A Dissertation
titled
Angular Momentum Algebra for Symbolic Expansions in
Atomic Structure Theory

by
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As partial fulfillment of the requirements for the
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An Abstract of

Angular Momentum Algebra for Symbolic Expansions in Atomic Structure Theory

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Computer programs based on multiconfiguration methods have become standard tools in atomic structure theory. Reliable predictions of atomic properties require very large configuration expansions. The computational resources required often exceed the capabilities of conventional computers. There is a need to restructure existing computer programs to take advantage of modern high-performance computational technology.

This dissertation deals with one important aspect of the effort to implement two widely used atomic structure packages (MCHF and GRASP92) on distributed memory parallel computers: the method for handling the angular momentum algebra.

In the existing algorithms, the angular integrations required for the Hamiltonian matrix elements are computed for each pair of configurations, even though the results may be identical or very similar for all configurations of a given type. This redundancy leads to a significant increase in computer resource requirements, because the angular matrix elements, which are repeatedly reused in the calculation, need to be stored
in computer memory or on disk. At present, the size (and, therefore, accuracy) of the calculations is limited by the large amounts of angular data produced. The aim of the research reported in this dissertation is to provide the theoretical basis for a computational method to curtail the growth of stored angular data with the size of the calculation.

The multiconfiguration basis is often generated by one- and two-particle replacements from a reference set to correlation orbitals. The redundancy in the stored angular data could be removed by reformulating the algorithm to treat simultaneously all angular matrix elements that differ only in the quantum numbers of the correlation orbitals. To accomplish this, we expand N-electron matrix elements of a general symmetric two-body scalar operator, an example of which is the Hamiltonian, in terms of two-electron matrix elements. Using diagrammatic methods of angular momentum theory, we derive the explicit dependence of the expansion coefficients on the quantum numbers of the correlation orbitals. Both relativistic (jj-coupled) and nonrelativistic (LS-coupled) multiconfiguration bases are considered. In addition, we report on a preliminary computer program that illustrates the application of this new method in parallel computations.
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Chapter 1

Introduction

Atomic theorists face a problem that cannot be solved exactly – the N-fermion problem. Approximations are necessary to describe the atom quantitatively. Variational multiconfiguration methods [1, 2] are widely accepted as a generally applicable, robust way to predict atomic properties. This chapter summarizes these methods in light of the research project to be discussed below, formulates the research objectives, and introduces some of the tools used to achieve these objectives.

1.1 Background on variational multiconfiguration methods in atomic structure

In the attempt to find an approximate solution to the many-body problem of atomic physics, it is natural to try to reduce one complex N-electron problem to N solvable one-electron problems. The assumption that each electron within the atom moves independently in the average field of the nucleus and all the other electrons is
known as the independent-particle model.

The independent-particle model itself is not enough to obtain tractable one-electron equations. In addition, it must be assumed that the potential in which each electron moves is spherically symmetric. This central-field approximation suggests the importance of angular momentum theory in atomic physics. From quantum mechanics we know that if a particle moves in a spherically symmetric potential, its angular momentum is conserved. The angular part of the particle’s wave function, then, does not depend on the exact form of the radial potential, and is known analytically. In the case of an atomic electron, the angular wave function is a product of a spherical harmonic and a spin eigenfunction in the nonrelativistic (Schrödinger) description, and consists of two spinor spherical harmonics in the relativistic (Dirac) description [3]. Angular momentum theory is the key to our problem; therefore, the central field approximation is essential to our work.

To build an N-electron wave function from one-electron orbitals, as described above, one has to take into account a few more physical considerations. Electrons are indistinguishable, and Fermi-Dirac statistics requires that an N-electron state be antisymmetric under the interchange of the labels on any two electrons. In addition, the total angular momentum of an isolated atom is conserved; therefore, the angular momenta of the individual electrons should be coupled to produce an eigenstate of the total angular momentum operator for the atom. A coupled antisymmetric wave function constructed from one-electron orbitals is called a configuration state function.

Not only atomic wave functions, but also physical operators can be expressed as linear combinations of products of angular and radial factors. This leads to separation
of the atomic structure problem into an “angular problem” and a “radial problem” [4]. This separation is crucial for our research.

How are the radial distributions of one-electron orbitals determined? Variational self-consistent field methods give the “best” solution within the framework of the independent-particle central-field approximation. By requiring that the energy be stationary under small changes in the one-electron radial distributions, subject to the normalization and orthogonality constraints, one obtains a set of coupled integro-differential equations for the desired radial distributions. These equations are then solved iteratively until the radial distributions are self-consistent. The variational self-consistent field method based on the non-relativistic atomic Hamiltonian is known as the Hartree-Fock method. Its relativistic counterpart, based on the Dirac-Coulomb Hamiltonian, is the Dirac-Fock method.

Of course, the independent-particle model is only an approximation. Departures from it represent correlation in the motion of electrons. Providing a quantitative description of correlation effects represents one of the most challenging problems in atomic structure theory. Variational self-consistent field methods address this problem by constructing a multiconfiguration basis set. When a single configuration state function cannot adequately describe an atomic state, a linear combination of such functions allows one to get an improved solution. Additional configuration state functions can contain one-electron orbitals which are not occupied in the minimal description of an atomic system – correlation orbitals. Computational methods based on these ideas are known as multiconfiguration self-consistent field methods. Two widely used computer programs based on these methods are the MCHF Atomic Structure
Figure 1-1: The multiconfiguration self-consistent field procedure

Package [5] (nonrelativistic) and GRASP92 [2] (relativistic). Figure 1-1 depicts the core steps in the multiconfiguration self-consistent field algorithm. This algorithm is an iterative procedure of computing matrix elements of the Hamiltonian in the basis of chosen configuration state functions, diagonalizing the Hamiltonian matrix to find a selected eigenvector, and solving self-consistent field equations to get improved radial distributions until the radial distributions and the eigenvector converge. For the purposes of the present work, it is important to notice that the angular integrals, needed in every iteration, are computed once and for all, and stored before the iterative process begins.
1.2 Symbolic states

The multiconfiguration method is based on the familiar quantum mechanical concept that an unknown quantum state can be expanded in terms of a complete set of orthonormal basis states:

\[ | \Psi \rangle = \sum_i c_i | \Phi_i \rangle, \text{ where } \sum_i | c_i |^2 = 1. \]  

(1.1)

Configuration state functions provide a convenient basis to describe an atomic state. In theory, this basis is infinite. In practice, however, the expansion needs to be truncated, and it is desirable to limit the basis on physical grounds.

The minimal description of an atomic system includes one or several configuration states, known as the reference set. Perturbation theory suggests that electron correlations can be accounted for by the inclusion of additional basis states. Assuming that correlation effects are described by a two-electron operator, configuration state functions contributing to the first-order correction cannot differ from the zeroth order wave function by more than two electrons. Therefore, the first order correction includes configuration states that are generated from the reference set by replacing one or two occupied orbitals with correlation orbitals. In multiconfiguration terminology, this procedure is known as single and double substitution.

The concept of a symbolic state [6] offers a systematic and elegant way to generate a multiconfiguration expansion composed of configuration state functions interacting\(^1\)

\(^1\)To clarify the terminology, we point out that the off-diagonal elements of the Hamiltonian matrix in the basis of configuration states are known as \textit{configuration-interaction} matrix elements. Atomic physicists use the term “interacting configuration states” to mean that the Hamiltonian matrix
with the reference set. This can be conveniently accomplished through the use of mixed-shell coefficients of fractional parentage \( \text{mcfp} \) [7]. A brief overview of this technique is given in Appendix B. Each reference state \( \Psi_{\text{ref}} \) is expanded in terms of states \( \{ (\Psi_{\text{sub}}) J_{\text{sub}}, (\psi_p) J_{\text{v}} \} J_{\text{tot}} \) by “pulling out” one or two electrons; i.e., uncoupling one electron or a pair of electrons from \( \Psi_{\text{ref}} \), separately coupling the “pullout” state \( \psi_p \) and the remaining subconfiguration \( \Psi_{\text{sub}} \), then coupling the two constituents together:

\[
| \Psi_{\text{ref}}(1, \ldots, N) J_{\text{tot}} \rangle = \sum_{(\psi_p) J_{\text{v}}} \left( \sum_{(\psi_p) J_{\text{v}}} (\Psi_{\text{ref}} \psi_p) \right) \left\{ \{ (\Psi_{\text{sub}}) J_{\text{sub}}, (\psi_p) J_{\text{v}} \} J_{\text{tot}} \right\}
\]

Here, \( (\Psi_{\text{ref}} \psi_p) \) is a mixed-shell coefficient of fractional parentage. It is worth emphasizing that while \( \Psi_{\text{ref}}, \Psi_{\text{sub}}, \) and \( \psi_p \) are fully antisymmetric, the newly formed N-electron states are \textit{not}, just like in the usual fractional parentage expansion.

Each state in the expansion of Equation (1.2) corresponds to a \textit{symbolic state} \( | \{ (\Psi_{\text{sub}}) J_{\text{sub}}, (\psi_v) J_{\text{v}} \} J_{\text{tot}} \rangle \), which interacts with at least one state in the reference set.\(^2\) By definition, a symbolic state is fully antisymmetric. A new one- or two-electron state \( (\psi_v) J_{\text{v}} \) is obtained by replacing the “pullout” orbitals in \( (\psi_p) J_{\text{v}} \) with general, unspecified, and unoccupied correlation orbitals. Thus a symbolic state represents many, in fact an infinite number, of configuration state functions all at once. In the two-electron case, \( (\psi_v) J_{\text{v}} \) corresponds to a symmetry-adapted pair-correlation

\(^2\)For a detailed discussion of the interaction of symbolic states with the reference set, see Chapter 2.
function [1].

To reiterate, a symbolic state is defined by set values of $(\psi_{sub})J_{sub}$, $J_v$, and $J_{tot}$, while the correlation orbitals in $(\psi_v)J_v$ are left unspecified.

While the symbolic-state formulation of the multiconfiguration expansion is appealing *per se* for physical reasons, its real virtue becomes apparent in its practical application.

### 1.3 Research objective

The problem this research project sets out to solve is very practical: to overcome the limitations of the angular-integration algorithm presently used in computer programs based on variational multiconfiguration methods, in particular, MCHF Atomic Structure Package [5] and GRASP92 [2].

In the existing algorithms, the required angular integrations are performed for each pair of configuration state functions, even though the results may be identical or very similar for all configurations of a given type. Since the results of angular integrations need to be saved and reused, this redundancy leads to a significant increase in computer memory or disk requirements. At present, the size (and, therefore, accuracy) of the calculations is limited by the large amounts of angular data produced. The aim of this project is to provide the theoretical basis for a computational method to curtail the growth of stored angular data with the size of the calculation.

The concept of a symbolic state is just the right tool to tackle this problem: the redundancy in the stored angular data could be removed by reformulating the angu-
lar computations to treat simultaneously all cases which differ only in the quantum
numbers of the correlation orbitals.

In this project, N-electron matrix elements of the Hamiltonian operator are ex-
panded in terms of two-electron matrix elements. We separate the expansion coeffi-
cients into two kinds of quantities: (1) analytic factors which are explicit expres-
sions involving the quantum numbers of the correlation orbitals, and (2) numerical
factors, independent of the correlation orbitals, containing the complications of an-
tisymmetrization and angular momentum coupling. This separation allows the size
of a calculation to be increased without recomputing the angular coefficients, and
without increasing the amount of stored angular data.

The need for restructuring angular integrations is especially evident in relativis-
tic multiconfiguration calculations. A relativistic configuration expansion contains
almost twice as many one-electron orbitals as its non-relativistic counterpart, and
a significantly larger number of basis states. Ref. [3] gives a striking illustration of
the above statement. A nonrelativistic multiconfiguration expansion of $1s^2 \, 2p \, 2P^o$
formed by all possible one-, two-, and three-electron replacements into the orbital set
$\{1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f\}$ contains 205 configuration state functions. The
corresponding relativistic expansion is a lot larger – 1048 configuration state func-
tions!

In the next few chapters we derive the analytical results using diagrammatic meth-
ods of angular momentum algebra [8]. Both nonrelativistic (LS-coupled) and relativis-
tic (jj-coupled) multiconfiguration expansions are considered. The jj-coupled case,
which turns out to be conceptually simpler, is explained in detail. The LS-coupled
case is handled by similar techniques, and only the final results are presented. Although tedious details of the derivations have been left out, it is still possible to lose the context of the discussion. The reader lost among the trees of angular momentum algebra is invited to return to this Introduction to see the forest.
Chapter 2

Symbolic-state expansion for relativistic multiconfiguration calculations

In this chapter, we compute the Hamiltonian matrix for a relativistic multiconfiguration expansion formulated in terms of jj-coupled symbolic states built on Dirac orbitals. We expand the resulting N-electron matrix elements in terms of two-electron matrix elements. The expansion coefficients contain all complications of angular momentum coupling and antisymmetrization, and are independent of the particular operator involved. (In the derivation we consider a general scalar two-body operator.) Furthermore, we derive the explicit dependence of the expansion coefficients on the quantum numbers of correlation orbitals. As mentioned in the Introduction, this last step is of great practical value for multiconfiguration self-consistent field calculations:
it eliminates the need to store angular data arising from each and every pair of configuration state functions. Instead, only the information defined by a pair of symbolic states needs to be stored, allowing us to enlarge the size of the calculation without increasing the amount of stored angular data.

2.1 Mathematical formulation of the problem

Let us consider a multiconfiguration expansion of an atomic state written in terms of symbolic states:

$$| \Psi_{atom} \rangle = \sum_{ref} c_{ref} | \Psi_{ref} \rangle + \sum_d c_d | \Psi_d \rangle + \sum_s c_s | \Psi_s \rangle .$$  \hspace{1cm} (2.1)

Here, $| \Psi_{ref} \rangle$ is a configuration state function belonging to the reference set. The expansion coefficients $c_{ref}, c_d, c_s$ are called mixing coefficients. The ket $| \Psi_d \rangle$ represents a symbolic state formed by a two-electron replacement from the reference set – a double-substitution symbolic state, and $| \Psi_s \rangle$ is a single-substitution symbolic state obtained in a similar way:

$$| \Psi_d \rangle = | \{ ( \Psi_{sub} ) J_{subn} ( n_1 l_{1j_1}, n_2 l_{2j_2} ) J_v \} J_{tot} \rangle ,$$ \hspace{1cm} (2.2)

$$| \Psi_s \rangle = | \{ ( \Psi_{sub} ) J_{subn} ( n_v l_j j_v ) \} J_{tot} \rangle .$$ \hspace{1cm} (2.3)

In the double-substitution symbolic state, $\Psi_{sub}$ represents an arbitrary $(N-2)$-electron subconfiguration of a reference state; $(n_1 l_{1j_1}, n_2 l_{2j_2})J_v$ is a coupled pair of correlation orbitals, which is subsequently coupled to the subconfiguration. Having
said this, the structure of $| \Psi_s \rangle$ is self-explanatory. It is worth emphasizing again that, whereas the reference set is given, the quantum numbers of the correlation orbitals remain unspecified.

We consider a symmetric two-body operator $G = \sum_{i<j}^{N} G_{ij}$ which commutes with the total angular momentum of the atom, or, in other words, is a scalar in its tensor properties. The general form of such an operator is

$$G_{ij} = \sum_{g} \left( G^{(g)}(i) \cdot G^{(g)}(j) \right) R_{g}(r_i, r_j), \quad (2.4)$$

where $G^{(g)}$ is a spherical tensor operator of rank $g$.\(^1\) We want to express a matrix element of this operator between the described $N$-electron states in terms of matrix elements between coupled and antisymmetric two-electron states:

$$\langle \Psi' | G | \Psi \rangle = \sum_{\alpha, \beta} K_{\alpha \beta}(\Psi', \Psi) \langle \psi_{\alpha}'(1, 2) | G_{12} | \psi_{\beta}(1, 2) \rangle. \quad (2.5)$$

Here $| \psi_{\alpha}(1, 2) \rangle$ is an antisymmetric coupled state of electrons 1 and 2, and we label all such states by the indices $\alpha, \beta$. This expansion is symbolic, since the quantum numbers of the correlation orbitals are not specified. We want to determine which two-electron states $\psi_{\alpha}'$, $\psi_{\beta}$ occur in this expansion, and to study the dependence of the coefficients $K_{\alpha \beta}$ on the quantum numbers of the correlation orbitals.

