QUANTUM CHEMISTRY GROUP
FOR RESEARCH IN ATOMIC, MOLECULAR AND SOLID-STATE THEORY
UPPSALA UNIVERSITY, UPPSALA, SWEDEN

Angular Momentum Wave Functions Constructed by Projection Operators

By

Per-Olov Löwdin

Technical Note No. 12

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WRIGHT AIR DEVELOPMENT CENTER of the AIR RESEARCH
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Abstract.

The conventional method of constructing wave functions of pure angular momentum for a composite system is based on the idea of coupling the angular momenta of the constituents. Instead of this synthetic method, an analytical approach is here introduced. It is pointed out that an arbitrary trial wave function for the total system in a unique way must be resolvable into orthogonal components of pure angular momentum associated with different quantum numbers. A particular component can be selected by means of certain "projection operators", which annihilate all components except the one desired. Such a projection operator is simply a product of commuting factors, each one of which annihilates a specific eigenfunction to the angular momentum under consideration.

Physically this idea is of importance, since one can now start out from a rough model wave function based essentially on qualitiative arguments, for instance of the independent-particle type, and then obtain a mathematically and physically much better trial function by selecting the particular component of the original function which has the correct symmetry type desired.

The projection operators are studied in some detail both as products and in expanded form. The case of degenerate subspaces of the same angular momentum quantum numbers is discussed, and the problem of constructing an orthogonal subset of functions is solved by a simple elimination procedure; the connection with the conventional seniority idea is briefly discussed.

I. INTRODUCTION.

The angular momentum for a composite system is conventionally studied by coupling the angular momenta for the constituents. The treatment of the operators is elementary and straightforward, whereas the construction of the associated wave functions in this approach represents a rather complicated problem. In combining two angular momenta, $\mathcal{M}_1$ and $\mathcal{M}_2$, the wave functions associated with the operator $\mathcal{M} = \mathcal{M}_1 + \mathcal{M}_2$ are obtained from the wave functions belonging to $\mathcal{M}_1$ and $\mathcal{M}_2$ respectively, by means of the vector-coupling formulas containing the so-called Clebsch-Gordon or Wigner coefficients [1]. This problem has been investigated extensively by several authors, and particularly beautiful work has been carried out by Wigner [2] by means of group theory.

[1] For a survey of the conventional theory of angular momentum, see e.g. A.R. Edmonds, "Angular Momenta in Quantum Mechanics" (Princeton University Press, Princeton 1957) or M.E. Rose, "Elementary Theory of Angular Momentum" (Wiley and Sons, New York 1957).

[2] E.P. Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren" (Vieweg und Sohn, Braunschweig 1931).

The wave functions belonging to a total angular momentum $\mathcal{M} = \mathcal{M}_1 + \mathcal{M}_2 + \mathcal{M}_3 + \cdots$ could now, in principle, be obtained from the wave functions of the separate terms by means of the vector-coupling formula by starting out from a certain component and then successively adding all the other components, one at a time. This

method becomes complicated already with three components, since there is no unique way of carrying out this coupling: one may combine $\mathcal{M}_1$ and $\mathcal{M}_2$ to a resultant $\mathcal{M}_{12}$ and couple this to $\mathcal{M}_3$, or one may couple $\mathcal{M}_1$ to the resultant $\mathcal{M}_{23}$ of combining $\mathcal{M}_2$ and $\mathcal{M}_3$. One obtains in this way two different sets of wave functions to $\mathcal{M}$, which are, of course, connected by a unitary transformation the elements of which are essentially the famous Racah coefficients [3].

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[3] G. Racah, Phys. Rev. 62, 438 (1942); 63, 367 (1943).

The coupling of four angular momenta becomes still more complicated.

It should be stressed that the vector-coupling formalism is basically a synthetic method for constructing wave functions of pure angular momentum for a composite system. In contrast to this approach, we will here describe a method of an analytic character which considers the composite system as an entity to which the various components contribute in an equivalent and not necessarily in an ordered way. We believe that such a treatment of the system as a collective without subgroups of components coupled in a perhaps artifical arrangement will be of essential physical importance, for instance in treating such properties as the total energy. The starting point is the fact that an arbitrary trial function for the total system must be resolvable in a unique way into orthogonal components of pure angular momentum $\mathcal{M}$ associated with different quantum numbers. Each one of these components may in principle be found by means of the projection operator formalism recently developed by the present author [4,5].

4) P.O. Löwdin, Phys. Rev. 97, 1509 (1955).

5) P.O. Löwdin, Adv. Physics 5, 1 (1956), particularly Sec. 3,1.

The basic idea is that the component of the symmetry type desired should be obtained from the original wave function by means of an operator $\mathcal{O}$ which annihilates all other components but lets the selected term survive the operation in an unchanged form; such a projection operator may here be constructed simply as a product of commuting factors each one of which annihilates a term of a specific symmetry type.

The method was first used for investigating the spin degeneracy problem[4] and explicit formulas for the singlet state were worked out; a complete treatment of this problem for all types of multiplicity will be given in a forthcoming paper[6]. In this connection we note that the

6) A preliminary report of some results have already been given in P.O. Löwdin, "Nature of Valence Bond Functions", Technical Note from the Quantum Chemistry Group of Uppsala University, 1957; Proc. Paris Symposium "Calcul des Fonctions d'Onde Moléculaires", 1957.

projection operator method has an essential physical importance, since it may be used to give a mathematically correct symmetry form also to a rough model wave function which is otherwise essentially based on qualitative arguments. In this way it is, for instance, possible to generalize the simple independent-particle-model to include certain correlation and exchange polarization effects[4,7],

7) P.O. Löwdin, "Generalizations of the Hartree-Fock Scheme", Technical Note from the Quantum Chemistry Group of Uppsala University; Annales Academiae Regiae Scientiarum Upsaliensis 2, (1958).

by permitting different orbitals for different spins. The projection operator method has also been successfully used for treating the translational symmetry [5] occurring in crystals.

We will now use this simple method for calculating the wave functions of the total angular momentum M of a composite system. The associated projection operators will be studied in some detail both as products and in expanded form. The purpose of the present paper is to present the basic theory with a few illustrating examples, whereas the main applications have appeared elsewhere or are reserved for forthcoming publications.

The applications to spin and isotopic spin have actually turned out to be very simple and, in the case of orbital angular momentum, the atomic state wave functions for the configurations p^n and d^n have already been derived[8]. Further applications on the atomic configuration

8) R. Fieschi and P.O. Löwdin, "Atomic State Wave Functions Generated by Projection Operators", Technical Note from the Quantum Chemistry Group of Uppsala University, (1957).

f^n and on the nuclear shell-model are now also in progress. For more complicated many-particle systems, the method is further being programmed for the electronic computer of the type Alwac III-E in the Quantum Chemistry Laboratory.

