

Matrix Elements in Configuration Interaction Calculations

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Abstracts

A method is proposed for the calculation of matrix elements among various states of atoms. A set of tensor operators is the only entity in the formalism, and all formulas involve merely the vacuum expectation values of these tensor operators and the recoupling transformation coefficients. Some numerical examples are given for the Coulomb interaction matrix elements.

On propose une méthode pour calculer les éléments de matrice entre des états d'atomes. La seule quantité requise consiste d'un ensemble d'opérateurs tensoriels et toutes les formules sont données en termes de valeurs moyennes de ces opérateurs tensoriels par rapport à l'état vide et de coefficients de transformation pour recouplage. On donne quelques exemples numériques pour les éléments de la matrice d'interaction de Coulomb.

Eine Methode für die Berechnung von Matrixelementen zwischen Atomzuständen wird vorgeschlagen. Die einzige gebrauchte Grösse ist ein Satz von Tensoroperatoren und alle Formeln werden mit Erwartungswerten von diesen Tensoroperatoren mit Rücksicht auf den Vakuumzustand und mit Transformationskopplungskoeffizienten ausgedrückt. Einige numerische Beispiele für die Matrixelemente der Coulombwechselwirkung werden gegeben.

1. Introduction

Configuration interaction calculations for atomic or molecular systems may be carried out, at least in principle, by an elementary method. We choose a set of Slater determinants or linear combinations of them as the basic configuration having the required symmetry. The matrix elements of the Hamiltonian can be found in terms of various integrals over spin orbitals.

Although the above procedure works well for small systems, it rapidly becomes cumbersome as the number of electrons or the orbital angular momentum increases, the difficulty being that the number of terms to be summed becomes very large.

Alternative, more powerful approaches have been developed for the calculation of matrix elements between states by several authors [1-5]. The basic methods used in their work involve recoupling transformations and separation of one or

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two electrons from the rest. Thus, the matrix elements are expressed in terms of Racah or Wigner coefficients and fractional parentage coefficients.

The matrix elements can, however, be evaluated quite straightforwardly by using only the recoupling transformation technique for a set of tensor operators.

In Section 2, the tensor operators which will be treated in this paper are described. In Section 3, two reduction formulas for the vacuum expectation value of an invariant tensor operator are derived. In Section 4, a few examples are given for the case of the Coulomb interaction among electrons.

The formulation is carried out for atomic systems in the *LS* coupling scheme, so the apparent group of the transformation is $O(3) \times SU(2)$ corresponding to the independent rotation of space and spin coordinate systems. It should be noted that most of the results are applicable to systems whose symmetry group is simply reducible [6].

2. Tensors

The field operator $\psi(x)$ and its Hermitian conjugate $\psi^\dagger(x)$ satisfy the commutation relations

$$(1) \quad \begin{aligned} [\psi(x), \psi(x')]_+ &= [\psi^\dagger(x), \psi^\dagger(x')]_+ = 0 \\ [\psi(x), \psi^\dagger(x')]_+ &= \delta_{x,x'} \end{aligned}$$

where x stands for space and spin coordinates (r, σ) . The Hamiltonian of the system is

$$(2) \quad \int \psi^\dagger(x) \left\{ -\frac{1}{2} \Delta - \frac{Z}{r} \right\} \psi(x) dx + \frac{1}{2} : \iint \rho(r) \frac{1}{|r-r'|} \rho(r') dv dv' :$$

assuming infinite nuclear mass and neglecting all relativistic effects. Here $\rho(r)$ is the charge density operator $\sum_\sigma \psi^\dagger(r, \sigma) \psi(r, \sigma)$, and the symbol $: \cdot :$ stands for the normal product.

This Hamiltonian is invariant under a rotation in space coordinates (including space inversion) as well as in spin space. Transformations of space and spin coordinates constitute the group $G = O(3) \times SU(2)$ where $O(3)$ and $SU(2)$ correspond to rotations in space coordinates and spin coordinates, respectively. The usual notation for atomic multiplets such as 1P , $^2S^0$, $^3D \cdots$ will be employed for specifying irreducible representations of the group G explicitly. Three symbols i_L , j_S and j_P will be used to indicate the orbital angular momentum, the spin angular momentum, and the parity of an irreducible representation j of the group G . The symbol j_P takes the value $+1$ or -1 according to whether the parity of the representation j is even or odd under the space inversion. The dimension $(2j_L + 1)(2j_S + 1)$ of the representation j will be denoted by $[j]$.

A basis set of an irreducible representation space of the above group G is usually called a double tensor when its representation matrix has some standard

form [8]. In this paper it will be called simply as a tensor and will be indicated by a boldface letter. The corresponding italic letter will be used as the symbol for its irreducible representation. The irreducible representation space spanned by the components of a tensor \mathbf{j} will be denoted by $\{\mathbf{j}\}$.

Throughout this paper, we shall only treat the algebra generated by the field operators $\psi(x)$, $\psi^\dagger(x)$ and the identity e , and this algebra A is, at the same time, considered as a representation space of the group G . Thus, any irreducible space $\{\mathbf{j}\}$ will be a subspace of A . The space $\{\mathbf{j}_1\}\{\mathbf{j}_2\}$ is clearly an invariant subspace of A , and in general it is reducible. To each irreducible subspace, a unique tensor \mathbf{j}_3 can be found with the help of the generalized Clebsch-Gordon coefficients of the group G and it will be denoted by $(\mathbf{j}_1\mathbf{j}_2)^{j_3}$. Components are

$$(j_3)_{m_3} = \sum_{m_1 m_2} (j_1 j_2 j_3 m_3 | j_1 m_1 j_2 m_2)_G (j_1)_{m_1} (j_2)_{m_2}$$

Since the algebra A is not commutative, $(\mathbf{j}_1\mathbf{j}_2)^{j_3}$ is, in general, not related to $(\mathbf{j}_2\mathbf{j}_1)^{j_3}$ by a simple phase factor.

