho\mu}{}^{\bar{N}\rho^\mu}\bar{\alpha}_{\rho\mu}\bar{S}_{\rho\mu}\bar{L}_{\rho\mu}l_{\rho\mu}|\}l_{\rho\mu}{}^{N\rho^\mu}\alpha_{\rho\mu}S_{\rho\mu}L_{\rho\mu})(l_{\sigma\mu}{}^{\bar{N}\sigma^\mu}\bar{\alpha}_{\sigma\mu}\bar{S}_{\sigma\mu}\bar{L}_{\sigma\mu}l_{\sigma\mu}|\}l_{\sigma\mu}{}^{N\sigma^\mu}\alpha_{\sigma\mu}S_{\sigma\mu}L_{\sigma\mu})$$
$$\times\langle\bar{S}_1\cdots(\bar{S}_{\rho i}\tfrac{1}{2}(N))S_{\rho i}\cdots\bar{S}_{b_i}\tfrac{1}{2}(N+1),S_i|\bar{S}_1\cdots(\bar{S}_{\rho\mu}\tfrac{1}{2}(N+\epsilon))S_{\rho\mu}\cdots(\bar{S}_{\sigma\mu}\tfrac{1}{2}(N+1-\epsilon))S_{\sigma\mu}\cdots,S_k\rangle$$
$$\times\langle\bar{L}_1\cdots(\bar{L}_{\rho i}l_{\rho i})L_{\rho i}\cdots\bar{L}_{b_i}l_i,L_i|P_\nu(\hat{r}_N\cdot\hat{r}_{N+1})|\bar{L}_1\cdots(\bar{L}_{\rho\mu}l_{\rho\mu}(N+\epsilon))L_{\rho\mu}\cdots(\bar{L}_{\sigma\mu}l_{\sigma\mu}(N+1-\epsilon))L_{\sigma\mu}\cdots,L_k\rangle, \quad (59)$$

where $\langle P_\nu\rangle$ can be evaluated using the method of Fano, Prats, and Goldschmidt as in Eq. (40).

Writing Eq. (53) as

$$L_{il,k}{}^C=\sum_\mu C_\mu{}^k\left\{\langle il|H_1|\mu\rangle+\left\langle il\left|\frac{1}{r}\right|\mu\right\rangle\right\}$$
$$\equiv\sum_\mu C_\mu{}^k\int dx_{N+1}V_{\mu,i}(r_{N+1})F_{il}(r_{N+1}), \quad (53a)$$

where the first term on the r.h.s. is written out explicitly in Eq. (56) and

$$\left\langle il\left|\frac{1}{r}\right|\mu\right\rangle=\prod_{\lambda=1s}^{\overrightarrow{N}}\delta(N_\lambda{}^i,N_\lambda{}^\mu+\delta_{\lambda\rho i}-\delta_{\lambda\rho\mu}-\delta_{\lambda\sigma\mu})\ [N_{\rho i}N_{\rho\mu}(N_{\sigma\mu}-\delta_{\rho\mu\sigma\mu})]^{1/2}(-1)^{\Delta P}\sum_{\epsilon=0,1}(-1)^\epsilon(1-\epsilon\delta_{\rho\mu\sigma\mu})$$
$$\times\sum_{\bar{\alpha}_{\rho i}\cdots\bar{L}_{\sigma\mu}}(l_{\rho i}{}^{N\rho^i}\alpha_{\rho i}S_{\rho i}L_{\rho i}\{|l_{\rho i}{}^{\bar{N}\rho^i}\bar{\alpha}_{\rho i}\bar{S}_{\rho i}\bar{L}_i l_{\rho i})(l_{\rho\mu}{}^{\bar{N}\rho^\mu}\bar{\alpha}_{\rho\mu}\bar{S}_{\rho\mu}\bar{L}_{\rho\mu}l_{\rho\mu}|\}l_{\rho\mu}{}^{N\rho^\mu}\alpha_{\rho\mu}S_{\rho\mu}L_{\rho\mu})$$
$$\times(l_{\sigma\mu}{}^{\bar{N}\sigma^\mu}\bar{\alpha}_{\sigma\mu}\bar{S}_{\sigma\mu}\bar{L}_{\sigma\mu}l_{\sigma\mu}|\}l_{\sigma\mu}{}^{N\sigma^\mu}\alpha_{\sigma\mu}S_{\sigma\mu}L_{\sigma\mu})\langle S_i|S_\mu\rangle^\epsilon\sum_\nu R_\nu(\rho_i F_{il}\eta\zeta)(l_{\rho i}\|C^\nu\|l_\eta)(l_\zeta\|C^\nu\|l_i)$$
$$\times[(2l_i+1)(2l_\zeta+1)]^{-1/2}\langle 0_i|0_\mu\rangle^\epsilon, \quad (60)$$

where the last factor is the orbital recoupling coefficient

$$\langle\bar{L}_1\cdots(\bar{L}_{\rho i}l_{\rho i})L_{\rho i}\cdots\bar{L}_{b_i}(l_\zeta\nu)l_i,L_i|\bar{L}_1\cdots[\bar{L}_\zeta(\nu l_{\rho i})l_\eta]L_\eta\cdots(\bar{L}_\zeta l_\zeta)L_\zeta\cdots L_k\rangle, \quad (60a)$$

where η is the subshell containing N in distribution ϵ and ζ is subshell containing $N+1$.