In the multiconfiguration basis defined by (2.1), the Hamiltonian matrix contains six kinds of matrix elements:

\(^1\) For more information on spherical tensor operators, see Appendix A.
\begin{itemize}
\item \( \langle \Psi_{ref} | G | \Psi_{ref} \rangle \)
\item \( \langle \Psi_d | G | \Psi_{ref} \rangle \)
\item \( \langle \Psi_s | G | \Psi_{ref} \rangle \)
\item \( \langle \Psi'_d | G | \Psi_d \rangle \)
\item \( \langle \Psi'_s | G | \Psi_s \rangle \)
\item \( \langle \Psi'_s | G | \Psi_d \rangle \).
\end{itemize}

Matrix elements of the first type, \( \langle \Psi_{ref} | G | \Psi_{ref} \rangle \), can be expanded in terms of two-electron matrix elements by use of a standard textbook approach ([9], for example). In the sections that follow, we focus on the five distinct types of matrix elements involving symbolic states.

At first glance, the problem seems daunting: the state of each electron is described by a 4-component Dirac spinor, the number of electrons is arbitrary, and the states in the reference set contain any number of closed and open shells.

A closer look shows that we do not have to deal with four components of Dirac spinors explicitly when we study the structure of the coefficients \( K_{\alpha\beta}(\Psi', \Psi) \) in (2.5), leaving the operator \( G \) general. Essential to this project are the facts that Dirac spinors are eigenstates of the one-electron angular momentum operators \( j^2 \) and \( j_\alpha \), and form an orthonormal basis set.

Graphical methods of angular momentum offer a convenient way to tackle the coupling details of the problem in all generality. However, many-electron states are not only coupled, but also antisymmetric under interchange on any two electron
coordinates. To take advantage of graphical angular momentum techniques, we have to attack antisymmetrization complexities first.

### 2.2 Antisymmetrization issues

We find that antisymmetrization details simplify significantly if the required matrix elements are expressed in terms of coupled but not fully antisymmetrized functions in which the correlation orbitals and the subconfiguration are separately antisymmetric. To disentangle the correlation orbitals from the subconfiguration in the double-substitution symbolic states, we make the following definitions:

\[
| \Phi_d \rangle \equiv \{ \Psi_{\text{sub}}(1, 2 \cdots N - 2) J_{\text{sub}}, \psi_v(N - 1, N) J_v \} J_{\text{tot}}, \tag{2.6}
\]

\[
| \Phi_d^X \rangle \equiv \{ \Psi_{\text{sub}}(1, 2 \cdots N - 3, N - 1) J_{\text{sub}}, \psi_v(N - 2, N) J_v \} J_{\text{tot}}. \tag{2.7}
\]

Here, \( \psi_v(N - 1, N) \) is a normalized, coupled, and antisymmetric state of the correlation pair with electron labels \( N - 1, N \), and \( \Psi_{\text{sub}}(1, 2 \cdots N - 2) \) is a normalized, coupled, and antisymmetric subconfiguration of electrons \( 1, 2, \ldots, N - 2 \). The state \( | \Phi_d^X \rangle \) is obtained from \( | \Phi_d \rangle \) by interchanging electron labels \( N - 2 \) and \( N - 1 \). The states \( | \Phi_d \rangle \) and \( | \Phi_d^X \rangle \) are obviously not fully antisymmetric.

The corresponding definitions for single-substitution symbolic states are:

\[
| \Phi_s \rangle \equiv \{ \Psi_{\text{sub}}(1, 2 \cdots N - 1) J_{\text{sub}}, \psi_v(N) j_v \} J_{\text{tot}}, \tag{2.8}
\]

\[
| \Phi_s^X \rangle \equiv \{ \Psi_{\text{sub}}(1, 2 \cdots N - 2, N) J_{\text{sub}}, \psi_v(N - 1) j_v \} J_{\text{tot}}. \tag{2.9}
\]
The fully antisymmetric states $|\Psi_d\rangle$, $|\Psi_s\rangle$ can be expressed in terms of partially antisymmetrized states like $|\Phi_d\rangle$, $|\Phi_s\rangle$ by summing over permutations of electron labels. Since $\psi_v$ and $\Psi_{sub}$ are already antisymmetric individually, we include only those permutations by which electron labels are moved from $\psi_v$ to $\Psi_{sub}$ and vice versa. Within both $\psi_v$ and $\Psi_{sub}$ the label ordering remains standard, with increasing numerical value of the electron labels.

Let us first consider a double-substitution symbolic state. We specify a permutation by an interchange of electron labels $N - 1, N$ with an arbitrary pair of $\Psi_{sub}$ electron labels $a, b$. Then, by counting the number of label interchanges required to get back to the original ordering, $\Psi_{sub}(1, 2 \cdots N - 2)\psi_v(N - 1, N)$, we can show that the sign of this permutation is $(-1)^{a+b-1}$. To preserve the normalization, we note that the number of such permutations is equal to the number of different label pairs; i.e., $N(N - 1)/2$. Thus the normalized, fully antisymmetric double-substitution symbolic state can be written as

$$|\Psi_d\rangle = \sqrt{\frac{2}{N(N - 1)}} \sum_{a < b} (-1)^{a+b-1} \{\Psi_{sub}(1, 2 \cdots \bar{a} \cdots \bar{b} \cdots N)J_{sub}, \psi_v(a, b)J_v\} J_{tot}. $$

(2.10)

Here, $\bar{a}, \bar{b}$ show that the label ordering does not include $a, b$. Similarly, the single-substitution symbolic state becomes

$$|\Psi_s\rangle = \sqrt{\frac{1}{N}} \sum_{a} (-1)^{N-a} \{\Psi_{sub}(1, 2 \cdots \bar{a} \cdots N)J_{sub}, \psi_v(a)J_v\} J_{tot}. $$

(2.11)

By summing over all allowed permutations, taking advantage of (2.10)-(2.11), and
using the crucial fact that the correlation orbitals are orthogonal to all the reference and subconfiguration orbitals, we may write the matrix elements of the operator $G$ in the form

$$
\langle \Psi_{ref} | G | \Psi_d \rangle = \sqrt{\frac{N(N-1)}{2}} \langle \Psi_{ref} | G_{N-1,N} | \Phi_d \rangle, \quad (2.12)
$$

$$
\langle \Psi_{ref} | G | \Psi_s \rangle = \frac{\sqrt{N(N-1)}}{2} \left[ \langle \Psi_{ref} | G_{N-1,N} | \Phi_s \rangle - \langle \Psi_{ref} | G_{N-1,N} | \Phi_s^X \rangle \right],
$$

$$
\langle \Phi'_d | G | \Phi_d \rangle = 2(N-2) \left[ \langle \Phi'_d | G_{N-2,N-1} | \Phi_d \rangle - \langle \Phi'_d | G_{N-2,N-1} | \Phi_d^X \rangle \right]
$$

$$
+ \frac{(N-3)(N-2)}{2} \langle \Phi'_d | G_{N-3,N-2} | \Phi_d \rangle
$$

$$
+ \langle \Phi'_d | G_{N-1,N} | \Phi_d \rangle, \quad (2.14)
$$

$$
\langle \Phi'_s | G | \Phi_s \rangle = (N-1) \left[ \langle \Phi'_s | G_{N-1,N} | \Phi_s \rangle - \langle \Phi'_s | G_{N-1,N} | \Phi_s^X \rangle \right],
$$

$$
+ \frac{(N-1)(N-2)}{2} \langle \Phi'_s | G_{N-2,N-1} | \Phi_s \rangle, \quad (2.15)
$$

$$
\langle \Phi'_s | G | \Phi_d \rangle = (N-2) \sqrt{2(N-1)} \langle \Phi'_s | G_{N-2,N-1} | \Phi_d \rangle
$$

$$
+ \sqrt{2(N-1)} \langle \Phi'_s | G_{N-1,N} | \Phi_d \rangle. \quad (2.16)
$$

In the next section we will consider each of these matrix elements in detail.

### 2.3 Dependence of matrix elements on correlation orbitals

As mentioned before, our task is to find out how the five kinds of matrix elements (2.12) – (2.16) depend on quantum numbers of correlation orbitals. This is conve-
niently achieved using two rather unconventional techniques – graphical methods of angular momentum, and mixed-shell coefficients of fractional parentage. The reader unfamiliar with graphical methods of angular momentum is referred to Appendix A for an brief overview. Mixed-shell coefficients of fractional parentage are discussed in Appendix B. The reader may wish to take a look at these two appendices before proceeding, since they provide relevant definitions, and introduce the notation.

2.3.1 Matrix elements connecting double-substitution symbolic states and reference states

In Chapter 1, we alluded to the connection between the mcfp expansion of a reference state and the symbolic states interacting with that reference state. We are now ready to discuss a matrix element constructed from a double-substitution symbolic state and a reference state in detail. In particular, we will derive the dependence of \( \langle \Psi_d | G | \Psi_{ref} \rangle \) on quantum numbers of correlation orbitals.

We start with the two-electron mcfp expansion of the reference state:

\[
| \Psi_{ref}(1,2\cdots N) J_{tot} \rangle = \sum \left( \langle \psi_1^{ref} | J_{ref}^{ref} \right) | \Psi_{sub}^{ref}, \psi_2^{ref} \rangle \left( \{ \Psi_{sub}^{ref}(1\cdots N - 2) J_{sub}^{ref}, \psi_2^{ref} (N-1, N) J_{2}^{ref} \} \right) J_{tot} \rangle.
\]

The sum here extends over all possible subconfigurations \( \psi_1^{ref} J_{ref}^{ref} \) and pullout states \( \psi_2^{ref} J_{2}^{ref} \). The subscript “2” here indicates that the pullout state is a two-
electron state. Substituting (2.17) and (2.2) into (2.12), we obtain

\[
\langle \Psi_{\text{ref}} | \mathbf{G} | \Psi_d \rangle = \sqrt{\frac{N(N-1)}{2}} \sum_{(\Psi_{\text{sub}}^{\text{ref}}), (\psi_{2}^{\text{ref}})} \left( \langle \Psi_{\text{ref}} | \right) \left( \Psi_{\text{sub}}^{\text{ref}} \right), (\psi_{2}^{\text{ref}}) \left( J_{2}^{\text{ref}} \right) \\
\times \langle \left\{ (\Psi_{\text{sub}}^{\text{ref}}) J_{\text{sub}}^{\text{ref}}, (\psi_{2}^{\text{ref}}) J_{2}^{\text{ref}} \right\} J_{\text{tot}} | G_{N-1,N} | \left\{ (\Psi_{\text{sub}}) \right. \left( \psi_{v} \right) J_{v} \left. \right\} J_{\text{tot}} \rangle .
\]

(2.18)

Although the electron labels have been omitted for brevity, it is important to keep in mind that the operator \( G_{N-1,N} \) acts only on the two-electron states \((\psi_{2}^{\text{ref}})J_{2}^{\text{ref}}\) and \((\psi_{v})J_{v}\). To isolate the two-electron matrix element, we uncouple the subconfiguration from the two-electron pair on both sides of the N-electron matrix element. Orthonormality of subconfigurations selects a single term \((\Psi_{\text{sub}})J_{\text{sub}}\) in the sum over subconfigurations \((\Psi_{\text{sub}}^{\text{ref}})J_{\text{sub}}^{\text{ref}}\). Can we simplify the sum over the pullout states \((\psi_{2}^{\text{ref}})J_{2}^{\text{ref}}\)?

In the mcft expansion of the reference state, the selected subconfiguration specifies the pullout orbitals uniquely. The total angular momentum of the pullout pair is fixed to \( J_{v} \) by the scalar nature of the operator. Thus the sum over the pullout states \((\psi_{2}^{\text{ref}})J_{2}^{\text{ref}}\) reduces to a single term as well. Applying the orthogonality relation for vector-coupling coefficients that appear upon uncoupling the subconfigurations from the pullout states, we get

\[
\langle \Psi_{\text{ref}} | \mathbf{G} | \Psi_d \rangle = \frac{\sqrt{N}}{2} \left( \langle \Psi_{\text{ref}} | \right) \left( \Psi_{\text{sub}} \right) J_{\text{sub}} ; (\psi_{2}^{\text{ref}}) J_{v} \\
\times \langle \left( \psi_{2}^{\text{ref}} \right) J_{v} | G | (\psi_{v}) J_{v} \rangle .
\]

(2.19)

Equation (2.19) explains why the procedure for symbolic-state generation described
in the Introduction yields double-replacement symbolic states that interact with the reference set.

Finally, let us point out that the mixed-shell coefficient of fractional parentage is closely related to a more familiar quantity – an overlap between two antisymmetric N-electron states

\[
\langle \Psi_d | \Psi_{ref} \rangle = \sqrt{\frac{N(N-1)}{2}} \left( \Psi_{ref} \right) (\Psi_{sub}) J_{sub}, \left( \psi_{2}^{ref} \right) J_{v} \right). \quad (2.20)
\]

Here,

\[
| \Psi_d \rangle = \mathcal{A} | \left\{ \left( \Psi_{sub} \right) J_{sub}, \left( \psi_{2}^{ref} \right) J_{v} \right\} J_{tot} \rangle \quad (2.21)
\]

is a fully antisymmetric state that is the same as \(| \Psi_d \rangle \), but with \( (\psi_v) J_v \) replaced by \( \left( \psi_{2}^{ref} \right) J_{v} \), a two-electron state formed from the orbitals present in \(| \Psi_{ref} \rangle \) and absent in \(| \Psi_d \rangle \). Equation (2.21) is easily derived using (2.10) and the definition of the mixed-shell coefficient of fractional parentage.

### 2.3.2 Matrix elements connecting single-substitution symbolic states and reference states

Our next goal is to find out how the matrix element \( \langle \Psi_{ref} | \mathbf{G} | \Psi_s \rangle \) depends on the correlation orbital of the symbolic state \(| \Psi_s \rangle \). We begin with (2.13), and isolate the parts of the matrix element on which the operator \( G_{N-1,N} \) acts. To accomplish this, we do two mcfp expansions: a two-electron mcfp expansion (2.17) of the reference state, and a one-electron mcfp expansion for the subconfiguration of the symbolic
state

\[ | \Psi_{\text{sub}}(1 \cdots N - 1) J_{\text{sub}} \rangle = \sum_{(\psi_{1}^{\text{sub}})^{J_{1}^{\text{sub}}}, \ (\psi_{s}^{\text{sub}})^{J_{s}^{\text{sub}}}} \left( \langle \Psi_{1}^{\text{sub}} , \psi_{s}^{\text{sub}} \rangle \right) | \Psi_{\text{sub}} \rangle \ | \{ \Psi_{1}^{\text{sub}} (1 \cdots N - 2) J_{1}^{\text{sub}} , \psi_{s}^{\text{sub}} (N - 1) J_{s} \} J_{\text{sub}} \rangle. \]  

(2.22)

Next, we recouple \( | \Phi_{s} \rangle \) and \( | \Phi_{s}^{X} \rangle \) to form a coupled state of two electrons with labels \( N - 1, N \) by use of

\[ \left| \{ J_{1}^{\text{sub}} , J_{\text{sub}}, j_{v} \} J_{\text{tot}} \right\rangle = \sum_{J_{G}} \left| \{ J_{1}^{\text{sub}} , (j_{s}j_{v}) J_{G} \} J_{\text{tot}} \right\rangle \]

\[ \times \left\langle \{ J_{1}^{\text{sub}} , (j_{s}j_{v}) J_{G} \} J_{\text{tot}} \left| \{ J_{1}^{\text{sub}} , J_{\text{sub}}, j_{v} \} J_{\text{tot}} \right\} \right\rangle, \]  

(2.23)

and combine the contributions from \( | \Phi_{s} \rangle \) and \( | \Phi_{s}^{X} \rangle \) into an antisymmetric two-electron state

\[ | (\psi_{s}) J_{G} \rangle = \frac{1}{\sqrt{2}} \left[ \left| \{ \psi_{1}^{\text{sub}} (N - 1) j_{s}, \psi_{v} (N) j_{v} \} J_{G} \right\rangle \right. \]

\[ - \left. \left| \{ \psi_{1}^{\text{sub}} (N) j_{s}, \psi_{v} (N - 1) j_{v} \} J_{G} \right\rangle \right]. \]  

(2.24)

Now we can follow reasoning similar to that which led to (2.19). The result is

\[ \langle \Psi_{\text{ref}} | G | \Psi_{s} \rangle = \frac{\sqrt{N (N - 1)}}{\sqrt{2}} \sum_{(\psi_{1}^{\text{sub}})^{J_{1}^{\text{sub}}}, \ (\psi_{s}^{\text{sub}})^{J_{s}^{\text{sub}}}} \left( \langle \psi_{2}^{\text{ref}} \rangle J_{G} \right) \left( \langle \psi_{s} \rangle J_{G} \right) \]

\[ \times \left( \Psi_{\text{ref}} \left| \{ \psi_{1}^{\text{sub}} \}_1 J_{1}^{\text{sub}} , (\psi_{2}^{\text{ref}})_2 J_{G} \right\rangle \left( \langle \psi_{s}^{\text{sub}} \rangle J_{1}^{\text{sub}} , (\psi_{s}^{\text{sub}}) J_{s} \right\rangle \right) \Psi_{\text{sub}} \]

\[ \times \left\langle \{ J_{1}^{\text{sub}} , (j_{s}j_{v}) J_{G} \} J_{\text{tot}} \left| \{ J_{1}^{\text{sub}} , J_{\text{sub}}, j_{v} \} J_{\text{tot}} \right\} \right\rangle. \]  

(2.25)
Here, \( j_s \) runs over all the orbitals of the \((N-1)\)-electron symbolic-state subconfiguration \( \Psi_{\text{sub}} \). Orthogonality of the \((N-2)\)-electron subconfigurations eliminates the sum over subconfigurations of the reference state \( \Psi_{\text{ref}}^{\text{sub}} \). The two-electron state \( \psi_2^{\text{ref}} \) contains orbitals present in \( \Psi_{\text{ref}} \), but absent from \( \Psi_1^{\text{sub}} \).

