# Angular Momentum Wavefunctions Constructed by Projector Operators

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## 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 wavefunctions in this approach represents a rather complicated problem. In combining two angular momenta, $\mathbf{M}_1$ and $\mathbf{M}_2$, the wavefunctions associated with the operator $\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2$ are obtained from the wavefunctions belonging to $\mathbf{M}_1$ and $\mathbf{M}_2$, respectively, by means of the vector-coupling formulas containing the so-called Clebsch–Gordan 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.

The wavefunctions belonging to a total angular momentum $\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2+\mathbf{M}_3+\cdots$ could now, in principle, be obtained from the wavefunctions 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 $\mathbf{M}_1$ and $\mathbf{M}_2$ to a resultant $\mathbf{M}_{12}$ and couple this to $\mathbf{M}_3$, or one may couple $\mathbf{M}_1$ to the resultant $\mathbf{M}_{23}$ of combining $\mathbf{M}_2$ and $\mathbf{M}_3$. One obtains in this way two different sets of wavefunctions to $\mathbf{M}$, which are, of course, connected by a unitary transformation, the elements of which are essentially the famous Racah coefficients.[3] The coupling of four angular momenta becomes still more complicated.

The vector-coupling formalism is basically a synthetic method for constructing wavefunctions of pure angular momentum for a composite system. In contrast to this approach we describe here 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. Such a treatment of the system as a collective without subgroups of components coupled in a perhaps artificial arrangement is 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 $\mathbf{M}$ 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] The basic idea is that the component of the symmetry type desired should be obtained from the original wavefunction by means of an operator $O$ which annihilates all other components but lets the selected term survive the operation in an unchanged form; such a projection operator may 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 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 wavefunction 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] 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 wavefunctions of the total angular momentum $\mathbf{M}$ of a composite system. The associated projection

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[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, New Jersey, 1957) or M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc. New York, 1957).

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

[3] G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 637 (1943).

[4] P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

[5] P.-O. Löwdin, Advan. Phys. **5**, 1 (1956), particularly Sec. 3, 1.

[6] A preliminary report of some results has 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 Moleculaires," 1957.

[7] P.-O. Löwdin, "Generalizations of the Hartree–Fock Scheme," Technical Note from the Quantum Chemistry Group of Uppsala University; Ann. Acad. Reg. Sci. Upsalien. **2** (1958).

operators are studied in some detail both as products and in expanded form. The basic theory is presented with a few illustrative 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 wavefunctions for the configurations $p^n$ and $d^n$ have already been derived.[8] Further applications on the atomic configuration $f^n$ 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

A brief review of such basic properties of angular momentum as are of importance in constructing the projection operators follows essentially the ideas developed by Dirac,[9] but avoids the explicit introduction of matrices.

A general angular momentum $\mathbf{M}=(M_x, M_y, M_z)$ measured in units of $\hbar$ is defined by the commutation relation $\mathbf{M}\times\mathbf{M}=i\mathbf{M}$ or

$$M_xM_y-M_yM_x=iM_z \quad \text{(cyclic)}. \tag{1}$$

Fixing attention on $M_z$, in place of the two other components, we introduce the auxiliary operators

$$M_\pm=M_x\pm iM_y, \tag{2}$$

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

$$M^2=M_x^2+M_y^2+M_z^2 \tag{3}$$

$$=M_-M_++M_z^2+M_z \tag{4}$$

$$=M_+M_-+M_z^2-M_z. \tag{5}$$

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

$$M_zM_\pm=M_\pm(M_z\pm 1), \tag{6}$$

and $M_-$ and $M_+$ have therefore been called step-up and step-down operators, respectively, with respect to $M_z$. Using (6), we obtain

$$M_z\{M_+Y(M', M_z')\}=M_+(M_z+1)\,Y(M', M_z')$$

$$=(M_z'+1)\{M_+Y(M', M_z')\}, \tag{7}$$

showing that $M_+$ transforms the eigenfunction associated with the pair $(M', M_z')$ into an eigenfunction associated with the pair $(M', M_z'+1)$. Assuming that the function $Y(M', M_z')$ is properly *normalized* and using (4), we obtain the normalization integral for the new function

$$\int |M_+Y(M', M_z')|^2\,(dx)$$

$$=\int Y^*(M', M_z')M_-M_+Y(M', M_z')\,(dx) \tag{8}$$

$$=(M')^2-(M_z')^2-M_z'.$$

A corresponding theorem holds for $M_-$.