II. GENERAL PROPERTIES OF ANGULAR MOMENTUM.

Let us start by giving a brief review of such basic properties of angular momentum as are of importance in constructing the projection operators. The treatment in this section follows essentially the ideas developed by Dirac[9], but avoids the explicit introduction of matrices.

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9) P.A.M. Dirac, "Principles of Quantum Mechanics", (Clarendon Press, Oxford 1935), 2nd ed., p. 147.

A general angular momentum $\mathcal{M} = (\mathcal{M}_x, \mathcal{M}_y, \mathcal{M}_z)$ measured in units of $\hbar$ is defined by the commutation relation $\mathcal{M} \times \mathcal{M} = i\mathcal{M}$ or

$$\mathcal{M}_x\mathcal{M}_y - \mathcal{M}_y\mathcal{M}_x = i\mathcal{M}_z \quad \text{(cyclic)} \tag{1}$$

Fixing our attention on $\mathcal{M}_z$, we will, in place of the two other components, introduce the auxiliary operators

$$\begin{aligned} \mathcal{M}_+ &= \mathcal{M}_x + i\mathcal{M}_y, \\ \mathcal{M}_- &= \mathcal{M}_x - i\mathcal{M}_y, \end{aligned} \tag{2}$$

forming a pair of hermitean adjoint operators. The square of the total angular momentum is then given by the three relations

$$\mathcal{M}^2 = \mathcal{M}_x^2 + \mathcal{M}_y^2 + \mathcal{M}_z^2 = \tag{3}$$

$$= \mathcal{M}_-\mathcal{M}_+ + \mathcal{M}_z^2 + \mathcal{M}_z = \tag{4}$$

$$= \mathcal{M}_+\mathcal{M}_- + \mathcal{M}_z^2 - \mathcal{M}_z \tag{5}$$

Since $\mathcal{M}_z$ commutes with $\mathcal{M}^2$, it is feasible to consider the combined operator $(\mathcal{M}^2; \mathcal{M}_z)$ having the eigenfunctions $Y(\mathcal{M}'; \mathcal{M}'_z)$ associated with the eigenvalue pair $(\mathcal{M}')^2$ and $\mathcal{M}'_z$. From (1) and (2) follows further the commutation relations

$$\begin{aligned} \mathcal{M}_z \mathcal{M}_+ &= \mathcal{M}_+ (\mathcal{M}_z + 1) \\ \mathcal{M}_z \mathcal{M}_- &= \mathcal{M}_- (\mathcal{M}_z - 1) \end{aligned} \quad , \qquad (6)$$

and $\mathcal{M}_-$ and $\mathcal{M}_+$ have therefore been called step-up and step-down operators, respectively, with respect to $\mathcal{M}_z$. Using (6), we obtain

$$\mathcal{M}_z \{\mathcal{M}_+ Y(\mathcal{M}'; \mathcal{M}'_z)\} = \mathcal{M}_+ (\mathcal{M}_z + 1)\, Y(\mathcal{M}'; \mathcal{M}'_z) =$$

$$= (\mathcal{M}'_z + 1) \{\mathcal{M}_+ Y(\mathcal{M}'; \mathcal{M}'_z)\} \qquad (7)$$

showing that $\mathcal{M}_+$ transforms the eigenfunction associated with the pair $(\mathcal{M}', \mathcal{M}'_z)$ into an eigenfunction associated with the pair $(\mathcal{M}', \mathcal{M}'_z + 1)$. Assuming that the function $Y(\mathcal{M}', \mathcal{M}'_z)$ is properly <u>normalized</u> and using (4), we obtain the normalization integral for the new function

$$\int |\mathcal{M}_+ Y(\mathcal{M}'; \mathcal{M}'_z)|^2 (dx) =$$

$$= \int Y^*(\mathcal{M}'; \mathcal{M}'_z)\, \mathcal{M}_- \mathcal{M}_+ Y(\mathcal{M}'; \mathcal{M}'_z)\, (dx) =$$

$$= (\mathcal{M}')^2 - (\mathcal{M}'_z)^2 - \mathcal{M}'_z \,. \qquad (8)$$

A corresponding theorem holds for $\mathcal{M}_-$.

Because of the step-up and step-down properties, one could be inclined to draw the conclusion that the number of eigenvalues $\mathcal{M}'_z$ associated with a particular $\mathcal{M}'$ would be unlimited, but this is not the case. According to (4) and (5), the eigenfunctions to $(\mathcal{M}^2, \mathcal{M}_z)$ are also eigenfunctions to the operators $\mathcal{M}_-\mathcal{M}_+ = \mathcal{M}_+^\dagger\mathcal{M}_+$ and $\mathcal{M}_+\mathcal{M}_- = \mathcal{M}_-^\dagger\mathcal{M}_-$ and, since such operators can never have negative eigenvalues, one obtains the inequalities

$$\begin{aligned} (\mathcal{M}')^2 - (\mathcal{M}'_z)^2 - \mathcal{M}'_z &\geq 0 , \\ (\mathcal{M}')^2 - (\mathcal{M}'_z)^2 + \mathcal{M}'_z &\geq 0 , \end{aligned} \tag{8'}$$

showing that there definitely exist a largest and a smallest eigenvalue for $\mathcal{M}_z$, which will be denoted by $m_>$ and $m_<$, respectively.

Let us now consider the functions $\mathcal{M}_+ Y(\mathcal{M}', m_>)$ and $\mathcal{M}_- Y(\mathcal{M}', m_<)$. From (7) it follows that, unless these functions are vanishing identically, they are eigenfunctions associated with the eigenvalues $(m_> + 1)$ and $(m_< - 1)$, respectively, which is a contradictory result. Hence they must be vanishing and, taking their normalization integrals according to (8), we obtain

$$\begin{aligned} (\mathcal{M}')^2 - m_>^2 - m_> &= 0 , \\ (\mathcal{M}')^2 - m_<^2 - m_< &= 0 , \end{aligned} \tag{9}$$

which leads to $m_< = -m_>$. By means of (7) and

(9), it is then easily shown that the assumption that $(m_> - m_<)$ is not an integer leads to a contradiction, and hence we have

$$m_> - m_< = 2k \,, \quad k = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots \tag{10}$$

and further $m_> = +k$, $m_< = -k$, and

$$\mathcal{M}' = \sqrt{k(k+1)} \,. \tag{11}$$

If the value of k is fixed, the possible values of $\mathcal{M}'_z$ are thus

$$m = k, k-1, k-2, \ldots -k+1, -k \,, \tag{12}$$

giving the multiplicity $(2k+1)$.