We can express the above result in terms of overlaps between antisymmetric states. Using

\[
\langle \{ (\Psi_1^{\text{sub}}) J_1^{\text{sub}}, (\psi_1^{\text{sub}}) j_s \} J_{\text{sub}} | (\Psi_{\text{sub}}) J_{\text{sub}} \rangle = \sqrt{N-1} \left( \langle (\psi_1^{\text{sub}}) J_1^{\text{sub}}, (\psi_1^{\text{sub}}) j_s \rangle \langle \Psi_{\text{sub}} | \Psi_{\text{sub}} \rangle \right),
\]

(2.26)

and a relation similar to (2.20), we obtain

\[
\begin{align*}
\langle \Psi_{\text{ref}} | G | \Psi_s \rangle &= \sum_{(\psi_1^{\text{sub}}) J_1^{\text{sub}}, j_s, J_G} (-1)^{j_h + j_v + J_1^{\text{sub}} + J_{\text{tot}}} [J_{\text{sub}}, J_G]^{1/2} \left\{ J_1^{\text{sub}} \quad j_s \quad J_{\text{sub}} \right\} \left\{ j_v \quad J_{\text{tot}} \quad J_G \right\} \\
& \times \langle (\psi_1^{\text{sub}}) J_{\text{tot}} | \{ (\Psi_1^{\text{sub}}) J_1^{\text{sub}}, (\psi_2^{\text{ref}}) J_G \} J_{\text{tot}} \rangle \\
& \times \langle \{ (\Psi_1^{\text{sub}}) J_1^{\text{sub}}, (\psi_1^{\text{sub}}) j_s \} J_{\text{sub}} | (\Psi_{\text{sub}}) J_{\text{sub}} \rangle \langle (\psi_2^{\text{ref}}) J_G | G | (\psi_s) J_G \rangle.
\end{align*}
\]

(2.27)

In the above equation, the recoupling coefficient has been written in terms of a 6j-symbol, and the symbol \([J_{\text{sub}}, J_G]\) stands for \((2J_{\text{sub}} + 1)(2J_G + 1)\).
2.3.3 Matrix elements connecting double-substitution symbolic states

Let us turn our attention to the matrix elements connecting double-substitution symbolic states. We start with (2.14)

$$\langle \Psi^I_d \mid G \mid \Psi_d \rangle = \mathcal{M}_{vv} + \mathcal{M}_{ss} + \mathcal{M}_{sv}, \quad (2.28)$$

where

$$\mathcal{M}_{vv} = \langle \Phi^I_d \mid G_{N-1,N} \mid \Phi_d \rangle, \quad (2.29)$$

$$\mathcal{M}_{ss} = \frac{(N-3)(N-2)}{2} \langle \Phi^I_d \mid G_{N-3,N-2} \mid \Phi_d \rangle, \quad (2.30)$$

$$\mathcal{M}_{sv} = 2(N-2) \left[ \langle \Phi^I_d \mid G_{N-2,N-1} \mid \Phi_d \rangle - \langle \Phi^I_d \mid G_{N-2,N-1} \mid \Phi^X_d \rangle \right]. \quad (2.31)$$

Here, $\mathcal{M}_{ss}$, $\mathcal{M}_{vv}$ represent interactions within subconfigurations and correlation pairs, respectively, and $\mathcal{M}_{sv}$ describes the interaction between a subconfiguration and a correlation pair. The first two terms, $\mathcal{M}_{ss}$ and $\mathcal{M}_{vv}$, are almost trivial. We uncouple the subconfigurations from the correlation pairs, take into account orthonormality of the functions on which the operator $G$ does not act (subconfigurations in the $\mathcal{M}_{vv}$ term, and correlation pairs in the $\mathcal{M}_{ss}$ term), and use the orthogonality relation for vector-coupling coefficients that appear upon uncoupling the subconfigurations from the correlation pairs. The results are

$$\mathcal{M}_{vv} = \langle (\Psi^I_{sub})_I^{J_{sub}} \mid (\Psi^I_{sub})_I^{J_{sub}} \rangle \langle (\psi^I_v)_I^{J_v} \mid G \mid (\psi_v)_I^{J_v} \rangle, \quad (2.32)$$
\[ \mathcal{M}_{ss} = \langle (\Psi_{\text{sub}}') J_{\text{sub}}' | G | (\Psi_{\text{sub}}) J_{\text{sub}} \rangle \langle (\psi_v') J_v' | (\psi_v) J_v \rangle. \] (2.33)

Dealing with the interaction between a subconfiguration and a correlation pair requires some effort. Assuming that the general form of the operator \( G_{ij} \) that conserves \( \mathbf{J} \) is

\[ G_{ij} = \sum_g \left( G^{(g)}(i) \cdot G^{(g)}(j) \right) R_g(r_i, r_j) \]
\[ = \sum_g (-1)^g [g]^{1/2} [G^{(g)}(i) \times G^{(g)}(j)]^{(0)} R_g(r_i, r_j), \] (2.34)

we represent the nature of angular momentum coupling in the \( \mathcal{M}_{sv} \) term by use of diagrams, as explained in Appendix A. We focus on the part of the N-electron matrix element that depends upon the correlation orbitals and the operator:

\[ \mathcal{M}_{sv} = 2 (N-2) A_{N-3} A_{N-3} \sum_{j_s, j_v} \sum_{j_1, j_2} (c f p)(c f p)' \]
\[ \times \sum_{j_v=\{j_1, j_2\}, \mathcal{J}_v=\{j'_1, j'_2\}} (j_v, \mathcal{J}_v)(j_1j_2) J_v (j'_v, \mathcal{J}'_v)(j'_1j'_2) J'_v \]
\[ \times \sum_g (-1)^g [g]^{1/2} \delta_{j_v, \mathcal{J}_v} \]

\[ \begin{cases} (\text{N-3)-electron overlap} \end{cases} \]

\[ \begin{array}{c}
\text{direct} \\
\text{matrix} \\
\text{element}
\end{array} \]
Here, \( j_s, j'_s \) are subconfiguration orbitals; \( j_s \) and \( j'_s \) run over all the subconfiguration subshells. Coefficients of fractional parentage occurring upon separating one \( j_s \) or \( j'_s \) electron from its subshell are denoted as \( (cfp), (cfp)' \), and the fractional parents are labeled \( fp, fp' \). Operators \( A_{N-3}, A'_{N-3} \) complete antisymmetrization of the subconfigurations by taking into account allowed permutations of electron labels, with the last label kept in the \( j_s, j'_s \) subshell. The sums over the correlation orbitals are indexed by \( j_v, j'_v \), and there are at most two values for each of these orbitals, namely, \( j_1, j_2 \) or \( j'_1, j'_2 \). Noninteracting electrons in correlation orbitals are labeled \( \overline{j_v}, \overline{j'_v} \); that is, if \( j_v = j_1 \), then \( \overline{j_v} = j_2 \), and so forth. The mixed-shell coefficient of fractional parentage for the correlation pair is represented by \( \langle j_v, \overline{j'_v}\rangle (j_1j_2) J_v \). This coefficient preserves the coupling order in the correlation pair: for both permutations of electron labels \( (N-1, N) \), the noninteracting electron is coupled second. Direct and exchange matrix element boxes contain radial integrals and reduced matrix elements.
of one-electron tensor operators. In particular,

\[
\begin{align*}
\text{direct matrix element} & = \frac{1}{|j_v', j_s, g|^{1/2}} \left\langle j_v' \left| G^{(g)} \right| j_v \right\rangle \left\langle j_s' \left| G^{(g)} \right| j_s \right\rangle R_g^{\text{direct}}, \\
\text{exchange matrix element} & = \frac{1}{|j_v', j_s, g|^{1/2}} \left\langle j_v' \left| G^{(g)} \right| j_s \right\rangle \left\langle j_s' \left| G^{(g)} \right| j_v \right\rangle R_g^{\text{exchange}}.
\end{align*}
\]

Here, \( R_g^{\text{direct}} \), \( R_g^{\text{exchange}} \) are two-electron radial integrals, the reduced matrix elements have been defined as in Cowan [9], and we have used the usual shorthand notation \((2j_1 + 1)(2j_2 + 1) = [j_1, j_2] \).

To derive explicit dependence of \( M_{sv} \) on the quantum numbers of correlation orbitals, we proceed in three steps: first, we extract the two-electron matrix element; next, we isolate the subconfiguration contribution; and last, we compute the remaining purely angular factors.

**Two-electron matrix element.** Using techniques described in Appendix A, each diagram in (2.35) can be cut on four lines \( j_v', j_v, j_s', j_s \) to separate the operator-dependent part. Noticing that the matrix element of \( G \) between coupled, antisymmetric, and non-equivalent two-electron states has the diagrammatic form

\[
\left\langle (j_s', j_v') G \right| \left( j_s, j_v \right) G \right\rangle = \sum_g (-1)^g [g]^{1/2}
\]

(2.38)
(2.35) can be reduced to

\[
\mathcal{M}_{sv} = 2(N - 2)A_{N-3}A'_{N-3} \sum_{j_s, j'_s} \sum_{(fp)} (cpf)(cpf') \times \sum_{j_v, j'_v} \langle j'_v, j'_v|j_s, j'_s \rangle \langle j'_v, j'_v|j_s, j'_s \rangle \sum_{j_G} \delta_{j_v, j'_v} (-1)^{2j_v} \frac{[J_G, J_v]^{1/2}}{[j_s, j'_s]^{1/2}}
\]

\[\langle (j'_s, j'_v)J_G | G | (j_s, j_v)J_G \rangle. \quad (2.39)\]

The new sum is over the possible two-electron quantum numbers \(J_G\) that result as the orbitals \(j_s, j_v\) and \(j'_s, j'_v\) are coupled in pairs.

**Contribution of subconfigurations.** To isolate the subconfigurations, we cut the diagram of (2.39) on four lines \(J'_{sub}, j'_s, j'_v, J_{sub}\). This yields

\[
\mathcal{M}_{sv} = 2 \sum_{j_s, j'_s} \sum_{j_v, j'_v} \Gamma_k(\Psi_{sub, j'_s}, \Psi_{sub, j_s}) \sum_{j_v, j'_v} \langle j_v, j'_v|j_s, j'_s \rangle \langle j'_v, j'_v|j_s, j'_s \rangle \langle j'_v, j'_v|j_s, j'_s \rangle \langle j'_v, j'_v|j_s, j'_s \rangle \times \sum_{j_G} (-1)^{2j'_v + 2j_s + 2j_v} \frac{|k, J_G|^{1/2}}{|J_{sub, j'_v}|^{1/2}} \langle (j'_v, j'_v)J_G | G | (j_s, j_v)J_G \rangle
\]
Here, the quantity $\Gamma_k(\Psi'_{sub}, j'_s; \Psi_{sub}, j_s)$ depends on all the internal couplings required to specify the two subconfigurations, and does not depend on the quantum numbers of correlation orbitals:

$$\Gamma_k(\Psi'_{sub}, j'_s; \Psi_{sub}, j_s) = (N - 2) \frac{[J'_{sub}]^{1/2}}{[j'_{s}]^{1/2}} A_{N-3} A'_{N-3}$$

$$\times \sum_{j_{p}, (j_{p})'} (cf p)(cf p)' \ . \ \ (2.41)$$

The possible values of $k$ in the sum of (2.40) are limited by a triangle relation $(j'_s k j_s)$.

The quantity $\Gamma_k$ can also be seen in another context, which provides an efficient way to compute it. Suppose we want to compute a matrix element of a one-body operator of rank $k$

$$W_q^{(k)} = \sum_{i=1}^{N_{sub}} u_q^{(k)}(i) \ \ (2.42)$$

between two $N_{sub}$-electron subconfigurations $|\psi_{sub}J_{sub}\rangle$ and $|\psi'_{sub}J'_{sub}\rangle$. The graph-
ical analysis yields

\[
\langle (\Psi_{sub}^t) J_{sub}^t | W^{(k)} | (\Psi_{sub}) J_{sub} \rangle = \sum_{J_v, J_s} \Gamma_k (\Psi_{sub}^t, J_v^t; \Psi_{sub}, J_s) \langle j_s^t | u^{(k)} | j_s \rangle. \tag{2.43}
\]

Here, \( \langle \cdot | \cdot \rangle \) denote standard reduced matrix elements.

**Remaining angular factors.** We still have to work out an algebraic expression for the diagram of (2.40). By straightforward application of the diagram reduction rules outlined in Appendix A, we get

\[
\begin{align*}
&\times [k, J_G, j_v^t, J_v, J_v^t, J_{sub}]^{1/2} \\
&\times \left\{ \begin{array}{ccc}
J_v & k & J_v^t \\
J_v^t & J_{tot} & J_{sub}
\end{array} \right\} \left\{ \begin{array}{ccc}
J_v & k & J_v^t \\
J_v^t & J_{tot} & J_{sub}
\end{array} \right\} \left\{ \begin{array}{ccc}
j_s & k & j_s^t \\
j_s & J_G & j_v
\end{array} \right\}.
\tag{2.44}
\end{align*}
\]

**Final results.** Now we are ready to write the final expression:

\[
\mathcal{M}_{sv} = \sum_{J_v, J_s, j_v, j_v^t, J_G} \mathcal{C}_{sym} \langle (j_v^t, j_v) | J_G | G | (j_s, j_v) | J_G \rangle, \tag{2.45}
\]
where

\[
\mathcal{C}_{\text{sym}} = 2 \delta_{j_v,j'_v,j'_2} \left( J_v, J'_v \right) \left( j'_v, J'_v \right) \sum_{k} \Gamma_k (\Psi'_{\text{sub}}, j'_s; \Psi_{\text{sub}}, j_s) \times [J_G, k] [J_v, J'_v]^{1/2} (-1)^{k+J_{\text{tot}}+J'_v+J_{\text{sub}}+J_v-J_s-J_G} \times \begin{array}{ccc}
J_v & k & J'_v \\
J'_{\text{sub}} & j'_{\text{sub}}
\end{array} \begin{array}{ccc}
J_v & k & J'_v \\
J'_v & J_v & j_v
\end{array} \begin{array}{ccc}
j_s & k & j'_s \\
j'_v & J_G & j_v
\end{array}.
\]

(2.46)

The expression is rather complicated in appearance, but it is completely general and convenient to use in a computer program.