The space spanned by hermitian adjoint operators of the components of a tensor \mathbf{j} is irreducible, but the set \mathbf{j} itself cannot be regarded as a tensor because the representation matrix will then become the complex conjugate of the standard one. Since the complex conjugate representation of a simply reducible group is equivalent to the original one, we can find a unitary matrix U_j so that $U_j^* \mathbf{j}^\dagger$ becomes a tensor [7]. Following Wigner [6] we choose $(U_j)_{\kappa\lambda} = [j]^{1/2} (00 | j\kappa j\lambda)_G$. The new tensor $U_j^* \mathbf{j}^\dagger$ will be denoted by $\tilde{\mathbf{j}}$. From the properties of the Clebsch-Gordon coefficients and the above definition, it follows [6, 7] that

$$\begin{aligned} (\tilde{\mathbf{j}}_1\tilde{\mathbf{j}}_2)^j &= (-1)^{j_1+j_2-j} (\mathbf{j}_2\mathbf{j}_1)^j \\ \tilde{\mathbf{j}} &= (-1)^{2j} \mathbf{j} \end{aligned} \quad (3)$$

and $(\tilde{\mathbf{j}}\tilde{\mathbf{j}})^e$ is positive definite. The symbol e stands for the identity representation.

Let V be an arbitrary finite dimensional invariant subspace of $\psi^\dagger(x)$. Since V is spanned by creation operators, $V\rangle$ is a set of one-electron states (\rangle stands for the vacuum). These states may be called one-electron states in the V shell. In general, an element of $\underbrace{VV \cdots V}_{n\text{-terms}}$ is a state vector representing n electrons in the V shell.

The identity e and V generate an algebra. It will be denoted by F_V and contains e , V , VV , \cdots as its subspaces. Physical meaning of $F_V\rangle$ is the set of all states consisting of V -shell electrons. Two elements a and b in F_V will be said to be orthogonal if $\langle a^\dagger b \rangle = 0$. The algebra generated by e , V , V^\dagger will be denoted by H_V . This is the set of all operators acting on the shell, and contains F_V and F_V^\dagger as its subspace. Any matrix element can be expressed as the vacuum expectation value of a product $\langle a^\dagger cb \rangle$ ($a, b \in F_V$ and $c \in H_V$) as long as V -shell electrons

are concerned. In the following, we shall instead evaluate the vacuum expectation value of an invariant $\langle (\tilde{\mathbf{g}}(\mathbf{h}\mathbf{f})^e)^e \rangle$, where $\tilde{\mathbf{g}}$, \mathbf{f} and \mathbf{h} are tensors in F_V^\dagger , F_V and H_V , respectively. It will be written as $\langle \tilde{\mathbf{g}}\mathbf{h}\mathbf{f} \rangle$, since among all possible ways of forming products, only two products $(\tilde{\mathbf{g}}(\mathbf{h}\mathbf{f})^e)^e$ and $((\tilde{\mathbf{g}}\mathbf{h})^f\mathbf{f})^e$ can have nonzero vacuum expectation values and they are identical [6, 8].

Since the total number operator

$$N = \int \psi^\dagger(x) \psi(x) dx$$

commutes with all the group operations, tensors can be chosen to satisfy the following eigenvalue equation:

$$N\mathbf{j} - \mathbf{j}N = n(\mathbf{j})\mathbf{j}$$

The eigenvalue $n(\mathbf{j})$ is the number of creation operators minus the number of annihilation operators appearing in \mathbf{j} .

A set of tensors with the following properties:

$$\mathbf{f}_1, \dots, \mathbf{f}_n \in F_V$$

$$\langle \tilde{\mathbf{f}}_i \mathbf{f}_j \rangle = \delta_{ij} \sqrt{[f_i]}$$

$$F_V = \{\mathbf{f}_1\} + \dots + \{\mathbf{f}_n\}$$

corresponds to an orthonormal and complete set of states in the V shell. The operator

$$(4) \quad \sum_i (-1)^{2f_i} \sqrt{[f_i]} (\mathbf{f}_i) \langle \tilde{\mathbf{f}}_i \rangle^e$$

is a projection operator because

$$\begin{aligned} & \sum_i \sum_j (-1)^{2f_i+2f_j} \sqrt{[f_i][f_j]} (\mathbf{f}_i) \langle \tilde{\mathbf{f}}_i \rangle^e (\mathbf{f}_j) \langle \tilde{\mathbf{f}}_j \rangle^e \\ &= \sum_{ij} \delta_{f_i, 2f_j} (-1)^{2f_i+2f_j} \sqrt{[f_i][f_j]} (\mathbf{f}_i) \langle \tilde{\mathbf{f}}_i \mathbf{f}_j \rangle \langle \tilde{\mathbf{f}}_j \rangle^e (-1)^{2f_i+2f_j} \sqrt{[e][e]} \begin{pmatrix} f_i & f_i & e \\ f_j & f_j & e \end{pmatrix} \\ &= \sum_{ij} \delta_{ij} (-1)^{2f_i} \sqrt{[f_i]} (\mathbf{f}_i) \langle \tilde{\mathbf{f}}_i \rangle^e \end{aligned}$$

and works as the identity in the V shell.