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

$$(M')^2-(M_z')^2-M_z'\geq 0,$$

$$(M')^2-(M_z')^2+M_z'\geq 0, \tag{8'}$$

showing the existence of a largest and a smallest eigenvalue of $M_z$, which will be denoted by $m_>$ and $m_<$, respectively.

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

$$(M')^2-m_>^2-m_>=0,$$

$$(M')^2-m_<^2+m_<=0, \tag{9}$$

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,

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[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).

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

and hence we have

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

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

$$M'=[k(k+1)]^{\frac{1}{2}}. \tag{11}$$

If the value of $k$ is fixed, the possible values of $M_z'$ are thus

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

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

In the following, instead of the eigenvalues $(M', M_z')$, we use the quantum numbers $(k, m)$ as index in the eigenfunctions which henceforth is denoted by $Y(k, m)$. Equation (8) may be written

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

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

$$M_{\pm}Y(k,m)=[(k\mp m)(k\pm m+1)]^{\frac{1}{2}}Y(k,m\pm 1). \tag{14}$$

The normalization condition actually leaves 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* implicitly contained in (14).

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

## III. DEFINITION OF PROJECTION OPERATORS

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

$$Y=\sum_k\sum_m C_{km}Y_{km}, \tag{15}$$

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

$$\{M^2-k(k+1)\}Y_{k,m}\equiv 0, \qquad \{M_z-m\}Y_{k,m}\equiv 0, \tag{16}$$

which means that the eigenfunction $Y_{k,m}$ is *annihilated* by the operator $\{M^2-k(k+1)\}$ or the operator $\{M_z-m\}$. It is hence possible to get out a specific component $C_{km}Y_{k,m}$ in (15) by annihilating all other components. This is actually accomplished by means of the two operators $O_k(M^2)$ and $O_m(M_z)$ defined by the products

$$O_k(M^2)=\prod_{l\neq k}\frac{M^2-l(l+1)}{k(k+1)-l(l+1)}, \tag{17}$$

$$O_m(M_z)=\prod_{\mu\neq m}\frac{M_z-\mu}{m-\mu}. \tag{18}$$

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 $C_{km}Y_{km}$. By using Eqs. (16)–(18), we obtain

$$O_k(M^2)\,O_m(M_z)\,Y=C_{km}Y_{km}, \tag{19}$$

giving the uniquely defined component of $Y$ having a pure angular momentum with the quantum numbers $k$ and $m$.

One can visualize the expansion problem (15) by thinking about a Hilbert space spanned by the mutually orthogonal unit vectors $Y_{k,m}$, in which it is required to resolve an arbitrary vector $Y$ into component vectors along the axes; see Fig. 1. Geometrically this is done by an orthogonal projection, and the operators $O$ in the left-hand side of (19) are therefore called *projection operators*. A repeated use of $O$ would not change the result, which leads to the relation

$$O^2=O, \tag{20}$$

which is characteristic for the projection operators.[10] We note that this relation is also of essential importance

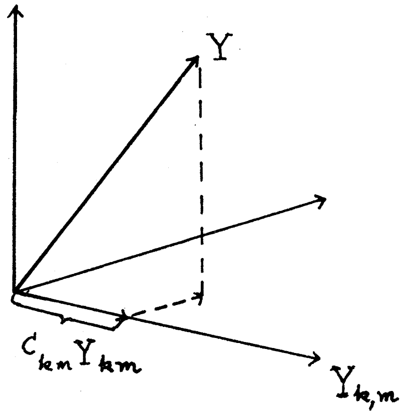

FIG. 1.

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

in simplifying the calculations of the energy and its matrix elements.[11]

By means of the addition theorem, it is usually possible to calculate which eigenvalues $(k, m)$ may occur in the system, and the product (17) can then be restricted to contain only a finite number of factors. However, even the infinite product is convergent, which is easily seen by writing (17) in the form

$$O_k(M^2)=\prod_{l\neq k}\left\{1-\frac{M^2-k(k+1)}{(l-k)(l+k+1)}\right\}. \qquad (21)$$