In summary, by expanding an \( N \)-electron matrix element in terms of two-electron matrix elements, we obtained explicit dependence of the matrix element \( \langle \Psi'_d | G | \Psi_d \rangle \) on the quantum numbers of the correlation orbitals.

### 2.3.4 Matrix elements connecting single-substitution symbolic states

Next we consider the matrix elements connecting single-substitution symbolic states. To derive the dependence of the matrix element (2.15) on the correlation orbitals, we retrace our steps taken in the treatment of the interaction between double-substitution symbolic states. Without repeating the details, we state the final result

\[
\langle \Psi'_s | G | \Psi_s \rangle = \mathcal{M}_{ss} + \mathcal{M}_{sv},
\]

(2.47)
where

\[
\mathcal{M}_{ss} = \langle (\Psi'_{\text{sub}})^J_{\text{sub}} | G | (\Psi_{\text{sub}})^J_{\text{sub}} \rangle \langle (\psi'_v)^j_{v} | (\psi_v)^j_v \rangle,
\]

(2.48)

\[
\mathcal{M}_{sv} = \sum_{\substack{j_s j'_s \\ k, j_G}} (-1)^{J_{\text{tot}}+J_{\text{sub}}-J_G-j_s} \left[ J_G, k \right] \left\{ \begin{array}{ccc} J_{\text{sub}} & k & J'_{\text{sub}} \\ J_v & j_v \end{array} \right\} \left\{ \begin{array}{ccc} j_v & k & j'_{v} \\ j_s & J_G & j_s \end{array} \right\} 
\times \Gamma_k(\Psi'_{\text{sub}}, j'_s, \Psi_{\text{sub}}, j_s) \langle (j'_s, j'_v) J_G | G | (j_s, j_v) J_G \rangle.
\]

(2.49)

Again, the possible values of $J_G$ are limited by triangle relations $(j_s j_v J_G)$ and $(j'_s j'_v J_G)$, the values of $k$ are defined by $(j_s k j'_s)$, and $j_s, j'_s$ run over all orbitals of their corresponding subconfigurations. The definition of $\Gamma_k(\Psi'_{\text{sub}}, j'_s, \Psi_{\text{sub}}, j_s)$ is given in (2.43).

### 2.3.5 Matrix elements connecting the two types of symbolic states

To complete our long discussion on the dependence of the matrix elements (2.12) - (2.16) upon correlation orbitals, we examine the matrix element $\langle \Psi'_s | G | \Psi_d \rangle$ between a single-substitution symbolic state and a double-substitution symbolic state.

We start with (2.16)

\[
\langle \Psi'_s | G | \Psi_d \rangle = \mathcal{M}_{svvw} + \mathcal{M}_{vvss},
\]

(2.50)

where

\[
\mathcal{M}_{svvw} = \sqrt{2(N-1)} \langle \Phi'_s | G_{N-1,N} | \Phi_d \rangle,
\]

(2.51)
\[ \mathcal{M}_{vuss} = (N - 2)\sqrt{2(N - 1)} \langle \Phi_s' | G_{N-2,N-1} | \Phi_d \rangle. \] (2.52)

The \( \mathcal{M}_{svv} \) term connects three correlation orbitals and one subconfiguration orbital, whereas \( \mathcal{M}_{vuss} \) connects three subconfiguration orbitals and one correlation orbital.

The \( \mathcal{M}_{svv} \) term can be handled in a manner similar to that which we used in Section 2.3.2 to study the matrix element between a single-replacement symbolic state and a reference state. We transform \( |\Phi_s'\rangle \) using (2.22) and (2.23), and isolate an electron pair on which the operator acts. We also observe that

\[ \langle (\psi_{sv}^t) J_v | G | (\psi_v) J_v \rangle = \sqrt{2} \left\{ \langle \psi_1^{t \text{ sub}} (N - 1) j_s^t, \psi_v (N) j_v^t \rangle J_v | G | (\psi_v) J_v \right\}, \] (2.53)

where \( (\psi_{sv}^t) \) is an antisymmetric two-electron state defined as in (2.24). With this in mind, we obtain

\[ \mathcal{M}_{svv} = \sqrt{N - 1} \left\{ \langle \Psi_{\text{sub}}^t J'_{\text{sub}} \{ | (\Psi_{\text{sub}}^t) J_{\text{sub}} \{ (\psi_1^{t \text{ sub}}) j_s^{'t} \rangle \right. \]

\[ \times \left. \langle J_{\text{sub}} (j_s^t j_v^t) J_v \rangle J_{\text{tot}} | \langle J_{\text{sub}} j_s^t J_{\text{sub}} j_v^t J_{\text{tot}} \rangle \right\} \]

\[ \times \langle (\psi_{sv}^t) J_v | G | (\psi_v) J_v \rangle . \] (2.54)

Here, all primed quantities pertain to the single-substitution symbolic state, and unprimed quantities belong to the double-substitution symbolic state. The orbital \( (\psi_1^{t \text{ sub}}) j_s^t \) is present in \( \Psi_{\text{sub}}^t \) but absent from \( \Psi_{\text{sub}} \).

Next we turn our attention to the \( \mathcal{M}_{vuss} \) term. Just as we did before, we isolate the electron pair on which the operator acts; in this case, the pair with electron
labels \( N - 2, N - 1 \). To accomplish this, we do three mcfp expansions: one for each subconfiguration, and one for the correlation pair of the double-replacement symbolic state. Although similar expansions have been used in previous sections, we repeat the equations for clarity of notation. In particular, the subconfiguration of the single-replacement symbolic state is expressed as

\[
|\Psi'_{\text{sub}}(1\cdots N-1)J'_{\text{sub}}\rangle = \sum_{(\Psi'_{N-3})J'_{N-3}, \left(\psi'_{\text{sub}}\right)J'_s} \left( (\Psi'_{N-3}) J'_{N-3}, \left(\psi'_{\text{sub}}\right) J'_s \right) \left( |\Psi'_{\text{sub}}(1\cdots N)\rangle \right) (\Psi'_{\text{sub}}) J'_{\text{sub}} \right),
\]

where \( (\psi'_{\text{sub}}) J'_s \) is a coupled and antisymmetric pair of subconfiguration electrons.

The subconfiguration of the double-replacement symbolic state becomes

\[
|\Psi_{\text{sub}}(1\cdots N-2)J_{\text{sub}}\rangle = \sum_{(\Psi'_{N-3})J'_{N-3}, \left(\psi'_{\text{sub}}\right)J_s} \left( (\Psi'_{N-3}) J'_{N-3}, \left(\psi'_{\text{sub}}\right) J_s \right) \left( |\Psi_{\text{sub}}(1\cdots N)\rangle \right) (\Psi_{\text{sub}}) J_{\text{sub}} \right),
\]

where \( (\psi'_{\text{sub}}) J_s \) is a selected orbital from the subconfiguration of the double-replacement symbolic state. The third mcfp expansion, for the correlation pair, is

\[
|\psi_v(N-1, N)J_v\rangle = \sum_{j_v = \{j_1, j_2\}} \langle j_v, \overline{j_v}\rangle \{j_1 j_2\} J_v \{\psi_v(N-1)j_v, \overline{\psi_v(N)}\overline{j_v}\} J_v.\]
Here, $j_v$ runs over the two orbitals of $| \langle \psi_v \rangle J_v \rangle$, and $\overline{j}_v$ is defined as the other correlation orbital: if $j_v = j_1$, then $\overline{j}_v = j_2$, and vice versa. The relation (2.57) ensures that the electron labeled $N-1$ is the first in the coupling order of the correlation pair.

Having separated electrons with labels $N-2, N-1$ from their subconfigurations, we still need to couple the active electrons together on the right-hand side of the matrix element. This is conveniently accomplished by use of the recoupling relation

$$
\left| \left\{ (J_{N-3}s) \ J_{\text{sub}}, (j_v, \overline{j}_v) \ J_v \right\} \right|_{\text{tot}} = \sum_{J_G, J_{\text{int}}} \left| \left\{ [J_{N-3}, (j_s j_v) \ J_G] \ J_{\text{int}}, \overline{J}_v \right\} \right|_{\text{tot}} \times \left\langle \left\{ (J_{N-3}s) \ J_{\text{sub}}, (j_v, \overline{j}_v) \ J_v \right\} \right|_{\text{tot}} \cdot (2.58)
$$

Notice that this step yields the desired electron pair $(j_s(N-2) j_v(N-1)) \ J_G$, which is coupled, but not antisymmetric.

Substituting (2.55) - (2.58) into (2.52) and keeping in mind (2.53), we get

$$
\mathcal{M}_{\text{vss}} = (N-2) \sqrt{N-1} \sum_{(\psi_{N-3}) J_{N-3}, j_v = \{j_1, j_2\}} \sum_{(\psi_{\text{sub}}^t) J_G} \langle j_1 j_2 \rangle \ J_v \langle \psi_v \rangle \ J'_v \langle \psi' \rangle \ J'_v \langle \overline{\psi}_v \rangle \ J_v
$$

$$
\times \left\langle \left\{ (\psi_{\text{sub}}^t) J_{\text{sub}} \right\} \ (\psi_{N-3}) J_{N-3} \right\rangle \ (\psi_{\text{sub}}^t) J_G \ (\psi_{\text{sub}}^t) J_{\text{sub}} \right\rangle \ J_G \ \left\langle (j_s j_v) \ J_G \ J_{\text{int}} \overline{J}_v \right\rangle \ J_{\text{tot}} \ \left\langle (j_{N-3}s) \ J_{\text{sub}}, (j_v, \overline{j}_v) \ J_v \right\rangle \ J_{\text{tot}}
$$

$$
\times \ \left\langle (\psi_{\text{sub}}^t) J_G \ | \ G \ | \ (\psi_{\text{sub}}) J_G \right\rangle \cdot (2.59)
$$

Here, $(\psi_{sv}) J_G$ is a coupled and antisymmetric two-electron state as in (2.24), the orthogonality of Dirac orbitals requires that the two $(N-3)$-electron states on both sides of the matrix element be the same, and the scalar nature of the operator sets
where $j'_s = J_G$ and $j'_s = J'_{sub}$. Also notice that for the $\mathcal{M}_{su}$ term to have a nonzero value, the two correlation orbitals on which the operator does not act have to be the same.

The recoupling coefficient is easily evaluated using angular momentum diagrams:

$$
\langle \{ [J_{N-3}, (j_s j_v) J_G] J'_s, j'_v \} J_{tot} \} \{ (J_{N-3}, j_s) J_{sub}, (j_v, j'_v) J_v \} J_{tot} \rangle =
$$

$$
= (-1)^{J_{N-3}+j_s+2j_v+j'_{sub}+j_{sub}+j'_v+j_v+J_{tot}} [J_{sub}, J_G, J'_s, J'_v, J_v]^{1/2}
$$

$$
\times \begin{pmatrix}
J_{N-3} & j_s & J_{sub} \\
j_v & J'_s & J_G \\
\end{pmatrix}
\begin{pmatrix}
J_{sub} & j_v & J'_s \\
\bar{j}_v & J_{tot} & J_v \\
\end{pmatrix}.
$$

(2.60)

Expressing the mcsp coefficients in terms of overlaps between antisymmetric states, we state the final results for the interaction between a single- and a double-replacement
symbolic state as

\[
\mathcal{M}_{svuv} = (-1)^{J_{sub} + J_v + J_{tot}} [J'_{sub}, J_v]^{1/2} \left\{ \begin{array}{ccc} J_{sub} & J'_s & J'_{sub} \\ J_v & J'_{tot} & J_v \end{array} \right\} \times \langle \{ (\Psi_{sub}) J_{sub}, j'_s \} J'_{sub} | (\Psi_{sub}) J_v | G \rangle \langle J'_v J_v \rangle;
\]

(2.61)

\[
\mathcal{M}_{vssv} = \sqrt{2} \sum_{\substack{(\Psi_{N-3})J_{N-3}, \\ \psi_2)J_G}} \langle \{ (\Psi_{N-3}) J_{N-3}, (\psi_2) J_G \} J'_s | (\Psi_{sub}) J'_v \rangle 
\times \langle \{ \psi_v \} J'_v | \langle \psi_v \rangle J_v \rangle \langle j_v, j_v \rangle \langle j_1 j_2 \rangle J_v 
\times (-1)^{J_{N-3} + J_s + 2j_v + J'_{sub} + J_{sub} + J'_v + J_{tot}} [J_{sub}, J'_v, J'_{sub}, J_v]^{1/2} 
\times \left\{ \begin{array}{ccc} J_{N-3} & j_s & J_{sub} \\ j_v & J'_{sub} & J_G \end{array} \right\} \left\{ \begin{array}{ccc} J_{sub} & j_v & J'_v \\ J_v & J_{tot} & J_v \end{array} \right\} \langle \psi'_2 J_G \rangle G \langle \psi'_{sv} J_G \rangle.
\]

(2.62)

2.3.6 Chapter summary

Starting with a relativistic multiconfiguration expansion based on symbolic states, and expressing \(N\)-electron matrix elements in terms of two-electron matrix elements, we have succeeded in exhibiting the explicit dependence of the Hamiltonian matrix on the quantum numbers of correlation orbitals. These results have been checked by an independent calculation using standard methods of Racah algebra. Implementation of these results in a variational multiconfiguration computer program is expected to improve the existing algorithm for angular integrations by allowing for more efficient use of computer memory and disk storage, thus increasing the size and accuracy of possible practical calculations of atomic structure and spectra. The next chapter
discusses some aspects of such implementation.
Chapter 3

Computational aspects

This chapter outlines a potential practical application of the matrix element expansions presented in Chapter 2 and Appendix C.

3.1 Variational multiconfiguration methods: outlook

As mentioned in the Introduction, variational multiconfiguration methods [1, 2] are some of the most powerful and widely used methods in atomic structure computations. The characteristic feature of these methods is the expansion of the desired N-electron atomic wave function in terms of configuration state functions, which are constructed from one-electron orbitals with known rotational symmetry. Atomic energy levels and their corresponding eigenstates are found through an iterative procedure of constructing the Hamiltonian matrix, diagonalizing it, and improving the radial distributions of one-electron orbitals.
To achieve the desired accuracy, we may need very large multiconfiguration expansions, which place sizeable demands on computer resources. The use of modern high-performance computational technology, such as massively parallel processing, could circumvent limitations associated with standard technology. However, for efficient use of the parallel hardware, the existing software has to be significantly restructured.

Parallel implementations [10, 11] of the MCHF Atomic Structure Package [5] indicate that the present algorithm for computing and storing angular matrix elements is inadequate for very large calculations [6]. Why? In the computation of the Hamiltonian matrix, the angular matrix elements do not change throughout the iterative procedure to determine the radial distributions. Thus, the values of the angular matrix elements have to be either stored or recomputed in every iteration. This last option is not very efficient, because one calculation may involve up to 100 iterations. In the present algorithm, the angular matrix elements are computed for every pair of configuration state functions, and stored in computer memory or on disk. This leads to a dramatic growth of angular data as the number of basis functions increases. The associated requirements of computer memory and disk space limit the size of the multiconfiguration expansion and, therefore, the accuracy of the calculation. This discussion is also applicable to the relativistic atomic structure package GRASP92 [2], which uses the same strategy for handling angular matrix elements as the MCHF Atomic Structure Package.