C. Terms Quadratic in C

The matrix elements of the two-electron operators which are quadratic in C, i.e., do not involve the continuum functions F, are precisely the quantities studied by Fano. From Eqs. (15) and (20) the terms quadratic in C are seen to be

$$L_{kl}{}^{C^2}=\sum_{\mu,\nu}\int\cdots\int dx\cdots dx_{N+1}C_\mu{}^kC_\nu{}^l\Phi_\mu(L_kS_k\pi_k)[H-E]\Phi_\nu(L_lS_l\pi_l). \quad (61)$$

The $(N+1)$ electron Hamiltonian will be expanded out as in Eq. (18). The matrix elements of $\sum_\alpha r_{N+1,\alpha}{}^{-1}$ will all contribute equally and the contribution to Eq. (61) will be

$$\sum_{\mu\nu}C_\mu{}^kC_\nu{}^lN\left\langle\Phi_\mu(L_kS_k\pi_k)\left|\frac{1}{r_{N,N+1}}\right|\Phi_\nu(L_lS_l\pi_l)\right\rangle=\sum_{\mu,\nu}C_\mu{}^kC_\nu{}^l(N+1)^{-1}\sum_{\bar{C}}[N_{\rho\mu}(N_{\sigma\mu}-\delta_{\rho\mu\sigma\mu})N_{\rho\nu}(N_{\sigma\nu}-\delta_{\rho\nu\sigma\nu})]^{1/2}$$
$$\times\prod_\lambda\delta(N_\lambda{}^\mu,N_\lambda{}^\nu+\delta_{\lambda\rho\mu}+\delta_{\lambda\sigma\mu}-\delta_{\lambda\rho\nu}-\delta_{\lambda\sigma\nu})\sum_{\epsilon_\mu-\epsilon_\nu}(-1)^{\Delta P}(1-\epsilon_\mu\delta_{\rho\mu\sigma\mu})(1-\epsilon_\nu\delta_{\rho\nu\sigma\nu})(-1)^{\epsilon_\mu-\epsilon_\nu}$$
$$\times\left\langle\phi_u(q_{\epsilon\mu}L_kS_k\pi_k)\left|\frac{1}{r_{N,N+1}}\right|\phi_u(q_{\epsilon\nu}L_\nu S_\nu\pi_\nu)\right\rangle, \quad (62)$$

where the quantities ϵ_μ, ϵ_ν, and ΔP are defined in Fano.

Using Fano's Eqs. (24), (34)–(36), and (41) we have

$$\left\langle \phi_u(q_{\epsilon_\mu} L_k S_k \pi_k) \left| \frac{1}{r_{N,N+1}} \right| \phi_u(q_{\epsilon_\nu} L_\nu S_\nu \pi_\nu) \right\rangle = \sum_{\bar{\alpha}_\rho \cdots \bar{L}_{\sigma_\nu}} (l_{\rho_\mu}{}^{N_{\rho\mu}} \alpha_{\rho_\mu} S_{\rho_\mu} L_{\rho_\mu} \{ | l_{\rho_\mu}{}^{\bar{N}_{\rho\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu} l_{\rho_\mu}) \times (l_{\sigma_\mu}{}^{N_{\sigma\mu}} \alpha_{\sigma_\mu} S_{\sigma_u} L_{\sigma_\mu} \{ | l_{\sigma_\mu}{}^{\bar{N}_{\sigma\mu}} \bar{\alpha}_{\sigma_\mu} \bar{S}_{\sigma_\mu} \bar{L}_{\sigma_\mu} l_{\sigma_\mu}) (l_{\rho_\nu}{}^{\bar{N}_{\rho\nu}} \bar{\alpha}_{\rho_\nu} \bar{S}_{\rho_\nu} \bar{L}_{\rho_\nu} l_{\rho_\nu} | \} l_{\rho_\nu}{}^{N_{\rho\nu}} \alpha_{\rho_\nu} S_{\rho_\nu} L_{\rho_\nu}) (l_{\sigma_\nu}{}^{\bar{N}_{\sigma\nu}} \bar{\alpha}_{\sigma_\nu} \bar{S}_{\sigma_\nu} \bar{L}_{\sigma_\nu} l_{\sigma_\nu} | \} l_{\sigma_\nu}{}^{N_{\sigma\nu}} \alpha_{\sigma_\nu} S_{\sigma_\nu} L_{\sigma_\nu})$$

$$\langle \bar{S}_1 \cdots (\bar{S}_{\rho_\mu \frac{1}{2}}(N+\epsilon_\mu)) S_{\rho_\mu} \cdots (\bar{S}_{\sigma_\mu \frac{1}{2}}(N+1-\epsilon_\mu)) S_{\sigma_\mu} \cdots \alpha_k S_k | \bar{S}_1 \cdots (\bar{S}_{\rho_\nu \frac{1}{2}}(N+\epsilon_\nu)) S_{\rho_\nu} \cdots (\bar{S}_{\sigma_\nu \frac{1}{2}}(N+1-\epsilon_\nu)) S_{\sigma_\nu} \cdots, \alpha_l S_l \rangle$$