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

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

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 of $M_z$, there is comparatively little use of the operator $O_m(M_z)$ except in an actual component analysis. In the following, we therefore assume that, from the beginning, the given function $Y$ is an eigenfunction of $M_z$ with the specific quantum number $m$. For simplicity, we 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 $k$ values range now from $k=m$ to a certain $k=k_{\max}$ evaluated from the addition theorem, and, since only the corresponding factors have to be included in the product (17), we obtain after replacing $l$ by $l+m$, that

$$O_k(M^2)=\prod_{l=0,n}^{(l\neq k-m)}\frac{M^2-(l+m)(l+m+1)}{k(k+1)-(l+m)(l+m+1)}, \qquad (23)$$

where $n=k_{\max}-m$. Since this operator is actually supposed to operate only on functions $Y$, which are eigenfunctions of $M_z$ associated with the eigenvalue $m$, we may write (23) in the form

$$O_{km}=\prod_{l=0,n}^{(l\neq k-m)}\frac{M^2-(M_z+l)(M_z+l+1)}{(k-m-l)(k+m+l+1)}, \qquad (24)$$

i.e., we have replaced $m$ by $M_z$ in the numerator but have left the denominator unchanged.

In the applications, the product forms (17) and (23) are 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 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

$$F_l\equiv M^2-(M_z+l)(M_z+l+1). \qquad (25)$$

Using (4), we obtain the special relation $F_0=M_-M_+$. By means of (6), we can further derive the more general commutation relations

$$\begin{aligned} f(M_z)M_+&=M_+f(M_z+1),\\ f(M_z)M_-&=M_-f(M_z-1), \end{aligned} \qquad (26)$$

for any polynomial function $f$ of $M_z$. Starting from $M_-M_+=F_0$ and using (26), we then obtain successively

$$\begin{aligned} &M_-M_+=F_0,\\ &M_-^2M_+^2=M_-F_0M_+=M_-M_+F_1=F_0F_1,\\ &M_-^3M_+^3=M_-(F_0F_1)M_+=M_-M_+F_1F_2=F_0F_1F_2, \qquad (27)\\ &\cdots\\ &M_-^qM_+^q=M_-(F_0F_1F_2\cdots F_{q-2})M_+\\ &\qquad=M_-M_+(F_1F_2F_3\cdots F_{q-1})\\ &\qquad=F_0F_1F_2F_3\cdots F_{q-1}. \end{aligned}$$

We can now expand the projection operators by means of the last formula.

Let us first consider the *principal case* $m=k$. This case 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

$$\begin{aligned} O_{kk}&=\prod_{l=1}^{n}\frac{M^2-(M_z+l)(M_z+l+1)}{(-l)(2k+l+1)}\\ &=\prod_{l=1}^{n}(-1)\frac{F_l}{l\cdot(2k+l+1)}\\ &=(-1)^n(2k+1)!\frac{F_1F_2F_3\cdots F_n}{n!(2k+n+1)!}, \end{aligned} \qquad (28)$$

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

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

$$F_p=F_0-p(2M_z+p+1), \tag{29}$$

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

$$\begin{aligned} F_1F_2F_3\cdots F_n &= F_1F_2F_3\cdots F_{n-1}F_0-F_1F_2\cdots F_{n-1}\cdot n(2M_z+n+1) \\ &= M_-^nM_+^n-n(2M_z+n+1)F_1F_2\cdots F_{n-1} \\ &= M_-^nM_+^n-n(2M_z+n+1)M_-^{n-1}M_+^{n-1} \\ &\quad +n(n-1)(2M_z+n+1)(2M_z+n)M_-^{n-2}M_+^{n-2}-+\cdots. \end{aligned} \tag{30}$$

For the projection operator (28), we obtain

$$\begin{aligned} O_{kk} &= (2k+1)!\left\{(-1)^n\frac{M_-^nM_+^n}{n!(2k+n+1)!}+(-1)^{n-1}\frac{M_-^{n-1}M_+^{n-1}}{(n-1)!(2k+n)!}+\cdots\right\} \\ &= (2k+1)!\sum_{\nu=0}^{k_{\max}-k}(-1)^\nu\frac{M_-^\nu M_+^\nu}{\nu!(2k+\nu+1)!} \end{aligned} \tag{31}$$