In the following we will, instead of the eigenvalues $(\mathcal{M}', \mathcal{M}'_z)$, use the quantum numbers (k, m) as index in the eigenfunctions which hence will be denoted by $Y(k, m)$. Equation (8) may be written

$$\int |\mathcal{M}_+ Y(k,m)|^2 (dx) = (k-m)(k+m+1) \tag{13}$$

and shows how the normalization integral is changed in the step-up procedure. For the properly normalized eigenfunctions, we hence get the connection formulas

$$\mathcal{M}_+ \underline{Y}(k,m) = \left\{(k-m)(k+m+1)\right\}^{1/2} \underline{Y}(k,m+1),$$
$$\mathcal{M}_- \underline{Y}(k,m) = \left\{(k+m)(k-m+1)\right\}^{1/2} \underline{Y}(k,m-1). \qquad (14)$$

Of course, the normalization condition leaves actually the eigenfunctions undetermined with respect to a phase factor $e^{i\alpha}$, but this factor is here chosen to be unity leading to the Dirac phase convention which is implicitly contained in (14).

In conclusion we note the existence of the addition theorem for angular momenta: if $\mathcal{M} = \mathcal{M}_1 + \mathcal{M}_2$, then $k = k_1+k_2, k_1+k_2-1, \ldots |k_1-k_2|$.

III. DEFINITION OF PROJECTION OPERATORS.

Let us now consider an arbitrarily given function $\underline{Y}$, and let us try to resolve it into components $C_{km}\underline{Y}_{km}$, which are eigenfunctions to $\mathcal{M}^2$ and $\mathcal{M}_z$, so that

$$\underline{Y} = \sum_k \sum_m C_{km}\underline{Y}_{km}, \qquad (15)$$

where the summation goes over all possible values of k and m. This can be done by observing that the eigenvalue relations for $\mathcal{M}^2$ and $\mathcal{M}_z$ may be written in the form

$$\{\mathcal{M}^2 - \ell(\ell+1)\}\underline{Y}_{\ell,m} \equiv 0\,, \quad \{\mathcal{M}_z - m\}\underline{Y}_{\ell,m} \equiv 0\,, \tag{16}$$

which means that the eigenfunction $\underline{Y}_{\ell,m}$ is annihilated by the operator $\{\mathcal{M}^2 - \ell(\ell+1)\}$ or the operator $\{\mathcal{M}_z - m\}$. It is hence possible to get out a specific component $C_{\ell m}\underline{Y}_{\ell,m}$ in (15) by annihilating all other components, and this is actually accomplished by means of the two operators $\mathcal{O}_\ell(\mathcal{M}^2)$ and $\mathcal{O}_m(\mathcal{M}_z)$ defined by the products

$$\mathcal{O}_\ell(\mathcal{M}^2) = \prod_{\chi \neq \ell} \frac{\{\mathcal{M}^2 - \chi(\chi+1)\}}{\ell(\ell+1) - \chi(\chi+1)}\,, \tag{17}$$

$$\mathcal{O}_m(\mathcal{M}_z) = \prod_{\mu \neq m} \frac{\{\mathcal{M}_z - \mu\}}{m - \mu}\,. \tag{18}$$

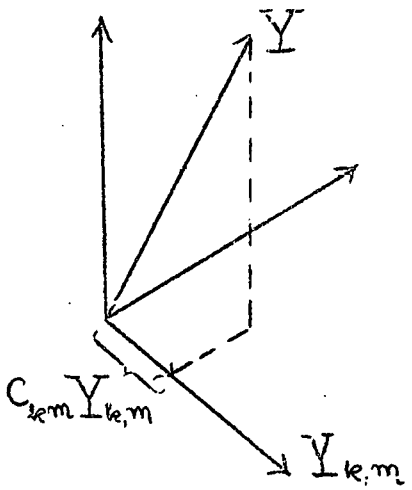
The numerators are products of the elementary annihilation operators defined by (16) over all quantum numbers except those characterizing the component desired, and the denominators have been chosen so that the operators have the value 1 when working on the term $C_{\ell m}\underline{Y}_{\ell m}$. By using eqs. (16)-(18), we hence obtain

$$\mathcal{O}_\ell(\mathcal{M}^2)\,\mathcal{O}_m(\mathcal{M}_z)\,\underline{Y} = C_{\ell m}\underline{Y}_{\ell m}\,, \tag{19}$$

giving the uniquely defined component of $\underline{Y}$ having a pure angular momentum with the quantum numbers ℓ and m.

One can visualize the expansion problem (15) by

thinking about a Hilbert space spanned by the mutually orthogonal unit vectors $Y_{\ell,m}$, in which it is required to resolve an arbitrary vector Y into component vectors along the axes. Geometrically this is done by an orthogonal projection, and the operators $\mathbb{O}$ in the left-hand side of (19) are therefore called <u>projection operators.</u> We note that a repeated use of $\mathbb{O}$ would not change the result, which leads to the relation



$$\mathbb{O}^2 = \mathbb{O} \qquad (20)$$

which is characteristic for the projection operators[10].

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[10] J.v. Neumann, Math. Grundlagen der Quantenmechanik (Dover Publications, New York 1943); p. 41.

We note that this relation is also of essential importance in simplifying the calculations of the energy and its matrix elements [11].

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[11] P.O. Löwdin, Phys. Rev. 97, 1509 (1955); see particularly eq. (37).

By means of the addition theorem, it is usually possible to calculate which eigenvalues (ℓ, m) may occur in the system, and the product (17) can then be restricted to contain only a finite number of factors. It is worthwhile

noting, however, that even the infinite product is convergent, which is easily seen by writing (17) in the form

$$O_{\ell}(M^2) = \prod_{\kappa \neq \ell} \left(1 - \frac{M^2 - \ell(\ell+1)}{(\kappa-\ell)(\kappa+\ell+1)} \right) . \qquad (21)$$

For only integral values of ℓ , the special case $\ell = 0$ has the particularly simple form

$$O_0(M^2) = \left(1 - \frac{M^2}{1\cdot 2}\right)\left(1 - \frac{M^2}{2\cdot 3}\right)\left(1 - \frac{M^2}{3\cdot 4}\right)\ldots \qquad (22)$$

In the right-hand member, the first factor will annihilate the triplet component, the second factor the quintet, the third the septet, etc., and only the singlet component will survive the operation being multiplied by the factor 1.