$$\times \sum_t [\delta_{\epsilon_\mu \epsilon_\nu} R_t(\rho_\mu \sigma_\mu \rho_\nu \sigma_\nu)[(2l_{\sigma_\mu}+1)(2l_{\rho_\nu}+1)]^{-1/2} (l_{\rho_\mu} \| C^t \| l_{\rho_\nu}) (l_{\sigma_\nu} \| C^t \| l_{\sigma_\mu}) \langle \bar{L}_1 \cdots (\bar{L}_{\rho_\mu} l_{\rho_\mu}) L_{\rho_\mu} \cdots [\bar{L}_{\sigma_\mu}(l_{\sigma_\nu} t) l_{\sigma_\mu}] L_{\sigma_\mu} \cdots$$

$$\bar{L}_{b_\mu}, \alpha_k L_k | \bar{L}_1 \cdots [\bar{L}_{\rho_\nu}(t l_{\rho_\mu}) l_{\rho_\nu}] L_{\rho_\nu} \cdots, \alpha_l L_l \rangle + (1-\delta_{\epsilon_\mu \epsilon_\nu}) R_t(\rho_\mu \sigma_\mu \sigma_\nu \rho_\nu)[(2l_{\sigma_\mu}+1)(2l_{\sigma_\nu}+1)]^{-1/2} (l_{\rho_\mu} \| C^t \| l_{\sigma_\mu}) (l_{\rho_\nu} \| C^t \| l_{\sigma_\mu})$$

$$\times \langle \bar{L}_1 \cdots (\bar{L}_{\rho_\mu} l_{\rho_\mu}) L_{\rho_\mu} \cdots [\bar{L}_{\sigma_\mu}(l_{\rho_\nu} t) l_{\sigma_\mu}] L_{\sigma_\mu} \cdot \alpha_k L_k | \bar{L}_1 \cdots (\bar{L}_{\rho_\nu} l_{\rho_\nu}) L_{\rho_\nu} \cdots [\bar{L}_{\sigma_\nu}(t l_{\rho_\mu}) l_{\sigma_\nu}] L_{\sigma_\nu} \cdots, \alpha_l L_l \rangle]. \quad (62a)$$

Within the distributions $q_{\lambda\mu}$ and $q_{\lambda\nu}$, $(N+1)$ and (N) are the interacting electrons. When Φ_μ and Φ_ν have identical configurations then there will be several ways of determining $\{\bar{N}_\lambda\}$, hence $\sum \bar{c}$ appearing in Eq. (62). When these functions differ by one jump, e.g.,

$$\left\langle 1s^2 2s^2 2p^q \left| \frac{1}{r_{N,N+1}} \right| 1s^2 2s 2p^q 3s \right\rangle,$$

then label $(N+1)$ could be assigned to $2s$ on the left and $3s$ on the right; the interacting label (N) could then be in any of the three common subshells and once again a $\sum \bar{c}$. For Φ_μ and Φ_ν differing by two electron jumps, there is a unique configuration of the spectators.

The matrix element of $H_1(x_{N+1})$ is

$$\langle \Phi_\mu | H_1 | \Phi_\nu \rangle = [\mathfrak{N}(N_\lambda{}^\mu) \mathfrak{N}(N_\lambda{}^\nu)]^{-1/2} \sum_{q_\mu q_\nu} (-1)^{P_{q^\mu} + P_{q^\nu}} \langle \phi_{\mu u}(q_\mu L_k S_k \pi_k) | H_1 | \phi_{\mu\nu}(q_\nu L_l S_l \pi_l) \rangle. \quad (63)$$

If Φ_μ and Φ_ν differ by a single electron jump, then this must be the interacting electron and there is a unique configuration of spectator electrons. For two or more electron jumps, the matrix element vanishes. For $\Phi_\mu = \Phi_\nu$, then $(N+1)$ will be found in the same subshell in Φ_μ and Φ_ν and there will be as many terms in $\sum \bar{c}$ as there are occupied subshells.

$$\langle \Phi_\mu | H_1 | \Phi_\nu \rangle = \sum_{\bar{c}} \mathfrak{N}(\bar{N}_\lambda)[\mathfrak{N}(N_\lambda{}^\mu) \mathfrak{N}(N_\lambda{}^\nu)]^{-1/2} \prod_\lambda \delta(N_\lambda{}^\mu, N_\lambda{}^\nu + \delta_{\rho_\mu \lambda} - \delta_{\rho_\nu \lambda})$$

$$\times (-1)^{\Delta P} \sum_{\bar{\alpha}_{\rho_\mu} \cdots \bar{L}_{\rho_\nu}} (l_{\rho_\mu}{}^{N_{\rho\mu}} \alpha_{\rho_\mu} S_{\rho_\mu} L_{\rho_\mu} \{ | l_{\rho_\mu}{}^{\bar{N}_{\rho\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu} l_{\rho_\mu}) (l_{\rho_\nu}{}^{\bar{N}_{\rho\nu}} \bar{\alpha}_{\rho_\nu} \bar{S}_{\rho_\nu} \bar{L}_{\rho_\nu} l_{\rho_\nu} | \} l_{\rho_\nu}{}^{N_{\rho\nu}} \alpha_{\rho_\nu} S_{\rho_\nu} L_{\rho_\nu})$$

$$\times \langle [\prod_{\lambda \neq \rho_\mu} \{ n l_\lambda{}^{\bar{N}_\lambda} \bar{\alpha}_\lambda \bar{S}_\lambda \bar{L}_\lambda | \bar{q}_\lambda) \times [\{ n l_{\rho_\mu}{}^{\bar{N}_{\rho\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu} | \bar{q}_\mu) \times \{ n l_{\rho_\mu} | N+1)]^{L_{\rho\mu} S_{\rho\mu}}]^{L_k S_k} H_1(N+1)$$