Symbolic-state expansion of the Hamiltonian matrix elements could be used to solve this problem. As illustrated in Figure 3-1, this expansion separates the angular matrix element into three parts. One part contains the information regarding the
\[
\langle \Psi' | H_{\text{int}} | \Psi \rangle = \sum_{\text{angular}} \begin{array}{c}
\text{Quantity} \\
\text{independent} \\
of \text{the} \\
correlation \\
orbitals}
\end{array} \times \begin{array}{c}
\text{Quantity} \\
\text{dependent} \\
on \text{the} \\
correlation \\
orbitals}
\end{array} \times \begin{array}{c}
\text{Two-electron} \\
\text{matrix} \\
element
\end{array}
\]

Figure 3-1: Separation of the angular matrix element

\((N-2)\)- or \((N-1)\)-electron subconfiguration of the reference state, and is completely independent of the quantum numbers of the correlation orbitals. The second part, which describes the correlation orbitals, is represented by an easily programmable formula. The third part, the two-electron matrix element, which may also depend on the correlation orbitals, can be evaluated separately. This break-up allows us to treat together all configuration state functions that are represented by a single symbolic state. It is now easy to see how such an approach curtails the growth of angular data with the problem size: for each pair of symbolic states, the quantities that do not depend on the correlation orbitals are stored in computer memory or on disk, and the rest of the angular quantities are computed as they are needed. When the basis set is increased by introducing more correlation orbitals, the amount of stored angular data remains unchanged.
3.2 Symbolic-state approach: sketch of a computer implementation

To illustrate how this new way of handling the angular momentum algebra could be implemented in a computer code, we wrote a Fortran 90 program to construct the angular matrix elements of the Hamiltonian matrix for a scalar operator $G$ in the basis of nonrelativistic symbolic states. The program is based on equations from Appendix C. It should be emphasized that we focus not on the numerical results, but rather on the matrix sparsity patterns, which are determined by the rotational symmetry of basis states. In this context, even the operator $G$ is not specified, although for practical purposes it is worth keeping the Coulomb interaction operator in mind as an example.

3.2.1 Input

The input to our program is a file supplied by a C program GAME [12] written by D. G. Ellis. By fully uncoupling configuration state functions, this program computes matrix elements of one- and two-body operators between general LS-coupled $N$-electron states in terms of one- or two-electron matrix elements.

For the present application, the GAME program provides information specifying the configuration-interaction blocks. A block is defined as a collection of matrix elements between two symbolic states. Recall that internal quantum numbers of the correlation orbitals are left unspecified in a symbolic state; therefore, a single matrix element between symbolic states becomes a rectangular block of matrix ele-
ments between configuration state functions once the quantum numbers specifying the correlation orbitals are assigned a range of values. The GAME program computes all the quantities in (C.5)-(C.9) that are independent of the quantum numbers of the correlation orbitals, including the coefficient \( \Gamma_{kk}^l \) which contains the details regarding the internal structure of the subconfigurations. The coefficient \( \Gamma_{kk}^l \) is found as a contribution of an electron pair \( l_c, l'_c \) to the matrix element of a one-body unit double-tensor operator according to (C.11)-(C.12).

The output file produced by the GAME program (a prototype of a file with potential use for large-scale MCHF calculations) is then read by our program. A sample file is shown in Appendix D.

### 3.2.2 Example: the Hamiltonian matrix for the ground state of the beryllium atom

Figure 3-2 shows the structure of the Hamiltonian matrix in the basis of LS-coupled symbolic states. Each point symbol on the plot represents a nonzero matrix element. The physical problem pictured here is electron correlation in the ground state of the beryllium atom. The reference set is assumed to be of the form

\[
\Psi_{\text{ref}} = c_1 \vert 1s^2 2s^2 1S^e \rangle + c_2 \vert 1s^2 2p^2 1S^e \rangle.
\]  

(3.1)
Figure 3-2: The sparsity structure of the Hamiltonian matrix for the ground state of the beryllium atom
We consider five double-substitution symbolic states interacting with the reference set:

\[
| (1s^2)^1S^e, (n_1l_1, n_2l_2)^1S^e \rangle \\
| (1s2s)^1S^e, (n_1l_1, n_2l_2)^1S^e \rangle \\
| (1s2s)^3S^e, (n_1l_1, n_2l_2)^3S^e \rangle \\
| (1s2p)^1P^o, (n_1l_1, n_2l_2)^1P^o \rangle \\
| (1s2p)^3P^o, (n_1l_1, n_2l_2)^3P^o \rangle.
\] (3.2)

All single-substitution symbolic states and those double-substitution states that are formed by replacement of both 1s (core) electrons have been omitted. Matrix elements involving reference states form a band that extends along the left vertical edge and the top horizontal edge of the matrix. This band is not shown. Numerical values of \(n_1, n_2\) range from 3 to 8, and \(l_1, l_2 \leq 3\). In practical applications, such matrices can be an order of magnitude larger; the present size of the matrix was chosen for graphing purposes. The five symbolic states give rise to the \(5 \times 5\) block structure of the matrix. The size of a diagonal block depends on the number of configuration state functions represented by a single symbolic state in the calculation. This number varies, because the number of orbital pairs \((n_1l_1, n_2l_2)\) that can yield specified values of \(L_vS_v\) is different for different symbolic states. For example, the third diagonal block, which corresponds to the matrix elements between the configuration state functions in the symbolic state \( | (1s2s)^3S^e, (n_1l_1, n_2l_2)^3S^e \rangle \), is smaller than
the first diagonal block, which represents matrix elements between the states of type
\[ \{|1s^2\rangle \, 1S^e, (n_1l_1, n_2l_2) \, 1S^e \} \, 1S^e \}; \] equivalent orbitals cannot be coupled to a triplet state \(^3S^e\) by the Pauli exclusion principle.

Each block consists of subblocks representing fixed orbital angular momentum quantum numbers \(l_1, l_2, l'_1, l'_2\). Varying values of \(n_1, n_2, n'_1, n'_2\) give rise to sparsity patterns within a subblock. Upon inspecting (C.5)-(C.9), one can see that in the case of orthogonal orbitals the off-diagonal blocks can only have nonzero contributions from the \(M_{\alpha\beta}\) term; therefore, at least one electron from the correlation pair has the same \(nl\) quantum numbers on both sides of the matrix element. This explains why there are many subblocks without a single nonzero matrix element.

### 3.2.3 Comparison of the data storage requirements

As mentioned earlier, the practical advantage of the symbolic-state multiconfiguration expansion over the traditional approach, in which every configuration state function is treated independently, is the capability to enlarge the multiconfiguration basis without increasing the amount of stored angular data. Let us use the beryllium example to compare the data storage requirements.

In the beryllium example, the multiconfiguration basis consists of 415 configuration state functions. Our sample matrix contains 57057 nonzero matrix elements; i.e., the matrix is \(57057 \div 415^2 \approx 33\%\) dense. If the angular data is stored on disk for each pair of configuration state functions separately, as it is done in the existing multiconfiguration atomic structure computer programs, there are at least 28736 entries in
the angular-coefficient file. (Since the matrix is symmetric, only the matrix elements on one side of the main diagonal need to be stored.) As seen from Appendix D, the new method based on symbolic states gives only 66 entries.

The difference between the traditional method and the new method becomes even more striking when the growth rates of the stored angular data are considered. Let us increase the range of the correlation orbitals to $3 \leq n_1, n_2 \leq 16$, $l_1, l_2 \leq 6$; i.e., double the maximum values of the quantum numbers describing the correlation orbitals. The multiconfiguration basis will now consist of 3671 configuration state functions. Assuming that the matrix is still 33% dense, the traditional method will lead to at least $2.2 \times 10^6$ entries in the angular-coefficient file! How many entries in the angular-coefficient file do we expect from the new method? Only 66 – in fact, the file of Appendix D suits the enlarged calculation.

This crude comparison of the data storage requirements convincingly illustrates the practical benefits of the symbolic-state matrix-element expansion.

Next let us look at a possible way to diagonalize a matrix with such sparsity structure.

### 3.2.4 Overview of the Davidson method for the large, sparse eigenvalue problem

The Davidson method [13] is commonly used in quantum chemistry and large-scale atomic structure calculations [10, 11] to find a few extreme eigenvalues and eigenvectors of a large (matrix dimension $10^3 \sim 10^6$), sparse ($\leq 30\%$ nonzero elements),
symmetric, diagonally dominant matrix. The main ideas of the method are briefly sketched below.

Given a real symmetric $N \times N$ matrix $A$, the eigenvalue equation $Ax = \lambda x$ is solved iteratively in a subspace of smaller dimensionality $P \ll N$. An orthonormal basis $B = \{b_1, b_2, \ldots, b_P\}$ is chosen, and an approximate eigenvector of the form $\tilde{x} = Bc$ is sought. Here, each $b_i$ is of length $N$, and $c$ is a vector of length $P$. An approximate (much smaller!) eigenvalue equation $B^T A B c = \tilde{\lambda} c$ is solved to get an approximation to the eigenpair $\tilde{\lambda}, \tilde{x}$ of the original matrix $A$. Next, the residual $(A - \tilde{\lambda} I) \tilde{x} = \text{Res}(\tilde{x})$ is computed and used in the construction of a new vector $B_{P+1} = (\tilde{\lambda} I - \text{diag}(A))^{-1} \text{Res}(\tilde{x})$ to be added to the subspace basis after orthogonalization. A matrix of diagonals $\text{diag}(A)$ is used as an easily invertible approximation of $A$. The process of solving an approximate eigenvalue problem in the increased subspace is repeated until convergence.

It is important to note that the original large matrix is accessed only through a matrix-vector multiplication operation. In fact, the implementation of the Davidson method [14] requires the user to provide a matrix-vector multiplication routine suited for the size and sparsity structure of the user’s matrix.

With the Davidson method for matrix diagonalization in mind, we have written a matrix-vector multiplication routine for the Hamiltonian matrix constructed in the basis of symbolic states. First, let us look at the way the matrix was stored in the computer memory.
3.2.5 The matrix storage scheme

A special data structure has been devised to store the matrix in computer memory in order to avoid filling the memory with zero entries. The matrix is stored as an array of pointers to the interaction blocks.\(^1\) Since the matrix is symmetric, it is sufficient to store the diagonal blocks and the blocks in the lower triangular part of the matrix. Each block is represented as an array of subblock information. Each element of the subblock array holds the contents of the subblock and the location of the subblock within the block. If a subblock does not contain any nonzero elements, it is not stored at all. Another array holds the sizes of the diagonal blocks, allowing us to find the location of any block within the full matrix. With this information, given the position of a matrix element in a subblock, it is straightforward to find the element’s position in the original matrix.

3.2.6 Matrix-vector multiplication algorithm

The basic unit of the calculation is set to be the matrix subblock, as defined in the beryllium example above. Both the multiplying vector \( \mathbf{x} \) and the product vector \( \mathbf{p} \) are partitioned into subvectors, corresponding to the subblocks of the matrix \( \mathbf{A} \). The matrix subblock indexed by the \( i^{th} \) subblock-row and the \( j^{th} \) subblock-column, \( A_{ij} \), contributes a vector \( A_{ij} \mathbf{x}_j \) to the matrix-vector product. Here \( \mathbf{x}_j \) is the \( j^{th} \) subvector of the multiplying vector \( \mathbf{x} \). The \( i^{th} \) subvector of the matrix-vector product is a sum

\(^1\)Recall that the block is a collection of matrix elements between two specified symbolic states.
of such contributions:

\[ p_i = \sum_j A_{ij}x_j. \]  \hfill (3.3)

Since only the lower triangular part of the symmetric matrix \( A \) is stored, the off-diagonal subblocks contribute to the matrix-vector product in two ways: \( A_{ij}x_j \) as a part of the product subvector \( p_i \), and \( A_{ji}^T x_i \) as a part of \( p_j \).

The basic idea of the matrix-vector multiplication algorithm is to multiply each subblock by an appropriate subvector and place the result in a proper position within the full matrix-vector product. With the matrix stored as a collection of subblocks, this operation is easily implemented in a computer program.

In addition, since each block of the matrix can be computed independently of all the other blocks, it is of interest to consider a parallel algorithm for the case of the matrix distributed among the processors.

The simplest possible parallelization was performed using MPI [15] as a message passing paradigm. Each processor node stores a few blocks of the matrix along with the full multiplying vector. The only necessary communication between processors is a collective computation operation MPI_REDUCE to sum the product vectors computed by individual processor nodes. Thus, the matrix-vector multiplication process can be depicted as:

Concurrently for all processors \( P \)

For all blocks assigned to \( P \) Do:

For all subblocks in a block Do:
Multiply a subblock by a subvector

Put the result into the matrix-vector product

End Do

End Do

Do global sum of matrix-vector products

3.2.7 Results and discussion

The program was tested on eight processor nodes of the IBM SP2 parallel supercomputer at the University of Michigan. The matrix sizes varied from $10^2$ to $10^4$. The speedup, defined as the ratio of the execution time on one node to the execution time on $n$ nodes, was found to be between three and four for eight processor nodes. The results are shown in Table 3.1. A much higher speedup is expected, since the problem of setting up the matrix is perfectly parallel, and the matrix-vector multiplication requires only minimal communication. An obvious source of parallelization inefficiency is poor load balancing. In the present code, each processor is assigned an equal number of blocks. The sample matrix of Figure 3-1 clearly shows that the diagonal blocks require a lot more work. Implementation of the load distribution technique that tries to balance the number of subblocks per processor should significantly improve the parallel performance.

The preliminary version of the program calls for many additional improvements, both algorithmic and conceptual. Listed below are the obvious algorithmic improvements:
Table 3.1: The speedup of the matrix-vector multiplication routine for 8 processor nodes of the IBM SP2 parallel supercomputer.

1. The diagonal blocks are symmetric and therefore do not need to be stored in full, as is done in the present program.

2. The sparsity structure of the subblocks could be taken into account.

In addition to these algorithmic improvements, the program needs to be expanded on a physical basis:

1. So far, we have considered only the configuration interaction between the double-substitution symbolic states, omitting the interaction of the symbolic states with the reference state. The formulas for these matrix elements are readily available in Appendix C, and could be easily incorporated into the program.

2. Matrix elements involving single-substitution symbolic states should be considered.

3. Finally, to treat the angular matrix quantitatively, the angular part of the two-electron matrix element needs to be taken into account.
Chapter 4

Conclusions

4.1 Summary

Multiconfiguration variational methods are widely accepted as a general and robust way to predict properties of complex atoms and ions. These methods are based on the independent-particle model, and the correlation in the motion of electrons is accounted for by enlarging the basis of configuration states. To achieve high accuracy, very large multiconfiguration expansions may be required. This dissertation describes a new method for handling the angular matrix elements in large-scale multiconfiguration atomic structure calculations.

We form the Hamiltonian matrix in the multiconfiguration basis of symbolic states, which are constructed from a set of reference configurations by replacing one or two occupied orbitals with general, unoccupied, and unspecified correlation orbitals. Expanding the $N$-electron matrix elements in terms of two-electron matrix elements by use of diagrammatic angular momentum techniques, we derive the explicit depen-
dence of the matrix elements on the quantum numbers of the correlation orbitals. In
Chapter 2 this expansion is derived for the multiconfiguration basis of relativistic jj-
coupled symbolic states, and in Appendix C the treatment is repeated for the basis of
nonrelativistic LS-coupled symbolic states. In addition, we demonstrate the sparsity
structure of the Hamiltonian matrix constructed in the basis of LS-coupled symbolic
states for a sample case of the beryllium atom.

4.2 Potential applications

This section lists some possible practical applications of the symbolic-state matrix-
element expansion described above.

The primary potential application – in fact, the motivation for this work – is the
need to restructure the present algorithms for computing the angular matrix elements
of the Hamiltonian matrix in multiconfiguration atomic structure calculations. In the
existing algorithms, many angular computations are redundant – the matrix elements
are computed for each pair of configuration states, neglecting the fact that different
configurations may have identical angular momentum properties. This redundancy
leads to a significant increase in computer resource requirements, because the angular
matrix elements, which are repeatedly reused in the calculation, need to be stored in
computer memory or on disk. The symbolic-state matrix-element expansion offers a
solution to this problem by

(a) isolating the part of the angular matrix element that depends on the pair
of symbolic states, but not on the correlation orbitals;
(b) providing explicit analytic formulas to evaluate the part of the matrix element that depends on the correlation orbitals, but not on the internal structure of the symbolic states.

With this approach, the angular data that needs to be stored is limited to the information independent of the correlation orbitals. The crucial benefit of the symbolic-state matrix-element expansion is the capability to enlarge the multiconfiguration basis (by adding new correlation orbitals) without increasing the amount of stored angular data.