When V is reducible, it may be decomposed into two invariant orthogonal subspaces V' and V'' . Tensors $\mathbf{f}' \in H_V'$ and $\mathbf{f}'' \in H_V''$ satisfy a simple commutative property because of the commutation relations (1):

$$(5) \quad (\mathbf{f}' \mathbf{f}'')^f = (-1)^{f'+f''-f+n(f')n(f'')} (\mathbf{f}'' \mathbf{f}')^f$$

From orthonormal and complete sets of F'_V and F''_V , an orthonormal complete set of F_V can be constructed by picking out all tensors of the type $(\mathbf{f}'_i \mathbf{f}''_j)^f$. The orthonormality can be demonstrated by calculating the expectation value $\langle (\tilde{\mathbf{f}}'_i \mathbf{f}''_j)^f (\mathbf{f}'_k \mathbf{f}''_l)^g \rangle$.

$$\begin{aligned} \langle (\tilde{\mathbf{f}}'_i \mathbf{f}''_j)^f (\mathbf{f}'_k \mathbf{f}''_l)^g \rangle &= \delta_{fg} (-1)^{f'_i + f''_j - f} \langle (\tilde{\mathbf{f}}'_j \tilde{\mathbf{f}}'_i)^f (\mathbf{f}'_k \mathbf{f}''_l)^f \rangle \\ &= \delta_{fg} \sum_h (-1)^{f'_i + f''_j - f + f'_i + f''_j + f'_k + f''_l + h + f''_j - f'_l + n(\mathbf{f}'') \{n(\tilde{\mathbf{f}}'_i) + n(\mathbf{f}'_k)\}} \\ &\quad \times \sqrt{[f][h]} \begin{Bmatrix} f''_j & f'_i & f \\ f'_k & f''_l & h \end{Bmatrix} \langle (\tilde{\mathbf{f}}'_i \mathbf{f}'_k)^h (\tilde{\mathbf{f}}'_j \mathbf{f}''_l)^h \rangle \end{aligned}$$

The intermediate state $(\tilde{\mathbf{f}}'_j \mathbf{f}''_l)^h$ is in F''_V , and should also be in F'_V in order to have nonzero matrix element to $\langle (\tilde{\mathbf{f}}'_i \mathbf{f}'_k)^h$. Therefore, it is the vacuum state.

$$\begin{aligned} \langle (\tilde{\mathbf{f}}'_i \mathbf{f}'_k)^h (\tilde{\mathbf{f}}'_j \mathbf{f}''_l)^h \rangle &= \delta_{he} \langle \tilde{\mathbf{f}}'_i \mathbf{f}'_k \rangle \langle \tilde{\mathbf{f}}'_j \mathbf{f}''_l \rangle \\ &= \delta_{he} \delta_{ik} \delta_{jl} \sqrt{[f'_i][f''_j]} \end{aligned}$$

Thus, we obtain

$$(6) \quad \langle (\tilde{\mathbf{f}}'_i \mathbf{f}''_j)^f (\mathbf{f}'_k \mathbf{f}''_l)^g \rangle = \delta_{fg} \delta_{ik} \delta_{jl} \delta(f'_i f''_j f) \sqrt{[f]}$$

where $\delta(f'_i f''_j f)$ is either 1 or 0 depending on the Kronecker product of the representations f'_i and f''_j contains the representation f or not. The completeness is apparent because $F_V = F'_V F''_V$.

3. Reduction Formulas

Since H_V equals $H'_V H''_V$, any tensor in H_V can be written as a linear combination of the following form:

$$\mathbf{h} = (\mathbf{h}' \mathbf{h}'')^h$$

where \mathbf{h}' and \mathbf{h}'' are tensors in H'_V and H''_V , respectively.

Therefore, it is sufficient to know the following matrix element:

$$(7) \quad \langle (\mathbf{g}' \mathbf{g}'')^g (\mathbf{h}' \mathbf{h}'')^h (\mathbf{f}' \mathbf{f}'')^f \rangle$$

for the computation of any matrix element in the V shell.

In order to reduce the matrix element (7) into matrix elements of subshells

V' and V'' , we first recouple the product of the last four tensors as follows:

$$\begin{aligned}
 ((\mathbf{h}'\mathbf{h}'')^h(\mathbf{f}'\mathbf{f}'')^f)^g = \sum_{r'r''} (-1)^{n(\mathbf{h}'')n(\mathbf{f}')} \{[h][f][r'][r'']\}^{1/2} \\
 \times \begin{pmatrix} h' & h'' & h \\ f' & f'' & f \\ r' & r'' & g \end{pmatrix} ((\mathbf{h}'\mathbf{f}')^{r'}(\mathbf{h}''\mathbf{f}'')^{r''})^g
 \end{aligned}$$

Substituting this expression into (7), we can evaluate the term almost identically as (6), and finally obtain the following formula:

$$\begin{aligned}
 (8) \quad \langle \widetilde{\mathbf{g}'}\mathbf{g}'' \rangle^g (\mathbf{h}'\mathbf{h}'')^h (\mathbf{f}'\mathbf{f}'')^f = (-1)^{n(\mathbf{h}'')n(\mathbf{f}')} \{[g][h][f]\}^{1/2} \\
 \times \begin{pmatrix} h' & h'' & h \\ f' & f'' & f \\ g' & g'' & g \end{pmatrix} \langle \widetilde{\mathbf{g}'}\mathbf{h}'\mathbf{f}' \rangle \langle \widetilde{\mathbf{g}''}\mathbf{h}''\mathbf{f}'' \rangle
 \end{aligned}$$

If the space V' further splits into two mutually orthogonal and irreducible subspaces, the term $\langle \widetilde{\mathbf{g}'}\mathbf{h}'\mathbf{f}' \rangle$ can be again expressed in terms of matrix elements defined in these two subshells of V' by using the same formula (8). The same can be done for V'' . In this way, formula (8) can be immediately generalized to treat any number of subshells in an arbitrary coupling scheme.