$$\times [\prod_{\lambda \neq \rho_\nu} (\bar{q}_\lambda | n l_\lambda{}^{\bar{N}_\lambda} \bar{\alpha}_\lambda \bar{S}_\lambda \bar{L}_\lambda \} \times [(\bar{q}_{\rho_\nu} | n l_{\rho_\nu}{}^{\bar{N}_{\rho\nu}} \bar{\alpha}_{\rho_\nu} \bar{S}_{\rho_\nu} \bar{L}_{\rho_\nu} \} \times (N+1 | n l_{\rho_\nu})]^{L_{\rho\nu} S_{\rho\nu}}]^{L_l S_l}, \quad (64)$$

which will include a spin recoupling coefficient

$$\langle \bar{S}_1 \cdots (\bar{S}_{\rho_\mu \frac{1}{2}}(N+1)) S_{\rho_\mu} \cdots \bar{S}_{b_\mu} \alpha_k S_k | \bar{S}_1 \cdots (\bar{S}_{\rho_\nu \frac{1}{2}}(N+1)) S_{\rho_\nu} \cdots \bar{S}_{b_\nu} \alpha_l S_l \rangle \quad (65)$$

and the factor

$$\langle P(n l_{\rho_\mu}) | H_1 | P(n l_{\rho_\nu}) \rangle \langle \bar{L}_1 \cdots (\bar{L}_{\rho_\mu} l_{\rho_\mu}) L_{\rho_\mu} \cdots \alpha_k L_k | \bar{L}_1 \cdots (\bar{L}_{\rho_\nu} l_{\rho_\nu}) L_{\rho_\nu} \cdots \alpha_l L_l \rangle. \quad (66)$$

Combining the above results together

$$\langle \Phi_\mu | H_1 | \Phi_\nu \rangle = \sum_{\bar{c}} (N+1)^{-1} [N_{\rho_\mu} N_{\rho_\nu}]^{1/2} \prod_\lambda \delta(N_\lambda{}^\mu, N_\lambda{}^\nu + \delta_{\lambda \rho_\mu} - \delta_{\lambda \rho_\nu}) (-1)^{\Delta P}$$

$$\times \sum_{\bar{\alpha}_{\rho_\mu} \cdots L_{\rho_\nu}} (l_{\rho_\mu}{}^{N_{\rho\mu}} \alpha_{\rho_\mu} S_{\rho_\mu} L_{\rho_\mu} \{ | l_{\rho_\mu}{}^{\bar{N}_{\rho\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu} l_{\rho_\mu}) (l_{\rho_\nu}{}^{\bar{N}_{\rho\nu}} \bar{\alpha}_{\rho_\nu} \bar{S}_{\rho_\nu} \bar{L}_{\rho_\nu} l_{\rho_\nu} | \} l_{\rho_\nu}{}^{N_{\rho\nu}} \alpha_{\rho_\nu} S_{\rho_\nu} L_{\rho_\nu})$$

$$\times \langle \bar{S}_1 \cdots (\bar{S}_{\rho_\mu \frac{1}{2}}) S_{\rho_\mu} \cdots \alpha_k S_k | \bar{S}_1 \cdots (\bar{S}_{\rho_\nu \frac{1}{2}}) S_{\rho_\nu} \cdots \alpha_l S_l \rangle \langle \bar{L}_1 \cdots (\bar{L}_{\rho_\mu} l_{\rho_\mu}) L_{\rho_\mu} \cdots \alpha_k L_k | \bar{L}_1 \cdots (\bar{L}_{\rho_\nu} l_{\rho_\nu}) L_{\rho_\nu} \cdots \alpha_l L_l \rangle$$

$$\times (-\tfrac{1}{2}) \int dr P_{n l_{\rho_\mu}}(r) \left[\frac{d^2}{dr^2} - \frac{l_{\rho_\mu}(l_{\rho_\mu}+1)}{r^2} + \frac{2Z}{r} \right] P_{n l_{\rho_\nu}}(r), \quad (67)$$

where

$$\Delta P=\sum_{\lambda=\min(\rho_\mu,\rho_\nu)}^{\max(\rho_\mu,\rho_\nu)}\bar{N}_\lambda.$$

Finally we have to evaluate the matrix element of H_N, the N-electron Hamiltonian:

$$\langle\Phi_\mu(L_kS_k\pi_k)|H_N|\Phi_\nu(L_lS_l\pi_l)\rangle=[\mathfrak{N}(N_\lambda{}^\mu)\mathfrak{N}(N_\lambda{}^\nu)]^{-1/2}\sum_{q_\mu q_\nu}(-1)^{P_{q^\mu}+P_{q^\nu}}\langle\phi_{u\mu}(q_\mu L_kS_k\pi_k)|H_N|\phi_{u\nu}(q_\nu L_lS_l\pi_l)\rangle. \quad (68)$$