Since there are usually no difficulties in constructing eigenfunctions to M_z , there is comparatively little use of the operator $O_m(M_z)$ except in an actual component analysis. In the following, we will therefore assume that, from the beginning, the given function $\underline{Y}$ is an eigenfunction to M_z with the specific quantum number m . For the sake of simplicity, we will further introduce the condition $m \geq 0$; the case of a negative m -value is then handled by reversing the Z-axis. The only possible ℓ -values range now from $\ell = m$ to a certain $\ell = \ell_{max}$ evaluated from the addition theorem, and, since only the corresponding factors have to be included in the product (17), we obtain, after replacing κ by $\kappa + m$, that

$$\mathcal{O}_k(\mathcal{M}^2) = \prod_{\chi=0,n}^{(\chi\neq k-m)} \frac{\{\mathcal{M}^2 - (\chi+m)(\chi+m+1)\}}{\{k(k+1) - (\chi+m)(\chi+m+1)\}}, \qquad (23)$$

where $n = k_{max} - m$. Since this operator is actually supposed to operate only on functions Y, which are eigenfunctions to $\mathcal{M}_z$ associated with the eigenvalue m, we have the freedom to write (23) under the form

$$\mathcal{O}_{km} = \prod_{\chi=0,n}^{(\chi\neq k-m)} \frac{\{\mathcal{M}^2 - (\mathcal{M}_z+\chi)(\mathcal{M}_z+\chi+1)\}}{(k-m-\chi)(k+m+\chi+1)}, \qquad (24)$$

i.e. we have replaced m by $\mathcal{M}_z$ in the numerator but left the denominator unchanged.

In the applications, the product forms (17) and (23) often convenient for direct practical use, and it seems as if these products also would render a good basis for the programming of the method for an electronic computer. In other cases, it is sometimes better to use an expanded form of the projection operator which will now be derived starting from the expression (24).

IV. EXPANSION OF THE PROJECTION OPERATORS.

Let us study the operator in the numerator of the product (24) by introducing the notation

$$F_\chi \equiv \mathcal{M}^2 - (\mathcal{M}_z + \chi)(\mathcal{M}_z + \chi + 1) \qquad (25)$$

Using (4), we obtain the special relation $F_0 = \mathcal{M}_- \mathcal{M}_+$. By means of (6), we can further derive the more general commutation relations

$$\begin{aligned} f(\mathcal{M}_z)\,\mathcal{M}_+ &= \mathcal{M}_+ f(\mathcal{M}_z + 1), \\ f(\mathcal{M}_z)\,\mathcal{M}_- &= \mathcal{M}_- f(\mathcal{M}_z - 1), \end{aligned} \qquad (26)$$

for any polynomial function f of $\mathcal{M}_z$. Starting from $\mathcal{M}_- \mathcal{M}_+ = F_0$ and using (26), we then obtain successively

$$\begin{aligned} &\mathcal{M}_- \mathcal{M}_+ = F_0, \\ &\mathcal{M}_-^2 \mathcal{M}_+^2 = \mathcal{M}_- F_0 \mathcal{M}_+ = \mathcal{M}_- \mathcal{M}_+ F_1 = F_0 F_1, \\ &\mathcal{M}_-^3 \mathcal{M}_+^3 = \mathcal{M}_- (F_0 F_1) \mathcal{M}_+ = \mathcal{M}_- \mathcal{M}_+ F_1 F_2 = F_0 F_1 F_2, \\ &\cdots \cdots \cdots \\ &\mathcal{M}_-^q \mathcal{M}_+^q = \mathcal{M}_- (F_0 F_1 F_2 \cdots F_{q-2}) \mathcal{M}_+ = \\ &\qquad = \mathcal{M}_- \mathcal{M}_+ (F_1 F_2 \cdots F_{q-1}) = \\ &\qquad = F_0 F_1 F_2 \cdots F_{q-1}. \end{aligned} \qquad (27)$$

By means of the last formula, we can now expand the projection operators.

Let us first consider the principal case $m = k$. This case is not only particularly simple but it forms also a convenient starting point for a study of the lower m -values by means of the step-down procedure based on the use of M_- . The projection operator (24) takes now the special form

$$\mathcal{O}_{kk} = \prod_{\chi=1}^{k_{max}-k} \frac{M^2 - (M_z+\chi)(M_z+\chi+1)}{(-\chi)(2k+\chi+1)} =$$

$$= \prod_{\chi=1}^{k_{max}-k} (-1)\frac{F_\chi}{\chi(2k+\chi+1)} =$$

$$= (-1)^n (2k+1)! \frac{F_1 F_2 F_3 \dots F_n}{n!\,(2k+n+1)!} , \qquad (28)$$

where $n = k_{max} - k$. From the definition (25) follows directly

$$F_\rho = F_0 - \rho(2M_z + \rho + 1) , \qquad (29)$$

and, by repeated use of this formula and (27) for $\rho = n, n-1, n-2, \dots 1$, we can then expand the product in (28):

$$F_1 F_2 F_3 \dots F_n =$$

$$= F_2 F_3 \dots F_{n-1} F_0 - F_1 F_2 \dots F_{n-1}\, n\,(2M_z + n + 1) =$$

$$= M_-^{\,n} M_+^{\,n} - n\,(2M_z + n + 1)\, F_1 F_2 \dots F_{n-1} =$$

$$= M_-^{\,n} M_+^{\,n} - n\,(2M_z + n + 1)\, M_-^{\,n-1} M_+^{\,n-1} + \tag{30}$$

$$+ n(n-1)(2M_z + n + 1)(2M_z + n)\, M_-^{\,n-2} M_+^{\,n-2} +$$

$$+ \dots \dots ,$$

For the projection operator (28), we hence obtain

$$O_{kk} = (2k+1)!\,\left\{ (-1)^n \frac{M_-^{\,n} M_+^{\,n}}{n!\,(2k+n+1)!} + (-1)^{n-1} \frac{M_-^{\,n-1} M_+^{\,n-1}}{(n-1)!\,(2k+n)!} + \dots \right\}$$

$$= (2k+1)!\, \sum_{\nu=0}^{k_{max}-k} (-1)^\nu \frac{M_-^{\,\nu} M_+^{\,\nu}}{\nu!\,(2k+\nu+1)!} , \tag{31}$$

which is the expansion desired.