The second, rather ugly, but useful formula for the calculation of matrix elements is

$$\begin{aligned}
 (9) \quad \langle \widetilde{\mathbf{g}}(\mathbf{h}_1\mathbf{h}_2)^h\mathbf{f} \rangle &= \sqrt{[h]} \sum_{\mathbf{k}} (-1)^{h_2+f+k} \begin{Bmatrix} h_1 & h_2 & h \\ f & g & k \end{Bmatrix} \langle \widetilde{\mathbf{k}}\mathbf{h}_1\mathbf{g} \rangle \langle \widetilde{\mathbf{k}}\mathbf{h}_2\mathbf{f} \rangle \\
 &= \sqrt{[h]} \sum_{\mathbf{k}} (-1)^{h_1+h_2+f+g} \begin{Bmatrix} h_1 & h_2 & h \\ f & g & k \end{Bmatrix} \langle \widetilde{\mathbf{g}}\mathbf{h}_1\mathbf{k} \rangle \langle \widetilde{\mathbf{k}}\mathbf{h}_2\mathbf{f} \rangle
 \end{aligned}$$

where the sum is taken over a complete orthonormal set of k . The proof is as follows. First, the left-hand side is recoupled into

$$\sum_{\mathbf{k}} (-1)^{h_1+h_2+f+g} \sqrt{[h][k]} \begin{Bmatrix} h_1 & h_2 & h \\ f & g & k \end{Bmatrix} \langle (\widetilde{\mathbf{g}}\mathbf{h}_1)^k(\mathbf{h}_2\mathbf{f})^k \rangle$$

The operator $\sum_{\mathbf{k}} (-1)^{2k} \sqrt{[k]} (\mathbf{k}) (\widetilde{\mathbf{k}})^e$ which works as the identity operator in the shell is inserted in the middle of the term $\langle (\widetilde{\mathbf{g}}\mathbf{h}_1)^k(\mathbf{h}_2\mathbf{f})^k \rangle$. Using the recoupling formula and (3), we obtain (9).

4. Examples

We rewrite the Coulomb interaction term in (2) in a suitable form for the use of formulas (8) and (9). Since the field operator ψ^\dagger is expressed as

$$\psi_{m_s}^\dagger(r) = \sum_{nlm_l} \bar{R}_{n_l}(r) \bar{Y}_{l, m_l}(\theta, \phi) A_{nlm_l, m}^\dagger$$

it can be regarded as a tensor of the symmetry 2S :

$$\psi^\dagger(r) = \sum_{nl} \sqrt{[l]} \bar{R}_{nl}(r) (\tilde{\mathbf{Y}}_l \mathbf{A}_{nl}^\dagger)^{{}^2S}$$

The charge density is therefore expressed as

$$\begin{aligned} \rho(r) &= \psi_{1/2}^\dagger(r) \psi_{1/2}(r) + \psi_{-1/2}^\dagger(r) \psi_{-1/2}(r) \\ &= -\sqrt{2} (\psi^\dagger(r) \psi(r))^{{}^1S} \\ &= -\sqrt{2} \sum_{nl n' l'} \sqrt{[l][l']} \bar{R}_{nl}(r) R_{n' l'}(r) ((\tilde{\mathbf{Y}}_l \mathbf{A}_{nl}^\dagger)^{{}^2S} (\tilde{\mathbf{A}}_{n, l}^\dagger \mathbf{Y}_{l'})^{{}^2S})^{{}^1S} \\ &= -\sqrt{2} \sum_k \sum_{nl n' l'} \sqrt{[k]} \bar{R}_{nl}(r) R_{n' l'}(r) ((\mathbf{A}_{nl}^\dagger \tilde{\mathbf{A}}_{n' l'}^\dagger)^{{}^1k} (\tilde{\mathbf{Y}}_l \mathbf{Y}_{l'})^{{}^1k})^{{}^1S} \end{aligned}$$

The term $1/|r - r'|$ can be expanded to the following sum:

$$\sum_k \frac{4\pi r_{<}^k}{\sqrt{[k]} r_{>}^{k+1}} (\tilde{\mathbf{Y}}_k(\theta, \phi) \mathbf{Y}_k(\theta' \phi'))^S$$

Substituting these expressions into the Coulomb interaction term in (2), and considering that $\int d\Omega (\mathbf{Y}_{l_1} \mathbf{Y}_{l_2} \mathbf{Y}_{l_3})^L$ is a non-zero only when L is S , we find

$$\begin{aligned} \frac{1}{2} \iint \frac{\rho(r) \rho(r')}{|r - r'|} dv dv' &= \sum_{knl n' l' n'' l'' n''' l'''} (4\pi)^3 [k]^{-3/2} (\tilde{\mathbf{Y}}_l \mathbf{Y}_{l'} \tilde{\mathbf{Y}}_k)^S (\mathbf{Y}_k \tilde{\mathbf{Y}}_{l''} \mathbf{Y}_{l'''})^S \\ (10) \quad &\times R^k(nl n' l', n'' l'' n''' l''') : ((\mathbf{A}_{nl}^\dagger \tilde{\mathbf{A}}_{n' l'}^\dagger)^{{}^1k} (\mathbf{A}_{n'' l''}^\dagger \tilde{\mathbf{A}}_{n''' l'''}^\dagger)^{{}^1k})^{{}^1S} : \end{aligned}$$

where R^k is the Slater integral:

$$R^k(nl n' l', n'' l'' n''' l''') = \int_0^\infty r^2 dr \int_0^\infty r'^2 dr' \frac{r_{<}^k}{r_{>}^{k+1}} \bar{R}_{nl}(r) R_{n' l'}(r) \bar{R}_{n'' l''}(r') R_{n''' l'''}(r')$$