Separating off the noninteracting electron we have

$$\begin{aligned}\langle\phi_{u\mu}(L_kS_k\pi_k)|H_N|\phi_{u\nu}(L_lS_l\pi_l)\rangle=&\sum_{\bar{\alpha}_{\rho_i}\cdots m_{\rho_\nu}}(l_{\rho_\mu}{}^{N_{\rho^\mu}}\alpha_{\rho_\mu}S_{\rho_\mu}L_{\rho_\mu}\{|l_{\rho_\mu}{}^{\bar{N}_{\rho^\mu}}\bar{\alpha}_{\rho_\mu}\bar{S}_{\rho_\mu}\bar{L}_{\rho_\mu}l_{\rho_\mu})\\&\times(l_{\rho_\nu}{}^{\bar{N}_{\rho^\nu}}\bar{\alpha}_{\rho_\nu}\bar{S}_{\rho_\nu}\bar{L}_{\rho_\nu}l_{\rho_\nu}|\}l_{\rho_\nu}{}^{N_{\rho^\nu}}\alpha_{\rho_\nu}S_{\rho_\nu}L_{\rho_\nu})(\bar{L}_{\rho_\mu}l_{\rho_\mu}M_{\bar{L}_\mu}m_{l_\mu}|L_{\rho_\mu}M_{L_\mu})(\bar{S}_{\rho_\mu\frac{1}{2}}M_{\bar{S}_\mu}m_{s_\mu}|S_{\rho_\mu}M_{S_\mu})\\&\times(\bar{L}_{\rho_\nu}k_{\rho_\nu}M_{\bar{L}_\nu}m_{l_\nu}|L_{\rho_\nu}M_{L_\nu})(\bar{S}_{\rho_\nu\frac{1}{2}}M_{\bar{s}_\nu}m_{s_\nu}|S_{\rho_\nu}M_{S_\nu})\langle nl_{\rho_\mu}|nl_{\rho_\nu}\rangle\langle\Phi_\mu(L_kS_k\pi_k\bar{q}_k)|H_N|\Phi_\nu(L_lS_l\pi_l\bar{q}_l)\rangle, \quad (69)\end{aligned}$$

where Φ is an unsymmetrized wave function of N electrons. In order to evaluate the "direct" terms we have made the assumption that

$$\int\cdots\int dx_1\cdots dx_N\psi(\gamma_i\mathbf{X})[H_N-\mathcal{E}]\psi(\gamma_j\mathbf{X})=0,$$

where $\psi(\gamma_i\mathbf{X})$ is a properly antisymmetrized wave function of N electrons [see Eq. (43)]. H_N is symmetric under interchange of labels of any pair of electrons and so it can be readily shown, using the expansion of Eq. (10), that this implies that

$$\int\cdots\int dx_1\cdots dx_N\psi_u(\gamma_i\mathbf{X})[H_N-\mathcal{E}]\psi_u(\gamma_j\mathbf{X})=0.$$

Hence we have

$$\langle\bar{\phi}_\mu(\bar{\gamma}_k\bar{q}_k)|H_N|\bar{\phi}_\nu(\bar{\gamma}_l\bar{q}_l)\rangle=E^{\bar{\gamma}_k}\delta_{\bar{\gamma}_l\bar{\gamma}_k}\delta_{\bar{q}_l\bar{q}_k}, \quad (70)$$

and

$$\begin{aligned}\langle\Phi_\mu(L_kS_k\pi_k)|H_N|\Phi_\nu(L_lS_l\pi_l)\rangle=[\mathfrak{N}(N_\lambda)]^{-1}&\sum_{q\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho}(l_\rho{}^{N_{\rho^\mu}}\alpha_\rho{}^\mu L_\rho{}^\mu S_\rho{}^\mu\{|l_\rho\bar{N}_\rho\bar{\alpha}_\rho\bar{L}_\rho\bar{S}_\rho l_\rho)\\&\times(l_\rho\bar{N}_\rho\bar{\alpha}_\rho\bar{L}_\rho\bar{S}_\rho l_\rho|\}l_\rho{}^{N_{\rho^\nu}}\alpha_\rho{}^\nu L_\rho{}^\nu S_\rho{}^\nu)E^{\bar{L}_\rho\bar{S}_\rho}\delta_{N\lambda\mu N\lambda^\nu}. \quad (71)\end{aligned}$$

The noninteracting electron $N+1$ may be found in any subshell for which $N_\lambda\neq0$, and from the symmetry of H_N (for a given configuration) each distribution of interacting electrons contributes equally, hence

$$\begin{aligned}\langle\Phi_\mu(L_kS_k\pi_k|H_N|\Phi_\nu(L_lS_l\pi_l)\rangle=\frac{1}{N+1}\sum_{\lambda=1_s}^{b}N_\lambda\sum_{\bar{\alpha}_\lambda\bar{L}_\lambda\bar{S}_\lambda}&(l_\lambda{}^{N\lambda\mu}\alpha_\lambda{}^\mu S_\lambda{}^\mu L_\lambda{}^\mu|\}l_\lambda\bar{N}_\lambda\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda l_\lambda)\\&\times(l_\lambda\bar{N}_\lambda\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda l_\lambda|\}l_\lambda{}^{N\lambda^\nu}\alpha_\lambda{}^\nu S_\lambda{}^\nu L_\lambda{}^\nu)E^{\bar{L}_\lambda\bar{S}_\lambda}\delta_{N\lambda\mu N\lambda^\nu}. \quad (72)\end{aligned}$$