Let us now also consider the more general case $0 \leq m < k$. By means of (24)-(27) and the expansion of (28) for $p = n - k + m = k_{max} - k$, we obtain

$$\mathcal{O}_{kmn} = \prod_{\varkappa=0,r}^{(\varkappa \neq k-m)} \frac{\mathcal{M}^2 - (\mathcal{M}_z+\varkappa)(\mathcal{M}_z+\varkappa+1)}{k(k+1) - (m+\varkappa)(m+\varkappa+1)} =$$

$$= \prod_{\varkappa=0,n}^{(\varkappa \neq k-m)} \frac{F_\varkappa}{(k-m-\varkappa)(k+m+\varkappa+1)} =$$

$$= (k+m)! \frac{F_0 F_1 F_2 \dots F_{k-m-1}}{(k-m)!\ (2k)!} (-1)^{n-k+m} (2k+1)! \frac{F_{k-m+1} F_{k-m+2} \dots F_n}{(n-k+m)!\ (k+m+n+1)!} =$$

$$= (2k+1) \frac{(k+m)!}{(k-m)!} \mathcal{M}_-^{k-m} \mathcal{M}_+^{k-m} (-1)^\rho \frac{F_{k-m+1} F_{k-m+2} \dots F_{k-m+\rho}}{\rho!\ (2k+\rho+1)!} =$$

$$= (2k+1) \frac{(k+m)!}{(k-m)!} \mathcal{M}_-^{k-m} \left\{ (-1)^\rho \frac{F_1 F_2 \dots F_\rho}{\rho!\ (2k+\rho+1)!} \right\} \mathcal{M}_+^{k-m} =$$

$$= (2k+1) \frac{(k+m)!}{(k-m)!} \mathcal{M}_-^{k-m} \left\{ \sum_{\nu=0}^{\rho} (-1)^\nu \frac{\mathcal{M}_-^\nu \mathcal{M}_+^\nu}{\nu!\ (2k+\nu+1)!} \right\} \mathcal{M}_+^{k-m}$$

$$= (2k+1) \frac{(k+m)!}{(k-m)!} \sum_{\nu=0}^{k_{max}-k} (-1)^\nu \frac{\mathcal{M}_-^{k-m+\nu} \mathcal{M}_+^{k-m+\nu}}{\nu!\ (2k+\nu+1)!} \qquad (32)$$

The application of the operator expansion (32) to a given function Y is a straightforward procedure, since the action of the operators $\mathcal{M}_-$ and $\mathcal{M}_+$ can always be found by elementary methods for a specified type of angular momentum. For more complicated many-particle systems, the calculations may be lengthy and somewhat tedious, but they are never difficult and can be carried out by routine procedures. After evaluating the function $\{\mathcal{O}_{k m} Y\}$, the final expression is conveniently checked by investigating whether it is annihilated by the operator $[\mathcal{M}^2 - k(k+1)]$. By means of (4), the checking relation may also be written in the form

$$[\mathcal{M}_- \mathcal{M}_+ - (k-m)(k+m+1)] \{\mathcal{O}_{k m} Y\} \equiv 0 . \quad (33)$$

In theoretical investigations of expanded forms of angular momentum wave functions, this relation is also of basic importance for deriving recursion formulas between the coefficients. We note that, in the principal case $m = k$, a still simpler check is provided by the relation

$$\mathcal{M}_+ \{\mathcal{O}_{kk} Y\} \equiv 0 , \quad (34)$$

which is also of theoretical value.

If the system is composed so that $\mathcal{M} = \sum_i \mathcal{M}_i$, we have

$$\mathcal{M}_+ = \sum_i \mathcal{M}_+(i) , \quad \mathcal{M}_- = \sum_i \mathcal{M}_-(i) , \quad (35)$$

and the operators $\mathcal{M}_+^{\nu}$ and $\mathcal{M}_-^{\nu}$ may then be

expanded by means of the polynomial theorem in an entirely symmetric way. Choosing a starting function Y, which contains the various parts in an equivalent way, we can then by projection derive a function of pure total angular momentum to which the different constituents contribute symmetrically. This can be done even in the case of a degeneracy but, since one is usually interested in finding only a sufficiently large subset for calculating the energy, it is not always worthwhile to put in the amount of work required. We will return to this problem in the following section.

In the special case when $\mathcal{M} = \mathcal{M}_1 + \mathcal{M}_2$, one can by means of the binomial theorem obtain a projection operator expansion which is equivalent in the two constituents. By means of the relations (14), one can then derive an expression for the total wave function which corresponds to the ordinary vector-coupling formula. More details about the connection with the conventional theory will be given in a forthcoming paper.

V. COMPLETE MATRIX REPRESENTATION OF THE PROJECTION OPERATORS.

In order to study the theoretical properties of the projection operators $\mathcal{O}$ in greater detail, we will now introduce an orthonormal set of basis functions $\Phi_1, \Phi_2, \Phi_3 \ldots \Phi_\rho$ all having $\mathcal{M}_z = m$, which is complete enough to span the part of Hilbert space under consideration. In treating a many-particle system, this set is usually chosen to consist of Hartree products or

Slater determinants built up from one-particle functions, but even more elaborate basis functions are possible. The matrix elements of the projection operator $\mathbb{O}$ with respect to this basis are given by the relation

$$C_{\mu\nu} = \int \Phi_\mu^* \mathbb{O} \Phi_\nu \, (dx) \tag{36}$$

and form an hermitean matrix $\mathbb{C}$, which is idempotent as a consequence of the relation (20). The matrix relation $\mathbb{C}^2 = \mathbb{C}$ implies that

$$\sum_\alpha C_{\mu\alpha} C_{\alpha\nu} = C_{\mu\nu} . \tag{37}$$

It follows further that the matrix $\mathbb{C}$ has only the eigenvalues 0 or 1, and the latter has a multiplicity $g = 1,2,3,\cdots$ which is usually derivable in advance by means of simple combinatoric arguments. In the case when $g = 1$, we speak about a non-degenerate projection problem; otherwise about a degenerate one.

From relation (37) follows directly that each one of the column vectors

$$\mathbb{C}_\nu = \begin{pmatrix} C_{1\nu} \\ C_{2\nu} \\ C_{3\nu} \\ \vdots \\ C_{\rho\nu} \end{pmatrix} \tag{38}$$

is an eigenvector to the matrix $\mathbb{C}$ associated with the eigenvalue 1, but of these eigenvectors $\mathbb{C}_1, \mathbb{C}_2, \cdots \mathbb{C}_\rho$ can, of course, only g be linearly independent.

Let us now consider the projected functions $\Theta_1, \Theta_2, \Theta_3, \ldots \Theta_\rho$, which are defined by

$$\Theta_\nu = \mathbb{O}\,\Phi_\nu = \sum_\mu \Phi_\mu C_{\mu\nu} \,. \tag{39}$$

This relation implies that the vectors $\mathbb{C}_1, \mathbb{C}_2, \ldots$ are nothing but discrete representations of the functions $\Theta_1, \Theta_2, \ldots$ in a system with the basis Φ_μ. In order to study the linear dependence of these functions, one has to investigate their overlap matrix:

$$\Delta_{\mu\nu} = \int \Theta_\mu^* \Theta_\nu \, (dx) \tag{40}$$

By means of the quantum-mechanical "turn-over rule" and (20), we obtain directly

$$\begin{aligned} \Delta_{\mu\nu} &= \int (\mathbb{O}\Phi_\mu)^* (\mathbb{O}\Phi_\nu)\,(dx) = \\ &= \int \Phi_\mu^* \, \mathbb{O}^2 \Phi_\nu \,(dx) = \\ &= \int \Phi_\mu^* \, \mathbb{O}\, \Phi_\nu \,(dx) = C_{\mu\nu} \,, \end{aligned} \tag{41}$$

i.e. the overlap matrix Δ is identical with the matrix $\mathbb{C}$. This means that the overlap matrix has q eigenvalues equal to 1 and $(\rho - q)$ equal to zero. Between the functions Θ_ν, there are hence $(\rho - q)$ linear relations, whereas q of them are linearly independent.