The factor

$$H^k(l l', l'' l''') \equiv (4\pi)^3 [k]^{-3/2} (\tilde{\mathbf{Y}}_l \mathbf{Y}_{l'} \tilde{\mathbf{Y}}_k)^S (\mathbf{Y}_k \tilde{\mathbf{Y}}_{l''} \mathbf{Y}_{l'''})^S$$

depends on normalizations of spherical harmonics. Using the normalization of Condon and Shortley, we obtain

$$(11) \quad H^k(l l', l'' l''') = (-1)^{(l-l'+l''-l''')/2} \sqrt{[l][l'][l'']/[k]} F(kll') F(kl''l''')$$

where

$$F(a\ b\ c) = \begin{cases} 0 & \text{for } a + b + c \text{ odd} \\ \frac{g! \sqrt{(2g-2a)!(2g-2b)!(2g-2c)!}}{\sqrt{(2g+1)!(g-a)!(g-b)!(g-c)!}} & \text{for } 2g = a + b + c \text{ even} \end{cases}$$

As an example, we calculate the Coulomb interaction term between the following states:

$$\begin{aligned} \Phi &= \langle l^1(2p^5(2s^2\ 1s^2)^1S)^2P^1P \rangle \\ \Psi &= \langle 3p^1(2p^6(2s^1\ 1s^2)^2S)^2S^1P \rangle \end{aligned}$$

Here l shell is assumed to be different from the other shells.

Substituting (10) in $\langle \Psi V_{coul} \Phi \rangle$, we find the following two tensors give nonzero contribution:

$$\begin{aligned} \mathbf{h}_1 &= :((\mathbf{A}_{3p}^\dagger \tilde{\mathbf{A}}_l^\dagger)^k (\mathbf{A}_{2p}^\dagger \tilde{\mathbf{A}}_{2s}^\dagger)^k)^1S: \\ \mathbf{h}_2 &= :((\mathbf{A}_{3p}^\dagger \tilde{\mathbf{A}}_{2s}^\dagger)^k (\mathbf{A}_{2p}^\dagger \tilde{\mathbf{A}}_l^\dagger)^k)^1S: \end{aligned}$$

The first tensor is equal to

$$(-1)^{2P+2l-1k+1} ((\tilde{\mathbf{A}}_l^\dagger (\mathbf{A}_{3p}^\dagger (\mathbf{A}_{2p}^\dagger (\tilde{\mathbf{A}}_{2s}^\dagger \cdot 1)^2S)^1k)^2l)^1S$$

and Φ and Ψ can be expressed as

$$\begin{aligned} \Phi &= \langle l^1(3p^0(2p^5(2s^2\ 1s^2)^1S)^2P^2P^1P \rangle \\ \Psi &= \langle l^0(3p^1(2p^6(2s^1\ 1s^2)^2S)^2S^1P^1P \rangle \end{aligned}$$

Then using (8) five times, we obtain

$$\begin{aligned} \langle \Psi \mathbf{h}_1 \Phi \rangle &= (-1)^{2P+2l-1k+1+1+0+0+(-1)\cdot 5} \{ [1P][1S][1P][1P][1P][2P] \\ &\quad \times [2S][1k][2P][2S][2S][1S][1S][1S] \}^{1/2} \\ &\quad \times \begin{pmatrix} 2l & 2l & 1S \\ 2l & 2P & 1P \\ 1S & 1P & 1P \end{pmatrix} \\ &\quad \times \begin{pmatrix} 2P & 1k & 2l \\ 1S & 2P & 2P \\ 2P & 2S & 1P \end{pmatrix} \begin{pmatrix} 2P & 2S & 1k \\ 2P & 1S & 2P \\ 1S & 2S & 2S \end{pmatrix} \begin{pmatrix} 2S & 1S & 2S \\ 1S & 1S & 1S \\ 2S & 1S & 2S \end{pmatrix} \begin{pmatrix} 1S & 1S & 1S \\ 1S & 1S & 1S \\ 1S & 1S & 1S \end{pmatrix} \\ &\quad \times \langle \ell^0 \tilde{\mathbf{A}}_l^\dagger \ell^1 \rangle \langle \tilde{\mathbf{p}}^1 \mathbf{A}_p^\dagger \mathbf{p}^0 \rangle \langle \tilde{\mathbf{p}}^6 \mathbf{A}_p^\dagger \mathbf{p}^5 \rangle \langle \tilde{\mathbf{s}}^1 \tilde{\mathbf{A}}_s^\dagger \mathbf{s}^2 \rangle \langle \tilde{\mathbf{s}}^2 \mathbf{1s}^2 \rangle \end{aligned}$$