4. RADIAL EQUATIONS

A. Derivation

As in Smith *et al.*,[6] Eq. (16) can be written out explicitly with the help of Eqs. (50), (41), (53), and (61),

$$\begin{aligned}\delta\Big[\sum_{i,j}\int F_{ik}\mathcal{L}_{ij}F_{jl}dr+\sum_{j,\mu}C_\mu{}^k\int V_{\mu,j}F_{jl}dr+\sum_{i,\nu}C_\nu{}^l\\\times\int V_{\nu,i}F_{ik}dr+\sum_{i,\nu}C_\mu{}^kC_\nu{}^lA_{\mu\nu}-\tfrac{1}{2}K_{kl}\Big]=0, \quad (73)\end{aligned}$$

where

$$\begin{aligned}\mathcal{L}_{ij}=-\frac{1}{2}\Big[\frac{d^2}{dr^2}-\frac{l_i(l_i+1)}{r^2}+\frac{2Z}{r}+2(E-\mathcal{E}_i)\Big]\delta_{ij}\\+V_{ij}+W_{ij}, \quad (74)\end{aligned}$$

and $A_{\mu\nu}$ is defined in terms of Eqs. (62a), (67), and (72). For variations of $F_{m,n}$ of the form Eq. (19), Eq. (73) yields the integrodifferential equations

$$\sum_j\mathcal{L}_{ij}F_{jl}+\sum_\mu C_\mu{}^lV_{\mu,i}=0. \quad (75)$$

Variations of (73) with respect to $C_\lambda{}^m$ lead to

$$\sum_\nu A_{\mu\nu}C_\nu{}^l+\sum_j\int V_{\mu,j}F_{jl}dr=0. \quad (76)$$

The solutions of Eqs. (75) and (76) are to be subjected to the further requirement and that they are orthogonal to all subshells of the target system with the same orbital angular momentum, i.e., Eq. (13).

Introducing this requirement into (74) using

LaGrange multipliers, $\mathfrak{M}$ gives (75) to be

$$\sum_j \mathfrak{L}_{ij}F_{jl}+\sum_\mu C_\mu{}^l V_{\mu,i}+\sum_\lambda \mathfrak{M}_\lambda P_{nl\lambda}\delta_{l_i l_\lambda}=0. \quad (77)$$

B. Numerical Method

An algorithm for the solution of the system of second-order integro-differential equations $\mathfrak{L}_{ij}F_{jl}=0$ for $k_i^2>0$ has been given by Smith[15] and for $k_i^2<0$ by Smith and Burke.[16] Both these papers are based on iterative techniques. Noniterative techniques are implied in the work of Hartree[17,18] and have been developed for collision problems with $k_i^2>0$ by Marriott[19] and Omidvar[20] for the system $\mathfrak{L}_{ij}F_{jl}=0$. The noniterative alogrithm for the system of equations in (77) for all real nonzero k_i^2 has been developed by Smith *et al.*[6]

A FORTRAN program has been written to solve Eq. (77) and is currently being tested. Given a set of $(LS\pi)$, the configurations to be coupled together and their term values, the code calculates the number of channels and potentials and sets up the distinct exchange terms to be obtained as the solutions of differential equations. It then proceeds to solve the equations, using an extension to the algorithm presented in Smith *et al.*,[6] and prints out the partial-wave cross sections. Some of the early production runs with the code will be to calculate the total cross sections for the scattering of low-energy electrons by atomic oxygen in order to compare with the absolute measurements of Sunshine *et al.*[21] Calculations will also be carried out to determine the positions and widths of resonances in the photo-ionization continuum of *Ne I* (20–150 eV), as these have been observed by Codling *et al.*[22] Carroll *et al.*,[23] have observed a new Rydberg series in the absorption spectrum of atomic nitrogen which they attributed to transitions from the $^4S^0$ ground state of the nitrogen atom to the Rydberg terms $2s\,2p^3\,(^5S^0)np\,{}^4P$; it will be possible to calculate the parameters of these autoionized levels with the code.

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APPENDIX

Evaluation of the Recoupling Coefficients

The subshell angular momenta L_λ, S_λ together with the angular momenta l_T and $\frac{1}{2}$ of the projectile are coupled according to a prescribed coupling scheme to give total angular momenta L, S. If the intermediate couplings leading to a given L, S are not unique, then to each coupling there corresponds a distinct state Γ_i specified by the quantum numbers L, S, π together with an additional parameter α_i which specifies the coupling. We shall couple the vectors $L_1\cdots L_b$, l_i to give a total L_i according to the scheme

$$|(L_1L_2)(L_2{}^{\alpha_i}L_3)(L_3{}^{\alpha_i}\cdots L_\lambda)(L_\lambda{}^{\alpha_i}\cdots)(L_{b_i}{}^{\alpha_i}l_i)L_i\rangle, \quad (1a)$$

where $L_\lambda{}^{\alpha_i}$ denotes the result of coupling L_λ to the resultant of $L_1\cdots L_{\lambda-1}$. For the purposes of recoupling we may regard the continuum electron as being in a subshell $b+1$ where b is the outermost of the discrete orbitals and where $\bar{L}_{b+1}=0$, $L_{b+1}=l_i$. We shall define subshell ρ to contain electron N and σ to contain $N+1$. The general form of the orbital recoupling coefficient is

$$\langle \bar{L}_1\bar{L}_2\cdots L_{\rho_i-1}{}^{\alpha_i}[\bar{L}_{\rho_i}(l_{\rho_j}k)l_{\rho_i}]L_{\rho_i}L_{\rho_i}{}^{\alpha_i}\cdots\bar{L}_{\sigma_j}\cdots (\bar{L}_{\sigma_i}l_{\sigma_i})\cdots\bar{L}_{\sigma_j}\cdots,L_i|\,\bar{L}_1\bar{L}_2\cdots\bar{L}_{\rho_i}\cdots(\bar{L}_{\rho_j}l_{\rho_j})L_{\rho_j}\cdots \bar{L}_{\sigma_i}\cdots[\bar{L}_{\sigma_j}(kl_{\sigma_i})l_{\sigma_j}]L_{\sigma_j}L_{\sigma_j}{}^{\alpha_i}\cdots,L_j\rangle.$$