A fundamental problem is now the construction of an orthonormal subset of order q from the functions $\Theta_1, \Theta_2, \ldots \Theta_\rho$. The solution is unique except

for a unitary transformation, but the special choice is not exceedingly important if the subset will be used for calculating the energy, since another unitary transformation will then be carried out anyway. It would, of course, be of value if one could directly construct a subset which diagonalizes the Hamiltonian of order g in an exact or approximate way, and this would also prove the existence of g extra good quantum numbers. So far, such an approach has been successful in some special cases, and particularly the use of seniority numbers in the nuclear shell-model should be mentioned in this connection.

Here we will first leave the question of approximate good quantum numbers aside and concentrate our interest on the orthogonalization procedure. In constructing the subset of order g, we could either try to treat all the functions $\Phi_1, \Phi_2, \Phi_3, \ldots \Phi_g$ in an equivalent way, or we could orthogonalize them successively in order by means of the Schmidt process[12]. It should be observed

[12] For a discussion of the relation between symmetric and successive orthogonalization, see e.g. P.O.Löwdin, Adv. Phys. 5, 1 (1956), particularly Sec. 3,2.

that, in the treatment of projections, the latter may be replaced by a very simple elimination procedure, which is based on (20) and the "turn-over rule" used in (41).

Let us start by considering a degeneracy of order $g = 2$. The two functions Φ_1 and Φ_2, defined by

$$\textcircled{H}_1 = \textcircled{0}\Phi_1 = \Phi_1 C_{11} + \Phi_2 C_{21} + \Phi_3 C_{31} + \cdots$$
$$\textcircled{H}_2 = \textcircled{0}\Phi_2 = \Phi_1 C_{12} + \Phi_2 C_{22} + \Phi_3 C_{32} + \cdots \qquad (42)$$

may be assumed to be linearly independent[13]. It is then

[13] If $\textcircled{H}_2$ happens to be proportional to $\textcircled{H}_1$, we will instead consider $\textcircled{H}_3, \textcircled{H}_4, \cdots$ etc. until we find a function which is not proportional to $\textcircled{H}_1$; this must be the case, since otherwise $g = 1$.

possible to find two multipliers, d_{12} and d_{22}, so that Φ_1 can be eliminated from the second expansion:

$$\textcircled{H}_1 = \Phi_1 C_{11} + \Phi_2 C_{21} + \Phi_3 C_{31} + \cdots$$
$$\textcircled{H}_2' = \textcircled{H}_1 d_{12} + \textcircled{H}_2 d_{22} = 0 + \Phi_2 C_{21}' + \Phi_3 C_{31}' + \cdots \qquad (43)$$

The relation required is $C_{11} d_{12} + C_{12} d_{22} = 0$
with $C_{k2}' = C_{k1} d_{12} + C_{k2} d_{22}$ for $k \geq 2$.
We can now directly conclude that $\textcircled{H}_2'$ must be orthogonal to $\textcircled{H}_1$, since we have

$$\int \textcircled{H}_1^* \, \textcircled{H}_2' \, (dx) = \int (\textcircled{0}\Phi_1)^* \, \textcircled{0} \, (\Phi_1 d_{12} + \Phi_2 d_{22})(dx) =$$
$$= \int \Phi_1^* \, (\Phi_2 C_{21}' + \Phi_3 C_{31}' + \cdots)(dx) = 0 . \qquad (44)$$

The orthogonality is here accomplished simply by eliminating Φ_1 from the expansion of Θ_2' .

In the case of a degeneracy of order $g = 3$, we proceed analogously. Starting out from the relations

$$\begin{aligned}
\Theta_1 &= \mathrm{H}\Phi_1 = \Phi_1 C_{11} + \Phi_2 C_{21} + \Phi_3 C_{31} + \cdots, \\
\Theta_2 &= \mathrm{H}\Phi_2 = \Phi_1 C_{12} + \Phi_2 C_{22} + \Phi_3 C_{32} + \cdots, \\
\Theta_3 &= \mathrm{H}\Phi_3 = \Phi_1 C_{13} + \Phi_2 C_{23} + \Phi_3 C_{33} + \cdots,
\end{aligned} \tag{45}$$

we can, by introducing convenient multipliers, eliminate Φ_1 from the second expansion and Φ_1 and Φ_2 from the third expansion:

$$\begin{aligned}
\Theta_1 &= \Phi_1 C_{11} + \Phi_2 C_{21} + \Phi_3 C_{31} + \cdots \\
\Theta_2' = \Theta_1 d_{12} + \Theta_2 d_{22} &= 0 + \Phi_2 C'_{22} + \Phi_3 C'_{32} + \cdots \\
\Theta_3' = \Theta_1 d_{13} + \Theta_2 d_{23} + \Theta_3 d_{33} &= 0 + 0 + \Phi_3 C'_{33} + \cdots
\end{aligned} \tag{46}$$

as before, one can then directly prove that the three functions

$$\begin{aligned} \Theta_1 &= \mathbb{O}\,\Phi_1 , \\ \Theta_2' &= \mathbb{O}\left(\Phi_1 d_{12} + \Phi_2 d_{22}\right), \\ \Theta_3' &= \mathbb{O}\left(\Phi_1 d_{13} + \Phi_2 d_{23} + \Phi_3 d_{33}\right), \end{aligned} \tag{47}$$

are mutually orthogonal.

The case of a general degeneracy of order g is treated analogously by means of a Gaussian elimination procedure which can be carried out straightforwardly. The successive orthogonalization can hence be performed in a way which becomes exceedingly simple because of the general properties of the projections.

Let us finally consider the normalization integrals. By means of the "turn-over rule" and (20), we obtain

$$\begin{aligned} \int |\Theta_1|^2 (dx) &= C_{11} , \\ \int |\Theta_2'|^2 (dx) &= C_{22}' d_{22}^* , \\ \int |\Theta_3'|^2 (dx) &= C_{33}' d_{33}^* , \end{aligned} \tag{48}$$

as is seen from the following typical example:

$$\int |\Theta_3'|^2 (dx) = \int |\mathbb{O}(\Phi_1 d_{13} + \Phi_2 d_{23} + \Phi_3 d_{33})|^2 (dx)$$

$$= \int (\Phi_1 d_{13} + \Phi_2 d_{23} + \Phi_3 d_{33})^* (\Phi_3 c'_{33} + \Phi_4 c'_{43} + \cdots)(dx)$$

$$= C_{33} d^*_{33} .$$

The orthonormalization required is hereby concluded. It should be observed that the functions Θ_ν are above taken in a definite order and, in the examples, we will show that there is a close connection between this approach and the conventional "seniority" idea.