The generality of the symbolic-state matrix-element expansion leads to another practical advantage of this new method. This expansion separates the content of the physical interaction exhibited in the two-electron matrix elements from the effects of electron indistinguishability and angular momentum coupling contained in the expansion coefficients. The expansion is valid for any interaction in an atom described by a symmetric two-electron operator that is a scalar in its tensor properties.\(^1\) This makes it easier to include additional physical effects in the atomic structure calculation. Rather than dealing with complexities of \(N\)-electron matrix elements for each additional term in the Hamiltonian, one needs to evaluate only the two-electron matrix elements, which are much simpler to compute. The expansion coefficients are shared by all two-electron operators. An example of an operator that could in the future be included in the computation of the atomic wave function is that which represents the Breit interaction. Because of the considerable computational effort required, the

\(^1\)i.e., commutes with the total angular momentum of the atom: \(J\) in the case of \(jj\)-coupled symbolic states; \(L\) and \(S\) separately in the case of \(LS\)-coupled symbolic states.
Breit interaction is usually calculated perturbatively, after the wave function has been determined, and, therefore, affects only the total energy [16]. The importance of incorporating changes in the wave function due to the Breit interaction is discussed, for example, in [17].

Finally, such an expansion yields the Hamiltonian matrix with a block structure. This structure offers significant computational benefits, whose detailed description is beyond the scope of this dissertation. As the Hamiltonian matrix is distributed among the processors of a parallel computer, the block structure facilitates efficient parallel computation with minimal interprocessor communication. In addition, a known block structure could speed up the convergence of the Davidson algorithm for finding selected eigenvalues and eigenvectors [14] if the diagonal blocks, instead of the diagonal matrix elements, were used to compute a required approximation of the matrix inverse [6].

4.3 Outlook

While the matrix-element expansion for relativistic jj-coupled symbolic states is ready for practical implementation, a similar expansion for nonrelativistic LS-coupled symbolic states is not yet complete. An immediate and straightforward task is to include the single-replacement symbolic states. In addition, the coupling order of the subconfiguration and the correlation pair in the LS-coupled symbolic state should be changed to match the definition of the symbolic state given in the Introduction.

In the derivation of the symbolic-state matrix-element expansion, we have assumed
that the multiconfiguration basis is built on a single set of orthonormal one-electron orbitals. This condition, however, is not a requirement of the variational multiconfiguration methods. Moreover, since the motion of electrons is correlated, it is natural to assume that in a different configuration state an electron described by an orbital of a given type feels a somewhat different radial potential. Thus, it may be beneficial to relax the orthogonality condition for one-electron radial wave functions belonging to different configuration states (orbitals within a single configuration state are still kept orthogonal, and so are different configuration states [18]). Indeed, due to their flexibility, the non-orthogonal radial orbitals are successfully used to account for electron correlation efficiently in both MCHF and MCDF calculations [3, 17]. Although a general non-orthogonal extension of our method is an ambitious project, a preliminary attempt shows that the symbolic-state matrix-element expansion might be relatively easily generalized to allow for non-orthogonality among radial wave functions in different reference states, if all correlation orbitals are kept orthogonal to all reference orbitals.

Most important, the practicability of the symbolic-state matrix-element expansion needs to be proved by implementing this approach into the computer programs MCHF Atomic Structure Package [5] and GRASP92 [2].

In conclusion, this dissertation has laid the groundwork for a method that has the potential to remove some practical limitations of today’s multiconfiguration atomic
structure calculations. The full implementation of this method is still in the future; thus, it is not yet possible to give a quantitative measure of the method’s impact. Time will tell.
Appendix A

Graphical techniques of angular momentum

In the Introduction we have mentioned that the central field approximation separates the atomic structure problem into an “angular problem” and a “radial problem,” and that the angular problem can be solved exactly in an analytic form by means of angular momentum theory. Standard techniques to evaluate angular matrix elements are known as Racah algebra [19]. This Appendix discusses graphical angular momentum techniques, which, complementing the traditional Racah algebra, simplify evaluation of angular matrix elements.

Graphical methods of angular momentum algebra were first introduced in the 1960’s by a Lithuanian atomic theorist, Adolfas Jucys, and his collaborators. Their first book on this subject [20] was based on the graphical representation of the 3-j symbols. Later, in the 1970’s, the technique was reformulated to treat the vector-coupling coefficients as basic building blocks of angular momentum diagrams [8],
and this is the work we closely follow. A brief description of this method can be found in [21]. Variations of the graphical angular momentum techniques have been developed by a number of authors [22, 23, 24].

In spirit, Jucys’ angular momentum diagrams are similar to Feynman diagrams: pictures provide the “bird’s-eye” view of the problem, and the rules, associated with the pictures, help us solve the problem efficiently, without tedious computations. It is beyond the scope of this work to give a detailed account of the Jucys’ method. The purpose of the discussion that follows is to introduce the notation, and to give a brief outline of the technique.

A.1 Graphical representation of coupled angular momentum states

**Vector-coupling coefficient.** A vector-coupling coefficient is represented by three lines, one for each angular momentum involved. The lines meet at a vertex. For example,

\[
\langle j_1m_1j_2m_2 | jm \rangle = \begin{array}{c}
+ j_1m_1 \\
\downarrow j_2m_2 \\
\downarrow jm
\end{array}.
\]  

(A.1)

The resultant angular momentum is denoted by a heavy line. The sign of the vertex indicates the coupling order. Imagine sweeping the line representing the first angular momentum of the coupled pair into the line representing the second without crossing the heavy line. If the direction of the sweep is *counterclockwise*, the sign is “+,” if
clockwise, the sign is “−.” The angles between the lines have no significance. Since
the vector-coupling coefficient is a real quantity, \( \langle jm \mid j_1m_1j_2m_2 \rangle \) is represented by
the same diagram as \( \langle j_1m_1j_2m_2 \mid jm \rangle \).

**Coupled states.** Using (A.1), a coupled state of two angular momenta is written
as

\[
| j_1j_2jm \rangle = \sum_{m_1,m_2} | j_1m_1 \rangle | j_2m_2 \rangle | jm \rangle.
\]  

(A.2)

A state of three coupled angular momenta is represented by

\[
| (j_1j_2j_3)j_4jm \rangle = \sum_{m_1,m_2,m_3} | j_1m_1 \rangle | j_2m_2 \rangle | j_3m_3 \rangle \langle j_1m_1j_2m_2 \mid j_4m_4 \rangle (j_3m_3 | jm \rangle
\]

(A.3)

Note that a line connecting two vertices represents summation over the corresponding
magnetic quantum number.

It is now easy to generalize (A.3) to arbitrary coupling of any given number
of angular momenta. As an example, we consider a state of four coupled angular
momenta:

\[
| (j_1j_2)j_3j_4jm \rangle = \sum_{m_1,m_2,m_3,m_4} | j_1m_1 \rangle | j_2m_2 \rangle | j_3m_3 \rangle | j_4m_4 \rangle
\]
The diagram on the right-hand side of the last equation is the representation of the generalized Clebsch-Gordan coefficient, which occurs in the transformation between a state of \( n \) coupled angular momenta and a state of \( n \) uncoupled angular momenta.

It is worth emphasizing that here we deal with coupled, but not antisymmetrized angular momentum states.

A.2 Matrix elements of tensor operators and the Wigner-Eckart theorem

In atomic physics, it is customary to expand any given operator in the basis of spherical tensor operators, which have well-defined rotational properties. In particular, rules of their commutation with angular momentum operators are analogous to relations expressing the action of angular momentum operators on angular momentum eigenstates. Most important, matrix elements of spherical tensor operators between angular momentum eigenstates can be conveniently evaluated by use of Racah algebra.

One of the cornerstones of Racah algebra is the Wigner-Eckart theorem, which states that a matrix element of a spherical tensor operator between angular momentum eigenstates is a product of two factors: a “physical factor” and a “geometrical
factor:\)
\[
\langle j m \mid T_q^{(k)} \mid j' m' \rangle = [j \parallel T^{(k)} \parallel j'] \langle j' m' k q \mid j m \rangle. \tag{A.5}
\]
The first factor\(^1\) depends on the physical nature of the operator, and does not depend on the choice of coordinate axes. The second factor – a vector coupling coefficient – describes the rotational properties of the matrix element in the chosen coordinate system.

We have seen how coupled angular momentum states are represented graphically. To construct a diagram corresponding to an angular matrix element, we still need a graphical representation of the operator. A spherical tensor operator \(T_q^k\) is represented graphically by
\[
T_q^k = T \quad k q . \tag{A.6}
\]
Here, \(k\) and \(q\) indicate the rank and the component of the tensor operator, respectively.

Suppose that \(T_q^k\) acts in the space spanned by a set of basis functions \(|jm\rangle\). The graphical form of a matrix element of \(T_q^k\) in this basis resembles a vector-coupling coefficient diagram
\[
\langle jm \mid T_q^k \mid j' m' \rangle = \begin{array}{c}
\text{+} \\
T \\
_j m' \\
\text{+} \\
T_q^k \\
j m \\
k q \\
\end{array} . \tag{A.7}
\]
\(^1\)The reduced matrix element \([j \parallel T^{(k)} \parallel j']\) differs from its usual definition \(\langle j \parallel T^{(k)} \parallel j' \rangle\) [25] by a multiplicative factor: \([j \parallel T^{(k)} \parallel j'] = (2j + 1)^{-1} \langle j \parallel T^{(k)} \parallel j' \rangle\).
The diagrammatic form of the Wigner-Eckart theorem is then

\[
\begin{array}{c}
\text{+} \\
 T \\
\text{+} \\
 j' m'
\end{array}
\begin{array}{c}
\text{+} \\
 T' \\
\text{+} \\
 j'
\end{array}
\begin{array}{c}
\text{+} \\
 j m
\end{array}
= +
\begin{array}{c}
\text{+} \\
 T \\
\text{+} \\
 j
\end{array}
\begin{array}{c}
\text{+} \\
 j m
\end{array}
, \\
\begin{array}{c}
k q
\end{array}
\begin{array}{c}
k
\end{array}
\begin{array}{c}
+ j' m'
\end{array}
\begin{array}{c}
k q
\end{array}
\begin{array}{c}
j m
\end{array}

\text{(A.8)}
\]

where the first term on the right represents the reduced matrix element \([j \parallel T^{(k)} \parallel j']\).

Because of the Wigner-Eckart theorem, a matrix element of an irreducible tensor operator can be conveniently treated as an additional vertex in the angular momentum diagram.

Many interactions in atomic physics can be written as coupled tensor operators:

\[
[T^{(k_1)}(1) \times U^{(k_2)}(2)]^{(K)}_Q = \sum_{q_1, q_2} \langle k_1 q_1, k_2 q_2 | KQ \rangle \ T^{k_1}_{q_1} (1) \ U^{k_2}_{q_2} (2), \quad \text{(A.9)}
\]

where \(T^{k_1}_{q_1}(1)\) and \(U^{k_2}_{q_2}(2)\) operate on different parts of the system (e.g., two electrons).

The graphical representation of a coupled tensor operator is

\[
[T^{(k_1)} \times U^{(k_2)}]^{(K)}_Q = \begin{array}{c}
T \end{array} \begin{array}{c}
k_1 \\
k_2
\end{array} \begin{array}{c}
U
\end{array} \begin{array}{c}
KQ
\end{array} + \begin{array}{c}
KQ
\end{array} \quad \text{(A.10)}
\]

A.3 Diagram transformation rules

Angular momentum diagrams are constructed to aid the evaluation of angular matrix elements in terms of quantities that are easy to compute, such as 3n-j coefficients. The diagrammatic forms of 3n-j coefficients are well known [8], but, in
general, a diagram does not initially match any of the standard forms. Here one can make use of the diagram transformation rules, which are based on the properties of vector-coupling coefficients. We do not intend to present the transformation rules in either all generality or great detail. The few given examples are intended only to illustrate the techniques that are extensively used in our work.

One obvious example is the diagrammatic representation of the relation

$$\langle j_1 m_1 j_2 m_2 | j m \rangle = (-1)^{j_1+j_2-j} \langle j_2 m_2 j_1 m_1 | j m \rangle, \quad (A.11)$$

which is

$$\begin{array}{c}
\begin{array}{c}
\downarrow j_1 m_1 \\
\downarrow j m \\
\downarrow j_2 m_2
\end{array}
\end{array}\begin{array}{c}
\begin{array}{c}
\downarrow j_1 m_1 \\
\downarrow j m \\
\downarrow j_2 m_2
\end{array}
\end{array} = (-1)^{j_1+j_2-j} \begin{array}{c}
\begin{array}{c}
\downarrow j_2 m_2 \\
\downarrow j m \\
\downarrow j_1 m_1
\end{array}
\end{array}\begin{array}{c}
\begin{array}{c}
\downarrow j_2 m_2 \\
\downarrow j m \\
\downarrow j_1 m_1
\end{array}
\end{array}. \quad (A.12)$$

Another, less obvious but very useful rule allows one to change the positions of heavy lines for two adjacent vertices. For example,

$$\begin{array}{c}
\begin{array}{c}
\downarrow j_1 \\
\downarrow j_3 \\
\downarrow j_1'
\end{array}
\end{array}\begin{array}{c}
\begin{array}{c}
\downarrow j_2 \\
\downarrow j_2 \\
\downarrow +
\end{array}
\end{array} = \frac{(2j_3+1)(2j_3'+1)}{(2j_1+1)(2j_1'+1)} \begin{array}{c}
\begin{array}{c}
\downarrow j_1 \\
\downarrow j_3 \\
\downarrow j_1'
\end{array}
\end{array}\begin{array}{c}
\begin{array}{c}
\downarrow j_2 \\
\downarrow j_2 \\
\downarrow +
\end{array}
\end{array}. \quad (A.13)$$

Equation (A.13) is readily derived by use of the symmetry property

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_2+m_2} \sqrt{\frac{2j_3+1}{2j_1+1}} \langle j_2 - m_2 j_3 m_3 | j_1 m_1 \rangle \quad (A.14)$$

applied to the expressions associated with the diagrams on the left and right in (A.13), $\Sigma_{m_2} \langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle \langle j_3 m_3 | j_1 m_1 \rangle \langle j_2 m_2 j_3 m_3 | j_1 m_1 \rangle$ and $\Sigma_{m_2} \langle j_2 m_2 j_3 m_3 j_1 m_1 \rangle \langle j_2 m_2 j_3 m_3 | j_1 m_1 \rangle$. 

\[\begin{array}{c}
\begin{array}{c}
\downarrow j_1 m_1 \\
\downarrow j m \\
\downarrow j_2 m_2
\end{array}
\end{array}\begin{array}{c}
\begin{array}{c}
\downarrow j_1 m_1 \\
\downarrow j m \\
\downarrow j_2 m_2
\end{array}
\end{array} = (-1)^{j_1+j_2-j} \begin{array}{c}
\begin{array}{c}
\downarrow j_2 m_2 \\
\downarrow j m \\
\downarrow j_1 m_1
\end{array}
\end{array}\begin{array}{c}
\begin{array}{c}
\downarrow j_2 m_2 \\
\downarrow j m \\
\downarrow j_1 m_1
\end{array}
\end{array}. \quad (A.12)$$
As a last example, we illustrate the crucial step in the reduction of angular momentum diagrams – so-called diagram cutting. The aim of this operation is to isolate components of the graph that may be identified as standard quantities; e.g., reduced matrix elements of spherical tensor operators, or 3n-j coefficients. Diagram cutting is based on the fact that certain products of vector-coupling coefficients, summed over some, but not all, magnetic quantum numbers, can be expanded in terms of generalized Clebsch-Gordan coefficients, which form a complete and orthonormal set of quantities.

When is the diagram cutting a valid operation? We state without proof that one of the resultant pieces has to be of the normal form. A diagram is said to have a normal form if the following conditions are satisfied:

1. When all of its thin lines are disconnected, the diagram decomposes into representations of generalized Clebsch-Gordan coefficients.

2. All free thin lines of the diagram belong to a single generalized Clebsch-Gordan coefficient, which we denote as the “largest.”