The terms $\langle * \tilde{\mathbf{A}}^\dagger * \rangle$ and $\langle * \mathbf{A}^\dagger * \rangle$ are essentially fractional parentage coefficients [9]. Those which appear in the above have the following values:*

$$\langle \ell^0 \tilde{\mathbf{A}}_l^\dagger \ell^1 \rangle = \langle \tilde{\ell}^1 \mathbf{A}_l^\dagger \ell^0 \rangle = \langle \ell^{[2]l-1} \tilde{\mathbf{A}}_l^\dagger \ell^{[2]l} \rangle = -\langle \ell^{[2]l} \mathbf{A}_l^\dagger \ell^{[2]l-1} \rangle = \sqrt{[2]l}$$

All 9- j symbols can be easily evaluated† and we have

$$\langle \psi \mathbf{h}_1 \phi \rangle = -\delta_{Pk} \delta(PPl)/2$$

Since there are two identical terms in the sum (10), the coefficients to the Slater integrals $R^1(3pl, 2p2s)$ become

$$\frac{-2H^1(1l, 10)\delta(PPl)}{2} = \begin{cases} \frac{-1}{\sqrt{3}} & \text{for } l = 0 \\ -\sqrt{\frac{2}{3}} & \text{for } l = 2 \\ 0 & \text{for } l \neq 0 \text{ or } 2 \end{cases}$$

* For the zero-electron and one-electron states, we take \rangle and $\mathbf{A}_l^\dagger \rangle$. They are properly normalized to the square root of the dimension of the respective representations. The expectation value $\langle \tilde{\ell}^0 \tilde{\mathbf{A}}_l^\dagger \ell^1 \rangle$ becomes therefore $\langle \mathbf{A}_l^\dagger \mathbf{A}_l \rangle = \sqrt{[2]l}$. From (3) $\langle \tilde{\mathbf{g}} \mathbf{A}^\dagger \mathbf{f} \rangle = (-1)^{f+A+g} \langle \tilde{\mathbf{f}} \tilde{\mathbf{A}}^\dagger \tilde{\mathbf{g}} \rangle = (-1)^{f+A-g} \langle \tilde{\mathbf{f}} \tilde{\mathbf{A}}^\dagger \tilde{\mathbf{g}} \rangle$, so $\langle \tilde{\ell}^1 \mathbf{A}^\dagger \ell^0 \rangle = \sqrt{[2]l}$. Similarly, starting from a normalized $|l^{[2]l}\rangle$ and identifying $\tilde{\mathbf{A}}_l^\dagger \ell^{[2]l}$ as the $[2]l-1$ electron state, we have $\sqrt{[2]l} = \langle \tilde{\ell}^{[2]l-1} \tilde{\mathbf{A}}_l^\dagger \ell^{[2]l} \rangle = (-1)^{1S+2l+2l} \langle \tilde{\ell}^{[2]l} \tilde{\mathbf{A}}_l^\dagger \ell^{[2]l-1} \rangle = (-1)^{2l+2l+2l+2l} \langle \tilde{\ell}^{[2]l} \mathbf{A}_l^\dagger \ell^{[2]l-1} \rangle = -\langle \tilde{\ell}^{[2]l} \mathbf{A}_l^\dagger \ell^{[2]l-1} \rangle$.

† All 6- j and 9- j symbols that appear in the numerical examples can be evaluated from the formulas listed below except for the 9- j symbol in (13) whose numerical value is also given:

$$\begin{aligned} \begin{pmatrix} a & a & e \\ a & c & b \\ e & b & b \end{pmatrix} &= \begin{pmatrix} a & c & b \\ e & b & b \\ a & a & e \end{pmatrix} = \cdots = (-1)^{a+b-c} \begin{pmatrix} e & a & a \\ b & c & a \\ b & b & e \end{pmatrix} = \cdots = \frac{\delta(abc)}{[a][b]} \\ \begin{pmatrix} a & b & c \\ a & b & c \\ e & e & e \end{pmatrix} &= \begin{pmatrix} a & b & c \\ e & e & e \\ a & b & c \end{pmatrix} = \cdots = \frac{\delta(abc)}{\sqrt{[a][b][c]}} \\ \left\{ \begin{matrix} a & b & c \\ b & a & e \end{matrix} \right\} &= (-1)^{a+b+c} \frac{\delta(abc)}{\sqrt{[a][b]}} \\ \begin{pmatrix} 1 & 1 & 0 \\ 1 & \frac{3}{2} & \frac{1}{2} \\ 1 & \frac{3}{2} & \frac{1}{2} \end{pmatrix} &= \frac{1}{\sqrt{6}} \begin{pmatrix} \frac{3}{2} & \frac{3}{2} & 1 \\ 1 & 1 & \frac{1}{2} \end{pmatrix} = \frac{1}{12} \sqrt{\frac{5}{3}} \end{aligned}$$

The expectation value $\langle \tilde{\psi} h_2 \phi \rangle$ can be expressed by the use of (9) as

$$\begin{aligned} \langle \tilde{\psi} \mathbf{h}_2 \phi \rangle &= \sum_f \begin{Bmatrix} 1k^1 & 1k^1 & 1S \\ 1P & 1P & f \end{Bmatrix} \langle \tilde{\psi} (\mathbf{A}_{3p}^\dagger \tilde{\mathbf{A}}_{2s}^\dagger)^{1k\mathbf{f}} \langle \mathbf{f} (\mathbf{A}_{2p}^\dagger \tilde{\mathbf{A}}_l^\dagger)^{1k} \phi \rangle \\ &= \delta_{Pk} \begin{Bmatrix} 1P & 1P & 1S \\ 1P & 1P & 1S \end{Bmatrix} \langle \psi (\mathbf{A}_{3p}^\dagger \tilde{\mathbf{A}}_{2s}^\dagger)^{1p} \xi \rangle \langle \tilde{\xi} (\mathbf{A}_{2p}^\dagger \tilde{\mathbf{A}}_l^\dagger)^{1p} \phi \rangle \end{aligned}$$