VI. PARTIAL CONSTRUCTION OF THE PROJECTION OPERATOR MATRIX.

In the previous section, we have assumed that the complete matrix representation $\mathbb{C}$ of the projection operator $\mathbb{O}$ with respect to the basis $\Phi_1, \Phi_2, \ldots \Phi_p$ is available, at least in principle. This matrix is definitely of essential theoretical interest, but, from the practical point of view of constructing wave functions, it is hardly worthwhile to evaluate the entire matrix. The simplest way of getting the complete matrix for $\mathbb{O}$ is probably by repeated matrix multiplication according to (17) or (23), starting out from the complete matrix for $\mathbb{M}^2$. However, if the latter is explicitly known,

one can directly get all the eigenfunctions simply by solving the linear equation system corresponding to the eigenvalue problem, and the projection operators would then no longer be needed - except for theoretical considerations.

However, it should be observed that, in constructing the wave functions by means of the projection operator $\mathcal{O}$, the entire matrix $\mathcal{C}$ is by no means needed and that it is sufficient to know a rectangular submatrix of order $p \times q$, provided that the q column vectors contained are linearly independent. This means a considerable simplification of the problem. In a practical application, one starts out by taking the projections of the basis functions $\Phi_1, \Phi_2, \Phi_3, \cdots$ successively in order combined with the elimination procedure (46) and, unless there are accidental linear dependencies early in the projected system, the whole process is concluded after projecting q functions, where q is the order of the degeneracy usually derivable in advance by simple combinatorial arguments. Adjusting the normalization constants by means of (48), we obtain a convenient orthonormal subset of pure angular momentum wave functions describing the degenerate state.

Finally a few words should be said about the matrix elements of the energy, provided that $\mathcal{M}^2$ commutes with the Hamiltonian $\mathcal{H}_{op}$. Introducing the notation

$$\mathcal{H}_{\mu\nu} = \int \Phi_\mu^* \mathcal{H}_{op} \Phi_\nu (dx) \qquad (50)$$

and using the expansion (39), we obtain

$$\int \Theta_\alpha^* \mathcal{H}_{op} \Theta_\beta (dx) = \sum_{\mu\nu} c^\dagger_{\alpha\mu} \mathcal{H}_{\mu\nu} c_{\nu\beta} , \qquad (51)$$

which is a fairly complicated double sum. Using the "turn-over rule" and (20), we get instead

$$\int \Theta_\alpha^* \mathcal{H}_{op} \Theta_\beta (dx) = \int \Phi_\alpha^* \mathcal{H}_{op} \Theta_\beta (dx) =$$

$$= \sum_\nu \mathcal{H}_{\alpha\nu} c_{\nu\beta} , \qquad (52)$$

a single sum which is more easily evaluated, particularly since only a rectangular submatrix of order $p \times q$ of $\mathcal{H}_{\mu\nu}$ is now needed.

The non-diagonal matrix elements in (52) are usually fairly large, since the sum in the right-hand member contains the quantity $\mathcal{H}_{\alpha\alpha} c_{\alpha\beta}$. If one goes over to the orthonormal subset $\Theta_1, \Theta'_2, \Theta'_3, \ldots$, the corresponding non-diagonal elements will come out considerably smaller, even if they are not always small enough to render good or approximately good extra quantum numbers. All the basis functions $\Phi_1, \Phi_2, \Phi_3, \ldots$ are assumed to be eigenfunctions to M_z associated with the quantum number m, and, if they are built up from Hartree products or Slater determinants of one-particle functions with the individual quantum numbers $m(i)$, they must differ in at least two of these numbers, since $\sum_i m(i) = m$. This means that,

if $\mu \neq \nu$, the one-particle operators in the Hamiltonian do not contribute to $\mathcal{H}_{\mu\nu}$, which depends only on the two-particle operators or higher interactions in $\mathcal{H}_{op}$. Simplifying the non-diagonal elements of $\mathcal{H}_{op}$ with respect to the set $\Theta_1, \Theta_2', \Theta_3', \ldots$ by means of the "turn-over rule" and (20), we obtain

$$\int \Theta_1^* \mathcal{H}_{op} \Theta_2' (dx) = \int \Phi_1^* \mathcal{H}_{op} (\Phi_2 C_{22}' + \Phi_3 C_{32}' + \cdots)(dx)$$

$$= \mathcal{H}_{12} C_{22}' + \mathcal{H}_{13} C_{32}' + \mathcal{H}_{14} C_{42}' + \cdots .$$

The construction is such that one will never get a diagonal element $\mathcal{H}_{\alpha\alpha}$ in the expansion in the right-hand member, which prevents the non-diagonal elements from becoming large.

VII. A SPIN EXAMPLE.

In order to give some illustrations of the projection operator formalism, we will in conclusion give some very simple examples. Let us start by considering the total spin of a four-electron system with $S_z = 1$. Denoting the elementary spin functions by α and β , we may use a basic set consisting of the four functions:

$$\Phi_1 = \alpha\alpha\alpha\beta\,, \qquad \Phi_3 = \alpha\beta\alpha\alpha\,,$$
$$\Phi_2 = \alpha\alpha\beta\alpha\,, \qquad \Phi_4 = \beta\alpha\alpha\alpha\,, \tag{54}$$

where the implicit spin coordinates in order are ξ_1, ξ_2, ξ_3, and ξ_4. According to the addition theorem, one has $S = 2$ and $S = 1$, and straightforward application of formula (32) gives then

$$\mathbb{O}_{11}\,\alpha\alpha\alpha\beta = \frac{3}{4}\left\{\alpha\alpha\alpha\beta - \frac{1}{3}(\alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)\right\}, \tag{55}$$

$$\mathbb{O}_{21}\,\alpha\alpha\alpha\beta = \frac{1}{4}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)\,. \tag{56}$$

The complete matrices of $\mathbb{O}_{11}$ and $\mathbb{O}_{21}$ have hence the form

$$\mathbb{O}_{11} = \frac{1}{4}\times\begin{pmatrix} 3 & -1 & -1 & -1 \\ -1 & 3 & -1 & -1 \\ -1 & -1 & 3 & -1 \\ -1 & -1 & -1 & 3 \end{pmatrix}; \quad \mathbb{O}_{21} = \frac{1}{4}\times\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{pmatrix} \tag{57}$$