We note that there are three vectors to be recoupled, namely, l_N l_{N+1} and k. We must recouple l_N from ρ_i to ρ_j or vice versa when ρ_j lies inside ρ_i, as we do not know *a priori* which is the smaller, then recouple l_{N+1} from σ_i to σ_j and k from ρ_i to σ_j. To evaluate the above recoupling coefficient we generalize the method of Biedenharn[24] by first recoupling $l_{\mu_i}(=l_N)$ step by step from ρ_i to ρ_j, each intermediate recoupling contributing a Racah coefficient and then recouple the vectors $[\bar{L}_{\rho_j},(l_{\rho_j}k)l_{\rho_i}]L_{\rho_j}\rightarrow[(\bar{L}_{\rho_j}l_{\rho_j})L_{\rho_j},k]$. Next recouple k step by step from ρ_j to σ_i, couple it to $l_{\sigma_i}(=l_{N+1})$ to give l_{σ_j} and finally recouple l_{σ_j} from σ_i to σ_j. The recoupling coefficient will then have been expressed as a product or, in the case when the intermediate recoupling vector is not found on the r.h.s. of the coefficient, a sum of products of Racah coefficients. Three basic types of recoupling occur:

(*a*) *Direct:* in which $\max(\rho_i\rho_j)\leqslant\min(\sigma_i\sigma_j)$ as in Eqs. (49a), (56), (67), and, depending upon the particular configurations considered, in Eqs. (60a) and (62a), see Fig. 1(a). Alternatively we may have $\max(\sigma_i\sigma_j)\leqslant\min(\rho_i\rho_j)$ which can occur in Eqs. (60a) and (62a). In either case, we do not, at any stage in the recoupling, have to recouple both l_N and l_{N+1} through the same

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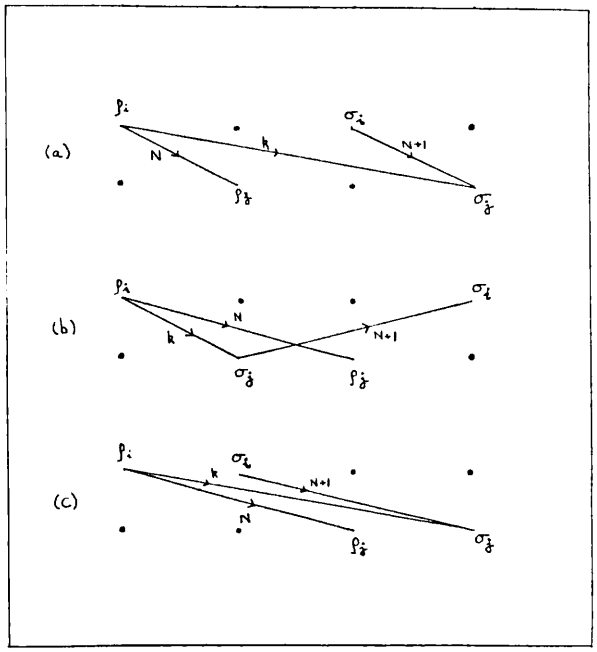

FIG. 1. Schematic representation of the three types of recoupling schemes encountered in the angular-momentum recoupling coefficients: (a) direct, (b) exchange, (c) translation.

range. This will give rise to a single product of Racah coefficients since we may use the property

$$\langle (L_{\lambda-1}{}^{\alpha i}L_\lambda)\tilde{L}_\lambda l_N;\ L_\lambda{}^{\alpha i}|\,(L_{\lambda-1}{}^{\alpha i}L_\lambda)L_\lambda{}^{\alpha i}l_N;\ L_\lambda{}^{\alpha i}\rangle = \delta_{\tilde{L}_\lambda L_\lambda}\alpha_j$$

to eliminate the summation over the intermediate couplings, $\tilde{L}$;

(*b*) *Exchange:* $\min(\rho_i\rho_j)\leqslant\min(\sigma_i\sigma_j)<\max(\rho_i\rho_j)$ as in Eq. (40) or alternatively $\min(\sigma_i\sigma_j)\leqslant\min(\rho_i,\rho_j)\leqslant\max(\sigma_i\sigma_j)$. Both cases may also occur in Eq. (60a) and (62a). In the former case we will have to recouple both l_{ρ_j} and l_{σ_i} through the range σ_j to ρ_j and will therefore have to sum over the intermediate couplings of this range. A schematic representations of these exchange recouplings are presented in Fig. 1(b);

(*c*) *Translation:* $\max(\rho_i\sigma_i)<\min(\rho_j\sigma_j)$ or alternatively $\max(\rho_j\sigma_j)<\min(\rho_i\sigma_i)$. This type of recoupling will only only occur in terms linear or quadratic in C, Eqs. (60a) and (62a), where both interacting electrons can appear in discrete orbitals. For example the recoupling coefficient of Eq. (60) arising from the configurations $1s^22s^22p^43skl-1s^22s^22p^6$ (where $\rho_i=3s$, $\sigma_i=kl$ continuum, and $\rho_j=\sigma_j=2p$), will be of this form. In the former case we will have to recouple both l_{ρ_i} and l_{σ_i} from σ_i to ρ_j. This is most easily achieved by coupling l_{ρ_i} $l_{\sigma_i}(\tilde{l}_i)$ and recoupling $\tilde{l}_i$ from σ_i to ρ_j then summing over all possible $\tilde{l}_i$. Schematically, these recouplings can be by Fig. 1(c).