where

$$\xi \rangle = (2p^6 2s^2 1s^2)^{1S} \rangle^{1S}$$

The second equality holds because it is the only term which does not vanish in the sum. Using (8) and the relationship $(\mathbf{A}_{2p}^\dagger \tilde{\mathbf{A}}_l^\dagger)^{1P} = (-1)^{2l+2P-1P+1} \times (\tilde{\mathbf{A}}_l^\dagger \mathbf{A}_{2p}^\dagger)^{1P}$, we obtain

$$\begin{aligned} \langle \psi \mathbf{h}_2 \phi \rangle &= \delta_{Pk} \begin{Bmatrix} 1P & 1P & 1S \\ 1P & 1P & 1S \end{Bmatrix} (-1)^{2l+2P-1P+1+1} \{[1P][1P][1S][1S][1P][1P]\}^{1/2} \\ &\quad \times \begin{pmatrix} 2P & 2S & 1P \\ 1S & 1S & 1S \\ 2P & 2S & 1P \end{pmatrix} \begin{pmatrix} 2l & 2P & 1P \\ 2l & 2P & 1P \\ 1S & 1S & 1S \end{pmatrix} \langle \tilde{\mathbf{p}}^1 \mathbf{A}_p^\dagger \mathbf{p}^0 \rangle \langle \tilde{\mathbf{s}}^0 \tilde{\mathbf{A}}_s^\dagger \mathbf{s}^1 \rangle \\ &\quad \times \langle \tilde{\mathbf{p}}^6 \mathbf{A}_p^\dagger \mathbf{p}^5 \rangle \langle \tilde{\mathbf{l}}^0 \tilde{\mathbf{A}}_l^\dagger \mathbf{l}^1 \rangle \\ &= \delta_{Pk} \delta(PPl) \langle -1 \rangle^l \end{aligned}$$

Thus, the coefficients to the integrals $R^1(3p2s, 2pl)$ are given by

$$2H^1(10, l0) \delta(Pl) = \begin{cases} \frac{2}{\sqrt{3}} & \text{for } l = 0 \\ 2\sqrt{\frac{2}{3}} & \text{for } l = 2 \\ 0 & \text{for } l \neq 0 \text{ or } 2 \end{cases}$$

We next consider the intershell interaction energy of the state

$$\phi \rangle = ((d^2; {}^3P)(p^3; {}^4S))^2P \rangle$$

as the second example. Tensors of the following type:

$$\mathbf{h}_\xi = ((\mathbf{A}_d^\dagger \tilde{\mathbf{A}}_d^\dagger)^\xi (\mathbf{A}_p^\dagger \tilde{\mathbf{A}}_p^\dagger)^{1S})^{1S}$$

have nonzero expectation values only when ξ is $1S$ or $3S$ because $4S$, ξ and $4S$ must satisfy the triangular condition. Since $(\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)^{1S}$ is $-1/(\sqrt{[2l]})$ times the

number operator of the l shell, it follows from (8) that

$$(12) \quad \begin{aligned} \langle \phi \mathbf{h}_{1S} \phi \rangle &= \sqrt{\frac{[{}^2P][{}^2P][{}^3P][{}^4S]}{[{}^3P][{}^4S][{}^2P][{}^2D][{}^2P]}} 2 \cdot 3 \\ &= 3\sqrt{\frac{2}{5}} \end{aligned}$$

The tensor $(\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)^3 S$ is proportional to the total spin operator [9] and we have

$$\langle \mathbf{g}(\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)^3 S \mathbf{f} \rangle = \langle \tilde{\mathbf{g}} \mathbf{f} \rangle \sqrt{2f_S(f_S + 1)/[l]}$$

when \mathbf{f} belongs to the l shell.* The expectation value of h_{3S} is therefore obtained by using (8) as

$$(13) \quad \begin{aligned} \langle \tilde{\phi} \mathbf{h}_{3S} \phi \rangle &= [{}^2P] \begin{pmatrix} {}^3S & {}^3S & {}^1S \\ {}^3P & {}^4S & {}^2P \\ {}^3P & {}^4S & {}^2P \end{pmatrix} \sqrt{2 \cdot 1 \cdot 2 \cdot 3 \cdot 2 \cdot \frac{3}{2} \cdot \frac{5}{2} \cdot 4 \cdot 3 / (5 \cdot 3)} \\ &= \sqrt{\frac{16}{3}} \end{aligned}$$

* From the definition of \mathbf{A}_l^\dagger and Clebsch-Gordon coefficients

$$(\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)_0^3 S = -\frac{1}{\sqrt{[2l]}} \langle A_{l,m_l}^\dagger \frac{1}{2} A_{l,m_l} - A_{l,m_l}^\dagger - \frac{1}{2} A_{l,m_l} - \frac{1}{2} \rangle = -\frac{2}{\sqrt{[2l]}} S_z$$

Thus, \mathbf{f} and \mathbf{g} must have the same symmetry in order to have a nonvanishing value and a particular component is given as

$$(A) \quad \langle g_{f_L f_S}^\dagger (\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)_0^3 S f_{f_L f_S} \rangle = -\frac{2}{\sqrt{[2l][f]}} f_S \langle \tilde{\mathbf{g}} \mathbf{f} \rangle$$