3. The total angular momentum magnetic quantum number of the largest generalized Clebsch-Gordan coefficient is equal to the sum of magnetic quantum numbers associated with all the other free lines of the diagram.
For example, the diagram $\mathcal{A}$ is of the normal form, but the diagram $\mathcal{B}$ is not:

\[
\mathcal{A} = + \quad j_3 \quad j_1 \quad j_1 \quad j_2 \quad j_3 m_{13} \quad j_1 m_{12} \quad j_2 m_2 \quad j_3 m_{13}
\]

\[
\mathcal{B} = + \quad j_5 \quad j_4 \quad j_2 m_2 \quad j_1 m_1 \quad j_4 m_4 \quad j_2 m_2 \quad j_3 m_3
\]

When the lines $j_1$ and $j_3$ of the diagram $\mathcal{A}$ are disconnected, the diagram decomposes into a vector-coupling coefficient $\langle j_1 m_1 j_3 m_3 | j_13 m_{13} \rangle$ and a generalized Clebsch-Gordan coefficient $\langle j_1 m_1 j_2 m_2 j_3 m_3 j_4 m_4 | \{j_1 j_2, j_3, j_4\} j_123 m_{123} \rangle$. Thus the diagram $\mathcal{A}$ satisfies the first condition of normal diagrams. The second condition is satisfied as well, since the diagram $\mathcal{A}$ has only one free thin line. The diagram $\mathcal{B}$ does not have any thin lines that could be disconnected to decompose it into generalized Clebsch-Gordan coefficients, and this breaks the first two conditions. To expose the quantitative difference between the two diagrams, let us check if the third condition is satisfied. We are interested in the relationship satisfied by the magnetic quantum numbers that are not summed over: $m_{13}, m_2, m_{123}$ in the case of the diagram $\mathcal{A}$, and $m_1, m_2, m_3$ in the case of the diagram $\mathcal{B}$. Recalling that the vector-coupling coefficient $\langle j_1 m_1 j_2 m_2 | j m \rangle$ has the property $m_1 + m_2 = m$, we get $m_{13} + m_2 = m_{123}$ for the diagram $\mathcal{A}$, but $m_1 + m_2 + m_3 = 0$ for the diagram $\mathcal{B}$. Thus the diagram $\mathcal{A}$ satisfies the third condition, but the diagram $\mathcal{B}$ does not.

Before cutting a closed diagram into two components, we may need to bring one of the components to the normal form by changing positions of heavy lines as described above.
If only three lines have to be cut to separate the diagram into two components, the normal component is proportional to a vector-coupling coefficient. Therefore, the diagram is expressible as a product of two simpler diagrams. For example,

\[
\begin{array}{c}
\begin{tikzpicture}
  \node (n1) at (0,0) {$j_1$};
  \node (n2) at (0,-1) {$j_2$};
  \node (n3) at (0,-2) {$j_3$};
  \node (n4) at (0,-3) {$j_4$};
  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);
\end{tikzpicture}
\end{array}
\begin{array}{c}
\begin{tikzpicture}
  \node (n1) at (0,0) {$j_1$};
  \node (n2) at (0,-1) {$j_2$};
  \node (n3) at (0,-2) {$j_3$};
  \node (n4) at (0,-3) {$j_4$};
  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);
\end{tikzpicture}
\end{array}
= \begin{array}{c}
\begin{tikzpicture}
  \node (n1) at (0,0) {$j_1$};
  \node (n2) at (0,-1) {$j_2$};
  \node (n3) at (0,-2) {$j_3$};
  \node (n4) at (0,-3) {$j_4$};
  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);
\end{tikzpicture}
\end{array}
+ \begin{array}{c}
\begin{tikzpicture}
  \node (n1) at (0,0) {$j_1$};
  \node (n2) at (0,-1) {$j_2$};
  \node (n3) at (0,-2) {$j_3$};
  \node (n4) at (0,-3) {$j_4$};
  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);
\end{tikzpicture}
\end{array}
. \quad (A.16)
\]

Here, the blocks represent closed parts of the diagram. It is assumed that the left block is of the normal form, and that in the left block \( j_1 \) is the total angular momentum of the largest generalized Clebsch-Gordan coefficient; therefore, \( m_2 + m_3 = m_1 \). The relation satisfied by the magnetic quantum numbers of the cut lines is reflected in the two new vertices on the right-hand side of (A.16).

An example of a diagram separable on four lines is

\[
\begin{array}{c}
\begin{tikzpicture}
  \node (n1) at (0,0) {$j_1$};
  \node (n2) at (0,-1) {$j_2$};
  \node (n3) at (0,-2) {$j_3$};
  \node (n4) at (0,-3) {$j_4$};
  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);
\end{tikzpicture}
\end{array}
\begin{array}{c}
\begin{tikzpicture}
  \node (n1) at (0,0) {$j_1$};
  \node (n2) at (0,-1) {$j_2$};
  \node (n3) at (0,-2) {$j_3$};
  \node (n4) at (0,-3) {$j_4$};
  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);
\end{tikzpicture}
\end{array}
= \sum_j \begin{array}{c}
\begin{tikzpicture}
  \node (n1) at (0,0) {$j_1$};
  \node (n2) at (0,-1) {$j_2$};
  \node (n3) at (0,-2) {$j_3$};
  \node (n4) at (0,-3) {$j_4$};
  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);
\end{tikzpicture}
\end{array}
+ \begin{array}{c}
\begin{tikzpicture}
  \node (n1) at (0,0) {$j_1$};
  \node (n2) at (0,-1) {$j_2$};
  \node (n3) at (0,-2) {$j_3$};
  \node (n4) at (0,-3) {$j_4$};
  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);
\end{tikzpicture}
\end{array}
. \quad (A.17)
\]

Again, it is assumed that the left block is of the normal form, and that in this block the angular momenta \( j_2 \) and \( j_3 \) belong to the generalized Clebsch-Gordan coefficient with
the total angular momentum $j_1$. Then, by the definition of the normal form, $m_2 + m_3 + m_4 = m_1$. This explains why the total angular momentum of the new generalized Clebsch-Gordan coefficients on the right-hand side of (A.17) is $j_1$. The sum extends over all possible values of $j$ in the chosen coupling scheme $\{j_3j_4j, j_2j_3 \}$. Notice that we do not need to know the detailed structure of the blocks, as long as one of them is of the normal form! This powerful feature of the diagrammatic method makes it particularly suited to our problem, where we deal with coupled states of an unspecified number of angular momenta.

To reiterate, we compute a matrix element of a spherical tensor operator between coupled angular momentum states by constructing the corresponding diagram and reducing it to graphical representations of familiar quantities (e.g., 3n-j coefficients).

We conclude this section with Brink and Satchler’s [22] statement on the advantages of the graphical method:

It should be emphasized that any calculation made using graphical methods can also be made using conventional algebraic techniques. To every graphical reduction there is a corresponding algebraic reduction because of the correspondence between graphs and algebraic formulae. The graphical method has two advantages over the algebraic method:

i. the notation is more compact because the redundant magnetic quantum numbers need not be written explicitly, and

ii. reductions can be made by recognizing geometrical patterns.
A.4 Example

To illustrate the ideas of the previous discussion, we derive Equation (11.47) in Cowan’s textbook [9]:

$$
\langle (\alpha_1j_1 \alpha_2j_2) jm \mid T^{(k)} \cdot W^{(k)} \mid (\alpha_1'j_1' \alpha_2'j_2') j'm' \rangle
= \delta_{jm,j'm'}(-1)^{j_1+j_2+j}\begin{bmatrix}
j_1 & j_2 & j \\
j_1' & j_2' & k
\end{bmatrix} \langle \alpha_1j_1 \parallel T^{(k)} \parallel \alpha_1'j_1' \rangle \langle \alpha_2j_2 \parallel W^{(k)} \parallel \alpha_2'j_2' \rangle.
$$

(A.18)

Here, the spherical tensor operator $T^{(k)}$ operates only within the subspace spanned by a set of basis functions $|\alpha_1j_1m_1\rangle$. Similarly, $W^{(k)}$ acts only in the $|\alpha_2j_2m_2\rangle$ subspace. The symbol $\alpha$ represents any additional quantum numbers needed to specify the basis state. The definition of the operator dot product is

$$
T^{(k)} \cdot W^{(k)} = (-1)^k[k]^{1/2}[T^{(k)} \times W^{(k)}]_0^{(0)},
$$

(A.19)

where the angular momentum quantum number enclosed in brackets $[k]$ is a shorthand notation for $(2k + 1)$.

The graphical representation of the matrix element on the left-hand side of (A.18) is

$$
\langle (\alpha_1j_1 \alpha_2j_2) jm \mid T^{(k)} \cdot W^{(k)} \mid (\alpha_1'j_1' \alpha_2'j_2') j'm' \rangle
= (-1)^k[k]^{1/2}\langle (\alpha_1j_1 \alpha_2j_2) jm \mid [T^{(k)} \times W^{(k)}]_0^{(0)} \mid (\alpha_1'j_1' \alpha_2'j_2') j'm' \rangle
$$
\[ (-1)^k [k]^{1/2} \delta_{k,k'} \] 
(A.20)

\[ (-1)^k \frac{1}{[k]^{1/2}} \delta_{k,k'} \times \langle j'm' \mid 00 \rangle = \delta_{jm,j'm'} . \quad (A.22) \]

The last step follows from the Wigner-Eckart theorem. The vector-coupling coefficient simplifies to

The next step is the diagram reduction. We cut out the reduced matrix elements using the Wigner-Eckart theorem. If the zero angular momentum line were thin, we could delete it using (A.22). To make the zero line thin, we change the positions of two heavy lines connected by a thin line \( k' \). We get
\[ \begin{align*}
\times \frac{[j_2]^{1/2}}{[k, j_2' ]^{1/2}} & \quad [j_1 \parallel T^{(k)} \parallel j_1'] [j_2 \parallel W^{(k')} \parallel j_2'] \quad \delta_{j, j'} \quad \delta_{k, k'} \quad j_1 \quad j_1' \quad j_2' \quad j_2 \\
& = \frac{[j_2]^{1/2}}{[k, j_2' ]^{1/2}} \quad [j_1 \parallel T^{(k)} \parallel j_1'] [j_2 \parallel W^{(k')} \parallel j_2'] \quad \delta_{j, j'} \quad \delta_{k, k'} \quad j_1 \quad j_1' \quad j_2' \quad j_2 .
\end{align*} \] (A.23)

The last diagram represents a recoupling coefficient for the transformation between two different coupling schemes of three angular momenta:

\[ \langle \{j'_1 k \} j_1, j_2 \mid \{j'_1, (k j_2) j_2' \} j \rangle = \langle \{j'_1 k \} j_1, j_2 \mid \{j'_1, (k j_2) j_2' \} j \rangle \]

\[ = (-1)^{j_k + j_{k+} + j_{k'k} + [j_1, j_2']}^{1/2} \begin{pmatrix} j_1 & j_2 & j \\ j_1' & j_2' & k \end{pmatrix} . \] (A.24)
Next we combine (A.20) – (A.24), noticing that \((-1)^{2k} = 1\) (the tensor rank is an integer), and taking into account the difference in the definitions of the reduced matrix element

\[
[ j_1 \parallel T^{(k)} \parallel j_1'] = [j_1]^{-1/2} \langle j_1 \parallel T^{(k)} \parallel j_1' \rangle.
\]  

(A.25)

This yields the desired relation (A.18).
Appendix B

Mixed-shell coefficients of fractional parentage

Coefficients of fractional parentage (cfp), usually defined for LS-coupled equivalent electrons [9], occur in the expansion of an antisymmetric \( w \)-electron state in terms of antisymmetric states of \( w - 1 \) electrons:

\[
|l^w \alpha LS\rangle = \sum_{\delta L S} \left|l^{w-1} \alpha^LS, l\rightangle LS \langle l^{w-1} \alpha^LS|l^w \alpha LS\rangle , \tag{B.1}
\]

where \( |l^{w-1} \alpha^LS\rangle \) is antisymmetric in electron labels \( 1, 2, \ldots w - 1 \), the singled-out electron is labeled \( w \), and \( |l^w \alpha LS\rangle \) is an antisymmetric function of \( w \) electrons. The symbol \( \alpha \) here represents all other quantum numbers needed to specify the state completely (the seniority quantum number, for example). For jj-coupled states, cfp’s
are defined in a similar way:

\[
|j^w \alpha J \rangle = \sum_{aJ} | \{ j^{w-1} \alpha aJ, j \} J \} (j^{w-1} \alpha aJ) \rangle \langle j^w \alpha J | .
\]  \hspace{1cm} (B.2)

L. Armstrong, Jr. [7] introduces mixed-shell coefficients of fractional parentage (MCFP), generalized in two ways: the requirement of electron equivalence is relaxed, and the possibility of separating more than one electron is considered. Following [7], we define one- and two-body mixed-shell coefficients of fractional parentage as follows:

\[
|T_N(1, 2 \cdots N) \rangle = \sum_{T_{N-1}, T_1} | \{ T_{N-1}(1, 2 \cdots N - 1), T_1(N) \} J \} (T_{N-1}, T_1) | T_N \rangle, \hspace{1cm} (B.3)
\]

\[
|T_N(1, 2 \cdots N) \rangle = \sum_{T_{N-2}, T_2} | \{ T_{N-2}(1, 2 \cdots N - 2), T_2(N - 1, N) \} J \} (T_{N-2}, T_2) | T_N \rangle. \hspace{1cm} (B.4)
\]

Here, for compactness, all quantum numbers needed to specify a general coupled and antisymmetric \( m \)-electron state have been written as \( T_m \). The sums extend in all possible ways to “separate”\(^1\) either one electron or an electron pair from the original \( N \)-electron state. Notice that the individual terms in the sums are not antisymmetric under the interchange of any two electron labels from the set \( \{1, 2 \cdots N\} \), but the sums are! Equations (B.3) and (B.4) are general, and applicable to both LS- and \( jj \)-coupled many-electron states.

Let us work out the \( N = 2 \) case explicitly, since mcfp’s provide a convenient way to treat equivalent and nonequivalent orbitals together. Here we use the \( jj \)-coupling

\(^1\) a more precise way of saying this might be “un-antisymmetrize and recouple”
scheme, as we do in Chapter 2, which presents the main results of this research project. Equation (B.3), specialized for the case of two \( jj \)-coupled electrons, is

\[
| (j_1, j_2) J \rangle = \sum_{j = \{j_1, j_2\}} | \{ j_1(1), j_2(2) \} J \rangle \langle \{ j_1, j \} | (j_1, j_2) J \rangle .
\]  

(B.5)

Here, if \( j = j_1 \), then \( \overline{j} = j_2 \), and vice versa. A normalized antisymmetric state of two \textit{nonequivalent} electrons can be written as

\[
| (j_1, j_2) J \rangle = \sqrt{\frac{1}{2}} \left[ | \{ j_1(1), j_2(2) \} J \rangle - | \{ j_1(2), j_2(1) \} J \rangle \right]
\]

\[
= \sqrt{\frac{1}{2}} \left[ | \{ j_1(1), j_2(2) \} J \rangle - (-1)^{j_1 + j_2 - J} \{ j_1(1), j_2(2) \} J \rangle \right].
\]  

(B.6)

The same argument, applied to a normalized antisymmetric state of two \textit{equivalent} electrons, gives

\[
| (j^2) J \rangle = \frac{1}{2} \left[ 1 - (-1)^{2j - J} \right] | \{ j(1), j(2) \} J \rangle .
\]  

(B.7)

Thus

\[
\langle j, \overline{j} | (j_1, j_2) J \rangle = \begin{cases} 
\frac{1}{2} \left[ 1 - (-1)^{2j - J} \right] & \text{if } j_1, j_2 \text{ are equivalent}, \\
\sqrt{\frac{1}{2}} \left\{ \delta_{jj_1} - \delta_{jj_2} (-1)^{j_1 + j_2 - J} \right\} & \text{otherwise}.
\end{cases}
\]  

(B.8)

How does one compute mixed-shell coefficients of fractional parentage? Since the standard coefficients of fractional parentage are well known, a convenient first step is to separate one electron from a group of equivalent electrons by use of the usual cfp expansion. Next, by recoupling three angular momenta, we interchange the coupling order of the singled-out electron and the immediately following group
<table>
<thead>
<tr>
<th>3s (2) 3p*(2) 3p (3) 4s (1)</th>
<th>[[ 0, 0] 0,3/2]3/2,1/2] 1 &gt;</th>
</tr>
</thead>
</table>

- 0.3952847  |{ 3s (1) 3p*(2) 3p (3) 4s (1) }[[1/2, 0]1/2,3/2] 2,1/2]3/2 , 3s } 1 >
- 0.2806751  |{ 3s (1) 3p*(2) 3p (3) 4s (1) }[[1/2, 0]1/2,3/2] 1,1/2]1/2 , 3s } 1 >
- 0.1020621  |{( 3s (1) 3p*(2) 3p (3) 4s (1) }[[1/2, 0]1/2,3/2] 1,1/2]3/2 , 3s } 1 >

Table B.1: Example of a one-electron mcfp expansion.