We note that $\mathbb{O}_{11} + \mathbb{O}_{21} \equiv \mathbb{1}$, giving the "resolution of the identity" for this simple case. The case $S = 2$ is non-degenerate $(g = 1)$ and is characterized by a uniquely determined function. The case $S = 1$ is triply degenerate $(g = 3)$, and, by successive elimination, we obtain the orthogonal subset

$$\begin{array}{lcccccc} & & \Phi_1 & \Phi_2 & \Phi_3 & \Phi_4 & \\ \hline \textcircled{H}_1 & = & \frac{3}{4} & -\frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} & \\ \textcircled{H}'_2 = \textcircled{H}_1 \cdot \frac{1}{2} + \textcircled{H}_2 \cdot \frac{3}{2} & = & 0 & 1 & -\frac{1}{2} & -\frac{1}{2} & (58) \\ \textcircled{H}'_3 = \textcircled{H}_1 + \textcircled{H}_2 + \textcircled{H}_3 \cdot 2 & = & 0 & 0 & 1 & -1 & \end{array}$$

The last function is of particular interest, since it may be written in the form

$$\textcircled{H}'_3 = \Phi_3 - \Phi_4 = \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha = \tag{59}$$
$$= (\alpha\beta - \beta\alpha)\alpha\alpha = (S=0)\times(S=1) .$$

It is hence the product of a pair singlet function and a pair triplet function and has the seniority $\nu = 2$, whereas $\textcircled{H}''_1$ and $\textcircled{H}''_2$ both have the seniority $\nu = 4$.

Since the spin projection operator commutes with the antisymmetrization operator, the formalism is directly generalizable to Slater determinants and has proven particularly valuable in studying the problem of the separation of space and spin [6]. Further details will be given elsewhere.

VIII. AN ORBITAL ANGULAR MOMENTUM EXAMPLE.

The atomic state wave functions for the configurations p^n and d^n have been treated in detail by the projection operator formalism in another paper[8], and here we will give only a single typical example of a degenerate case, namely the ^2D state of the configuration d^3. Denoting the orbital angular momentum by $\mathbf{L}$, we will study the principal case $L_z = L = 2$ by means of a basis consisting of the six Slater determinants:

$$\begin{aligned} \Phi_1 &= (2\,1\,|\,\bar{1}) \,, & \Phi_4 &= (1\,0\,|\,1) \,, \\ \Phi_2 &= (2\,0\,|\,0) \,, & \Phi_5 &= (2\,\bar{2}\,|\,2) \,, \\ \Phi_3 &= (2\,\bar{1}\,|\,1) \,, & \Phi_6 &= (1\,\bar{1}\,|\,2) \,. \end{aligned} \tag{60}$$

which span the subspace under consideration. We note that the notation $(2\,1\,|\,\bar{1})$ is an abbreviation for the Slater determinant

$$(2\,1\,|\,\bar{1}) \equiv (nd\,2\alpha \,,\, nd\,1\alpha \,,\, nd\,\bar{1}\beta) \,, \tag{61}$$

where each one-electron function is characterized by four quantum numbers $(n\,l\,m_l\,m_s)$.

By straightforward application of the expansion (31) applied to the different basic functions Φ_ν, we obtain the complete matrix representation:

$$\mathbb{O}_{22} = \frac{1}{42} \times \begin{pmatrix} 15 & -15 & 9 & 3\sqrt{6} & -3 & -6 \\ -15 & 15 & -9 & -3\sqrt{6} & 3 & 6 \\ 9 & -9 & 11 & -\sqrt{6} & -13 & 2 \\ 3\sqrt{6} & -3\sqrt{6} & -\sqrt{6} & 12 & 5\sqrt{6} & -4\sqrt{6} \\ -3 & 3 & -13 & 5\sqrt{6} & 23 & -10 \\ -6 & 6 & 2 & -4\sqrt{6} & -10 & 8 \end{pmatrix} \qquad (62)$$

The ^2D state of d^3 is doubly degenerate, and the idempotent matrix (62) has hence two eigenvalues equal to 1 and four eigenvalues equal to zero. In carrying out the elimination procedure (43), we note that $\mathbb{O}\Phi_2$ is proportional to $\mathbb{O}\Phi_1$ and that the projection of Φ_2 thus should be omitted. As basic subset, we will instead choose the following functions

$$\begin{matrix} & \Phi_1 & \Phi_2 & \Phi_3 & \Phi_4 & \Phi_5 & \Phi_6 \end{matrix}$$

$$\mathbb{O}_{22}\Phi_6 = \frac{1}{42} \times \begin{pmatrix} -6 & 6 & 2 & -4\sqrt{6} & -10 & 8 \end{pmatrix} \qquad (63)$$

$$\mathbb{O}_{22}(3\Phi_6 + 4\Phi_1) = 1 \times \begin{pmatrix} 1 & -1 & 1 & 0 & -1 & 0 \end{pmatrix}$$

where Φ_6 has been eliminated in the second function. In order to find out whether there is a connection with the seniority approach, we note that, for the configuration d^2, there is a ^1S function of the form

$$\{(0|0) + (2|\bar{2}) + (\bar{2}|2) - (1|\bar{1}) - (\bar{1}|1)\}/5, \qquad (64)$$

which may be obtained from $(2|\bar{2})$ by the operator $\mathbb{O}_{00}$. Starting out from the function $(2|$ corresponding to the ^2D state of a one-electron system, we can then construct a ^2D function with the seniority $\nu = 1$, namely:

$$^2D(d^1) \times {}^1S(d^2) = \tag{65}$$

$$= \{(20|0) + (2\bar{2}|2) - (21|\bar{1}) - (2\bar{1}|1)\}/5 ,$$

where the "product" in the left-hand member has a symbolic character. Except for the factor $-\frac{1}{5}$, this expression is identical with the second function in (63).

This example is typical for the connection with the seniority approach in treating the configuration d^n, which has been investigated in detail in its entirety. In the elimination procedure (46), the basic functions may always be chosen in such an order that the subset gives also the functions of lower seniority. We note that, with decreasing seniority, the number of projected determinants is increasing, and the functions of lowest seniority are hence the most complicated mathematically. The simplest way of getting their energy is probably to express them as sums of projected determinants and to simplify the integrals by means of the "turn-over rule" and (20). Particularly cumbersome are the valence bond functions in quantum chemistry, which are singlet spin functions of seniority zero[6], and the non-orthogonality problem connected with these functions is not yet fully solved.

The projection operator method for deriving wave functions has so far given several useful applications, and it is hoped that this approach in the future will contribute also to our theoretical understanding of the basic physical quantity called angular momentum.