On the other hand, an expectation value of a product of three tensor components can be derived from the Wigner-Eckart theorem:

$$\langle \tilde{g}_i h_j f_k \rangle = (g_{ijk} | 00) \langle \tilde{\mathbf{g}} \mathbf{h} \mathbf{f} \rangle$$

therefore

$$\begin{aligned} \langle g_{f_L f_S}^\dagger (\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)_0^3 S f_{f_L f_S} \rangle &= (-1)^{f_L + f_L + f_S + f_S} \langle \tilde{g}_{-f_L - f_S} (\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)_0^3 S f_{f_L f_S} \rangle \\ &= (-1)^{2f} \langle \tilde{\mathbf{g}} (\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)^3 S \mathbf{f} \rangle (f_L - f_L 00 f_L f_L | 00) (f_S - f_S 10 f_S f_S | 00) \\ &= (-1)^{2f} \langle \tilde{\mathbf{g}} (\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)^3 S \mathbf{f} \rangle (-1)^{2f_L} \frac{1}{\sqrt{[f_L]}} (-1)^{2f_S + 1} \sqrt{f_S(f_S + 1)[f_S]} \end{aligned}$$

Comparison of this with (A) yields

$$\langle \tilde{\mathbf{g}} (\mathbf{A}_l^\dagger \tilde{\mathbf{A}}_l^\dagger)^3 S \mathbf{f} \rangle = \langle \tilde{\mathbf{g}} \mathbf{f} \rangle \sqrt{2f_S(f_S + 1)/[l]}$$

The exchange-type matrix elements can now be calculated from (12) and (13):

$$\begin{aligned}
 \langle \Phi : ((\mathbf{A}_d^\dagger \tilde{\mathbf{A}}_p)^{1_k} (\mathbf{A}_p^\dagger \tilde{\mathbf{A}}_d)^{1_k})^{1_S} : \Phi \rangle \\
 &= \sum_{\xi} (-1)^{2D+2P+2P+2D+2P+2D-2D+1} \sqrt{[\xi][1k]} \begin{Bmatrix} 2D & 2P & 1k \\ 2P & 2D & \xi \end{Bmatrix} \langle \Phi \mathbf{h}_{\xi} \Phi \rangle \\
 &= \frac{\sqrt{[k]}}{2\sqrt{15}} \{-3\sqrt{\frac{2}{5}} + \sqrt{3} \cdot \sqrt{\frac{10}{3}}\} \\
 &= \frac{1}{5\sqrt{3}} \sqrt{\frac{2[k]}{3}}
 \end{aligned}$$

Therefore, the coefficients to $R^k(dp, pd) = G^k(dp)$ are

$$2H^k(21, 12) \cdot \frac{1}{5\sqrt{3}} \sqrt{\frac{2[k]}{3}} = \begin{cases} \frac{4}{15} \cdot \sqrt{6} & k = 1 \\ \frac{6}{35} \cdot \sqrt{6} & k = 3 \\ 0 & k \neq 1 \text{ or } 3 \end{cases}$$

The coefficient to $R^0(dd, pp) = F^0(dp)$ is from (12):

$$2H^0(22, 11) \cdot 3\sqrt{\frac{2}{5}} = 6\sqrt{6}$$

In these examples, $\langle \Psi V_{out} \Phi \rangle$ is calculated instead of its component $\langle \psi_i^\dagger V_{out} \phi_i \rangle$. The latter can be obtained by dividing the results by $\sqrt{[\phi]}$.

5. Concluding Remarks

The examples described in the previous section were purposely selected for easy hand calculation, yet they illustrate that there are numerous ways to evaluate the matrix elements of a given operator. The use of (9) enables one to express the expectation values of a tensor in terms of those of structurally simpler tensors. The expectation values in (8) are further simplified, because these are defined in a subspace. Thus, an almost arbitrarily chosen sequence of (8) and (9) will eventually terminate and lead to an expression in terms of the basic expectation values $\langle \mathbf{g} \mathbf{A}^\dagger \mathbf{f} \rangle$ defined in an irreducible shell no matter what the starting tensor is: it can be a three- or four-body interaction, a number nonconserving interaction, etc. Although the resulting expression involves only invariants, a redundant summation can be in some cases avoided by a proper choice of the sequence as was shown in the first example. In many cases it would be advantageous to recouple the tensor first so that formula (8) could be used, and to limit the use of (9) for an irreducible shell. However, there does not seem to be any sequence which is decisively superior to others, so a particular formula which will result from a certain choice of the reduction sequence will not be presented.

The second example differs from the first in that the reduction was not carried out thoroughly because one could evaluate the expectation values of $(\mathbf{A}^\dagger \tilde{\mathbf{A}}^\dagger)^{1S}$ and $(\mathbf{A}^\dagger \tilde{\mathbf{A}}^\dagger)^{3S}$ analytically. From a computational point of view, this saving of manipulation can be achieved simply by storing some of the expectation values. A CI program which was used in Reference [10] contains tables for some composite operators and an earlier version of the program contained tables for composite shells. For f electrons, however, a complete table of the basic expectation values $\langle \tilde{\mathbf{g}} | \mathbf{A}^\dagger \mathbf{f} \rangle$ requires several thousand numbers, even when it is compressed by combining tensors to quasi-spin multiplets. Thus, inclusion of extra tables for composite operators is not feasible. The advantage of including such tables for a CI is limited. Whereas these tables can be used effectively for the evaluation of diagonal elements or matrix elements among states having the same configuration, they are not useful for the evaluation of the other off-diagonal elements, which is a major part of the whole computation.

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