The general form of the spin recoupling coefficient is

$$\langle \bar{S}_1\cdots S_{\rho_i-1}{}^{\alpha i}(\bar{S}_{\rho_i\frac{1}{2}}(N))S_{\rho_i}\cdots\bar{S}_{\rho_j}\cdots S_{\sigma_i-1}{}^{\alpha i}(\bar{S}_{\sigma_i\frac{1}{2}}(N+1))\cdots S_{\sigma_i}S_{\sigma_i}{}^{\alpha i}\cdots,\alpha_i S_i|\,\bar{S}_1\cdots\bar{S}_{\rho_i}\cdots S_{\rho_j-1}{}^{\alpha j}(\bar{S}_{\rho_j\frac{1}{2}}(N))S_{\rho_j}\cdots\bar{S}_{\sigma_i}\cdots S_{\sigma_j-1}{}^{\alpha j}(\bar{S}_{\sigma_j\frac{1}{2}}(N+1))S_{\sigma_j}\cdots,\alpha_j S_j\rangle.$$

The evaluation can be carried out in the same way as the orbital recoupling coefficient, giving rise to the same 3 types of recoupling but will be simplified by the fact that there are only two vectors $\frac{1}{2}(N)$, $\frac{1}{2}(N+1)$ to be recoupled.

For example, the direct spin recoupling coefficient is, for $\rho_i<\rho_j$,

$$\langle \bar{S}_1\cdots S_{\rho_i-1}{}^{\alpha i}(\bar{S}_{\rho_i\frac{1}{2}}(N))S_{\rho_i}\cdots\bar{S}_{\rho_j}\cdots S_{b_i}{}^{\alpha i}\tfrac{1}{2}(N+1),S_i|\,\bar{S}_1\cdots\bar{S}_{\rho_i}\cdots(\bar{S}_{\rho_j\frac{1}{2}}(N))\cdots S_{b_j}{}^{\alpha j}\tfrac{1}{2}(N+1),S_j\rangle$$

$$=\langle S_{\rho_i-1}{}^{\alpha i},\bar{S}_{\rho_i\frac{1}{2}}(S_{\rho_i});S_{\rho_i}{}^{\alpha i}|\,S_{\rho_i-1}{}^{\alpha i}\bar{S}_{\rho_i}(S_{\rho_i}{}^{\alpha j}),\tfrac{1}{2};S_{\rho_i}{}^{\alpha i}\rangle\prod_{\lambda=\rho i+1}^{\rho_j-1}\langle S_{\lambda-1}{}^{\alpha j}\tfrac{1}{2}(S_{\lambda-1}{}^{\alpha i}),\bar{S}_\lambda;S_\lambda{}^{\alpha i}|\,S_{\lambda-1}{}^{\alpha j}\bar{S}_\lambda(S_\lambda{}^{\alpha j}),\tfrac{1}{2};S_\lambda{}^{\alpha i}\rangle$$

$$\times\langle S_{\rho_j-1}{}^{\alpha i}\tfrac{1}{2}(S_{\rho_j-1}{}^{\alpha i}),\bar{S}_{\rho_j};S_{\rho_j}{}^{\alpha i}|\,S_{\rho_j-1}{}^{\alpha j},\bar{S}_{\rho_j\frac{1}{2}}(S_{\rho_j});S_{\rho_j}{}^{\alpha i}\rangle\prod_{\lambda=1}^{\rho_i-1}\delta(S_\lambda{}^{\alpha i}S_\lambda{}^{\alpha j})\prod_{\lambda=\rho_j+1}^{b_i}\delta(S_\lambda{}^{\alpha i}S_\lambda{}^{\alpha j})\delta_{b_ib_j}\delta_{S_iS_j},$$

where the recoupling coefficients are given in terms of Racah coefficients by[24]

$$[(2S_{\rho_i}+1)(2S_{\rho_j}{}^{\alpha j}+1)]^{1/2}W(S_{\rho_i-1}{}^{\alpha i}\bar{S}_{\rho_i}S_{\rho_i}{}^{\alpha i}\tfrac{1}{2};\ S_{\rho_i}{}^{\alpha i}S_{\rho_i})\prod_{\lambda=\rho i+1}^{\rho_j-1}[(2S_{\lambda-1}{}^{\alpha i}+1)(2S_\lambda{}^{\alpha i}+1)]^{1/2}$$

$$\times W(S_{\lambda-1}{}^{\alpha i}\tfrac{1}{2}\bar{S}_\lambda S_\lambda{}^{\alpha j};\ S_{\lambda-1}{}^{\alpha j}S_\lambda{}^{\alpha i})[(2S_{\rho_j-1}{}^{\alpha i}+1)(2S_{\rho_j}+1)]^{1/2}(-1)^{S_{\rho i}+1/2-S_{\rho j}}W(S_{\rho_j-1}{}^{\alpha j}\tfrac{1}{2}S_{\rho_i}{}^{\alpha i}\bar{S}_{\rho_j};\ S_{\rho_j-1}{}^{\alpha i}S_{\rho_j}).$$