<table>
<thead>
<tr>
<th>3s (2) 3p*(2) 3p (3) 4s (1)</th>
<th>[[ 0, 0] 0,3/2]3/2,1/2] 1 &gt;</th>
</tr>
</thead>
</table>

- 0.1336306  |{ 3s (2) 3p*(2) 3p (2) 3p (2) }[[ 0, 0] 0, 0] 0 , (3p ,4s ) 1} 1 >
- 0.2112866  |{ 3s (2) 3p*(2) 3p (2) 3p (2) }[[ 0, 0] 0, 0] 0, 2 , (3p ,4s ) 1} 1 >
- 0.1128866  |{ 3s (2) 3p*(2) 3p (2) 3p (2) }[[ 0, 0] 0, 0] 0, 2 , (3p ,4s ) 2} 1 >

- 0.1336306  |{ 3s (2) 3p*(2) 3p (1) 4s (1) }[[ 0, 0] 0,3/2]3/2,1/2] 1 , (3p ,3p ) 0} 1 >
- 0.2112866  |{ 3s (2) 3p*(2) 3p (1) 4s (1) }[[ 0, 0] 0,3/2]3/2,1/2] 1 , (3p ,3p ) 2} 1 >
- 0.1128866  |{ 3s (2) 3p*(2) 3p (1) 4s (1) }[[ 0, 0] 0,3/2]3/2,1/2] 2 , (3p ,3p ) 2} 1 >

- 0.1336306  |{ 3s (2) 3p*(1) 3p (3) }[[ 0,1/2]1/2,3/2] 1 , (3p*,4s ) 0} 1 >
- 0.0944911  |{ 3s (2) 3p*(1) 3p (3) }[[ 0,1/2]1/2,3/2] 1 , (3p*,4s ) 1} 1 >
- 0.2112866  |{ 3s (2) 3p*(1) 3p (3) }[[ 0,1/2]1/2,3/2] 2 , (3p*,4s ) 1} 1 >

- 0.0944911  |{ 3s (2) 3p*(1) 3p (2) 4s (1) }[[ 0,1/2]1/2, 0]1/2,1/2] 0 , (3p*,3p ) 1} 1 >
- 0.0681633  |{ 3s (2) 3p*(1) 3p (2) 4s (1) }[[ 0,1/2]1/2, 0]1/2,1/2] 1 , (3p*,3p ) 1} 1 >
- 0.1494036  |{ 3s (2) 3p*(1) 3p (2) 4s (1) }[[ 0,1/2]1/2, 0]1/2,1/2] 1 , (3p*,3p ) 2} 1 >

Table B.2: Example of a two-electron mcfp expansion.
of equivalent electrons. We continue recoupling until the singled-out electron is the last to be coupled. This procedure, applied to all equivalent electron groups, yields a one-electron mcfp expansion. If a two-electron mcfp expansion is needed, the above steps are repeated, and then the two singled-out electrons are coupled together by use of another recoupling of three angular momenta. Without explaining the details regarding permutation signs and normalization, we illustrate one- and two-electron mcfp expansions of a $\tilde{j}$-coupled state by a numerical example (Tables B.1 and B.2). In each state involved, the coupling scheme, which includes angular momentum quantum numbers for equivalent electron groups, and the way the groups are coupled together, follows the list of orbitals. The $j$-value of an individual orbital is indicated by the presence of the “$-$” sign, or lack of it: the “$-$” sign next to the orbital means $j = l - \frac{1}{2}$, otherwise $j = l + \frac{1}{2}$. In Table B.2, the ellipsis shows that some terms in the mcfp expansion have been omitted for brevity. The numerical results have been checked using computer programs GRASP [26] and CESD97 [27].
Appendix C

Symbolic-state expansion for nonrelativistic multiconfiguration calculations

In Chapter 2, we studied the Hamiltonian matrix constructed in the basis of relativistic jj-coupled symbolic states. In particular, we derived the dependence of the matrix elements on the quantum numbers of the correlation orbitals. Here we consider a similar problem for the multiconfiguration basis of nonrelativistic LS-coupled symbolic states. Since the methods used here are essentially the same as those employed in Chapter 2, only the final results are presented.

Let $|\Psi_{ref}\rangle$ be an arbitrary LS-coupled antisymmetric configuration state function for $N$ electrons. A symbolic state $|\Psi\rangle$ is formed by a two-electron replacement from
\[ |\Psi_{ref}\rangle \text{ to an unoccupied pair of correlation orbitals } (n_1l_1, n_2l_2)L_vS_v: \]

\[ |\Psi\rangle = \{ (n_1l_1, n_2l_2)L_vS_v, (\Psi_{sub})L_cS_c \} LS \cdot \]  

We consider matrix elements of a symmetric two-body operator \( G = \sum_{i<j} G_{ij} \) between such \( N \)-electron states. We expand the \( N \)-electron matrix elements in terms of two-electron matrix elements, with expansion coefficients independent of the nature of the operator:

\[ \langle \Psi' | G | \Psi \rangle = \sum_{\alpha, \beta} K_{\alpha \beta} \langle \Psi' , \Psi \rangle \langle \psi'_\alpha (1, 2) L_\alpha S_\alpha | G_{12} | \psi_\beta (1, 2) L_\beta S_\beta \rangle . \]  

We derive this expansion for an operator that commutes with both \( L \) and \( S \):

\[ G_{12} = \sum_{g, \gamma} \left[ G_{\text{space}}^{(g)} (1) \times G_{\text{space}}^{(g)} (2) \right]^{(0)} \left[ G_{\text{spin}}^{(\gamma)} (1) \times G_{\text{spin}}^{(\gamma)} (2) \right]^{(0)} \mathcal{R}_{g\gamma} (r_1, r_2) . \]  

Here, \( g \) is the tensor rank of the operator that acts on the space coordinates, and \( \gamma \) is the tensor rank of the operator that acts on the electron spin. This form of the operator includes the Coulomb interaction, but is more general.

We consider two kinds of matrix elements, \( \langle \Psi | G | \Psi_{ref} \rangle \) and \( \langle \Psi' | G | \Psi \rangle \), and study their dependence on the quantum numbers of the correlation orbitals. The matrix element connecting a symbolic state and a reference state is

\[ \langle \Psi | G | \Psi_{ref} \rangle = \langle (l_1, l_2)L_vS_v | G | (l_1, l_2)L_vS_v \rangle \langle \Psi'' | \Psi_{ref} \rangle . \]
Here, $l_{c1}, l_{c2}$ are the two orbitals present in $|\Psi_{ref}\rangle$, but absent from $|\Psi\rangle$. The $N$-electron state $|\Psi''\rangle$ is of the same form as $|\Psi\rangle$, but in $|\Psi''\rangle$ a pair of correlation orbitals $(l_1, l_2)L_vS_v$ is replaced by a pair of occupied orbitals $(l_{c1}, l_{c2})L_vS_v$. This result assumes that the one-electron orbitals are orthogonal.

The matrix element between two symbolic states $\langle \Psi' | G | \Psi \rangle$ is given by

$$
\langle \Psi' | G | \Psi \rangle = M_{vv} + M_{cv} + M_{cc} .
$$

(C.5)

Here,

$$
M_{vv} = \langle (\Psi'_{sub})L_v^iS'_v | (\Psi_{sub})L_cS_c \rangle \langle (\psi'_{\nu})L_v^iS'_v | G | (\psi_{\nu})L_vS_v \rangle ,
$$

(C.6)

$$
M_{cc} = \langle (\Psi'_{sub})L_c^iS'_c | G | (\Psi_{sub})L_cS_c \rangle \langle (\psi'_{\nu})L_v^iS'_v | (\psi_{\nu})L_vS_v \rangle ,
$$

(C.7)

$$
M_{cv} = \sum_{l_c} \sum_{l'_{\nu}} \sum_{L_v} \sum_{S_G} C_{sym} \langle (l'_{\nu}, l_c^i) L_G S_G | G | (l_{\nu}, l_c) L_G S_G \rangle .
$$

(C.8)

In (C.8), $l_c, l'_c$ run over all subconfiguration orbitals, and $l_{\nu}, l'_{\nu}$ run over the two correlation orbitals. The values of $L_G, S_G$ are limited by triangle relations $(l_{\nu}l_cL_G), (l'_{\nu}l_c^iL_G)$, and $(l'_{22}S_G)$. The coefficient $C_{sym}$ is expressed as:

$$
C_{sym} = 2 \langle \bar{n}_{\nu} | \bar{n}_{\nu}^i \rangle \langle l_{\nu} | l'_{\nu} \rangle \langle l_1 l_2 | L_v S_v \rangle \langle \bar{l}_{\nu} l'_{\nu} | (l'_{1} l_2^i) L_v^i S'_v \rangle
$$

$$
\times \sum_{k, \kappa} \Gamma_{v\kappa} \langle (\Psi'_{sub})^i_{l_c^i} | (\Psi_{sub})_{l_c}^i \rangle \langle L_G, S_G, k, \kappa | L_v, S_v, L'_v, S'_v \rangle^{1/2}
$$

$$
\times \langle -1 \rangle^{L'_v + L_c + \bar{l}_{\nu} + l_{\nu}^i + L + L_v + k + L_G} (-1)^{S'_v + S_v + S + \nu + k + S_G}
$$

$$
\times \left\{ L_{v} \ k \ L_{v}' \right\} \left\{ L_{v} \ k \ L_{v}' \right\} \left\{ l_{c} \ k \ l_{c}' \right\}
$$

$$
\times \left\{ L_{c}' \ L \ L_{c} \right\} \left\{ l_{\nu}' \ L_{\nu} \ l_{\nu} \right\} \left\{ l_{v}' \ L_{G} \ l_{v} \right\}
$$
\[
\times \begin{pmatrix}
S_v & \kappa & S_v' \\
S_v' & S & S_v \\
S_c' & S & S_c
\end{pmatrix} \times \begin{pmatrix}
S_v & \kappa & S_v' \\
S_v' & S & S_v \\
S_c' & S & S_c
\end{pmatrix} \times \begin{pmatrix}
1/2 & \kappa & 1/2 \\
1/2 & 1/2 & 1/2 \\
1/2 & S_G & 1/2
\end{pmatrix}. \quad (C.9)
\]

In (C.9), \( (l_v^l, l_v^l)\left(l_1^l l_2^l\right) L_v S_v \) is the two-electron mixed-shell coefficient of fractional parentage:

\[
(\mathcal{I}_v^l, l_v^l)\left(l_1^l l_2^l\right) L_v S_v = \begin{cases}
\frac{1}{2} \left[ 1 + (-1)^{L_v + S_v} \right] & \text{if } l_1, l_2 \text{ are equivalent,} \\
\sqrt{\frac{\pi}{2}} \left\{ \delta_{l_v^l l_v^l} + \delta_{l_v^l l_v^l} (-1)^{l_1^l + l_2^l + L_v + S_v} \right\} & \text{otherwise.}
\end{cases}
\quad (C.10)
\]

The quantity \( \Gamma_{k\kappa}(\Psi_{\text{sub}}^l, l_v^l; \Psi_{\text{sub}}, l_c) \) is the coefficient in the expansion of a \((N - 2)\)-electron matrix element of a general one-body double-tensor operator,

\[
W_{qr}^{[k\kappa]} = \sum_{i=1}^{N-2} w_{qr}^{[k\kappa]}(i),
\quad (C.11)
\]

in terms of one-electron matrix elements:

\[
\langle \Psi_{\text{sub}}^l, l_v^l, S_v' || W^{[k\kappa]} || \Psi_{\text{sub}} L_v S_v \rangle = \sum_{l_c^l, l_c^l} \Gamma_{k\kappa}(\Psi_{\text{sub}}^l, l_v^l; \Psi_{\text{sub}}, l_c) \langle l_c^l || w^{[k\kappa]} || l_c^l \rangle. \quad (C.12)
\]

Here, \( k \) is the tensor rank of the operator with respect to the orbital angular momentum, and \( \kappa \) is the tensor rank with respect to the spin angular momentum. The possible values of \( k \) and \( \kappa \) in the sum of (C.9) are limited by triangle relations \((l_c^l k l_c^l)\) and \((\frac{1}{2} \kappa \frac{1}{2})\).
Appendix D

A sample file of angular coefficients

This appendix shows the angular-coefficient file for the beryllium example presented in Chapter 3. The numerical coefficients are obtained by evaluating all the quantities in (C.5)-(C.9) that are independent of the quantum numbers of the correlation orbitals.

Be IS subconfigurations

Symbolic CSF1: 1 | { (s1,n'1')1Se, (1s2)1Se } 1Se >
Symbolic CSF2: 1 | { (s1,n'1')1Se, (1s1,2m1)1Se } 1Se >
Symbolic CSF3: 1 | { (s1,n'1')3Se, (1s1,2m1)3Se } 1Se >
Symbolic CSF4: 0 | { (s1,n'1')Po, (1s1,2p1)Po } 1Se >
Symbolic CSF5: 0 | { (s1,n'1')3Po, (1s1,2p1)3Po } 1Se >

INTERACTION BLOCKS FOR G CONSERVING L, S

Block( 1X 1): < {(v1,v2)1Se, (C 1)1Se} 1Se | G | {(v3,v4)1Se, (C 1)1Se} 1Se >

Block( 2X 1): < {(v1,v2)1Se, (C 2)1Se} 1Se | G | {(v3,v4)1Se, (C 1)1Se} 1Se >

5.00000000000000E+00 A(k=0) < (v1,1a)1L | G | (v3,1a)1L > < v2 | v4>
1.60000000000000E+00 A(k=0) < (v1,1a)3L | G | (v3,1a)3L > < v2 | v4>

3.53553063903797E+00 A(k=0) < (v1,2a)1L | G | (v3,1a)1L > < v2 | v4>
1.06060017798212E+00 A(k=0) < (v1,2a)3L | G | (v3,1a)3L > < v2 | v4>
\begin{align*}
&4.3301270189221930E+001 \ A(k-0) \ < \ (v_1,1s)1L \ | G | (v_3,1s)1L > \ < v_2 | v_4>
&1.299035106676680E+000 \ A(k-0) \ < \ (v_1,1s)3L \ | G | (v_3,1s)3L > \ < v_2 | v_4>
&2.500000000000000E+001 \ A(k-0) \ < \ (v_1,2p)1L \ | G | (v_3,2p)1L > \ < v_2 | v_4>
&7.500000000000000E+001 \ A(k-1) \ < \ (v_1,2p)1L \ | G | (v_3,2p)1L > \ < v_2 | v_4>
&1.250000000000000E+000 \ A(k-2) \ < \ (v_1,2p)1L \ | G | (v_3,2p)1L > \ < v_2 | v_4>
&7.500000000000000E+001 \ A(k-0) \ < \ (v_1,2p)3L \ | G | (v_3,2p)3L > \ < v_2 | v_4>
&2.500000000000000E+000 \ A(k-1) \ < \ (v_1,2p)3L \ | G | (v_3,2p)3L > \ < v_2 | v_4>
&3.750000000000000E+000 \ A(k-2) \ < \ (v_1,2p)3L \ | G | (v_3,2p)3L > \ < v_2 | v_4>

\end{align*}
Bibliography


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