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

$$\begin{aligned} O_{km} &= \prod_{l=0,n}^{(l\neq k-m)}\frac{M^2-(M_z+l)(M_z+l+1)}{(k-m-l)(k+m+l+1)} \\ &= \prod_{l=0,n}^{(l\neq k-m)}\frac{F_l}{(k-m-l)(k+m+l+1)} \\ &= (k+m)!\frac{F_0F_1F_2\cdots F_{k-m-1}}{(k-m)!(2k)!}(-1)^{n-k+m}(2k+1)!\frac{F_{k-m+1}F_{k-m+2}\cdots F_n}{(n-k+m)!(n+k+m+1)!} \\ &= (2k+1)\frac{(k+m)!}{(k-m)!}M_-^{k-m}M_+^{k-m}(-1)^p\frac{F_{k-m+1}F_{k-m+2}\cdots F_{k-m+p}}{p!(2k+p+1)!} \\ &= (2k+1)\frac{(k+m)!}{(k-m)!}M_-^{k-m}\left\{(-1)^p\frac{F_1F_2\cdots F_p}{p!(2k+p+1)!}\right\}M_+^{k-m} \\ &= (2k+1)\frac{(k+m)!}{(k-m)!}M_-^{k-m}\left\{\sum_{\nu=0}^{p}(-1)^\nu\frac{M_-^\nu M_+^\nu}{\nu!(2k+\nu+1)!}\right\}M_+^{k-m} \\ &= (2k+1)\frac{(k+m)!}{(k-m)!}\sum_{\nu=0}^{k_{\max}-k}(-1)^\nu\frac{M_-^{k-m+\nu}M_+^{k-m+\nu}}{\nu!(2k+\nu+1)!}. \end{aligned} \tag{32}$$

The application of the operator expansion (32) to a given function $Y$ is a straightforward procedure, since the action of the operators $M_-$ and $M_+$ 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 $\{O_{km}Y\}$, the final expression is conveniently checked by investigating whether it is annihilated by the operator $[M^2-k(k+1)]$. By means of (4), the checking relation may also be written in the form

$$[M_-M_+-(k-m)(k+m+1)]\{O_kY\}=0. \tag{33}$$

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. In the principal case $m=k$, a still simpler check is provided by the relation

$$M_+\{O_{kk}Y\}\equiv 0, \tag{34}$$

which is also of theoretical value.

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

$$M_+=\sum_i M_+(i), \qquad M_-=\sum_i M_-(i), \tag{35}$$

and the operators $M_+{}^\nu$ and $M_-{}^\nu$ 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 return to this problem in the following section.

In the special case when $\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2$, 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 wavefunction which corresponds to the ordinary vector-coupling formula. More details about the connection with the conventional theory are given in a forthcoming paper; see the Discussion.

## V. COMPLETE MATRIX REPRESENTATION OF THE PROJECTION OPERATORS

In order to study the theoretical properties of the projection operators $O$ in greater detail, we now introduce an orthonormal set of basic functions $\phi_1$, $\phi_2$, $\phi_3, \cdots, \phi_p$ all having $M_z=m$, which is complete enough to span the part of Hilbert space under consideration. In particular, we will assume that the subspace is closed under the operations $M_x$, $M_y$, and $M_z$. This implies that, if one of these operations is applied to a basic function, the result may always be expressed as a linear superposition of the functions in the basic set. 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 basic functions are possible. The matrix elements of the projection operator $O$ with respect to this basis are given by the relation

$$c_{\mu\nu}=\int\phi_\mu{}^*O\phi_\nu(dx), \tag{36}$$

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

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

It follows further that the matrix $\mathbf{c}$ 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 case $g=1$, this is called a nondegenerate projection problem; otherwise a degenerate one.

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

$$\mathbf{c}_\nu=\begin{pmatrix} c_{1\nu}\\ c_{2\nu}\\ c_{3\nu}\\ c_{4\nu}\\ \cdot\\ \cdot\\ \cdot\\ c_{p\nu}\end{pmatrix}, \tag{38}$$

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

Let us now consider the projected functions $\Theta_1$, $\Theta_2$, $\Theta_3, \cdots, \Theta_p$ which are defined by

$$\Theta_\nu=O\phi_\nu=\sum_\mu\phi_\mu c_{\mu\nu}. \tag{39}$$

This relation implies that the vectors $\mathbf{c}_1, \mathbf{c}_2, \cdots$ are nothing but discrete representations of the functions $\Theta_1, \Theta_2, \cdots$ in a system with the basis $\phi_\mu$. 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

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

i.e., the overlap matrix $\boldsymbol{\Delta}$ is identical with the matrix $\mathbf{c}$. This means that the overlap matrix has $g$ eigenvalues equal to 1 and $(p-g)$ equal to zero. Between the functions $\Theta_\nu$, there are hence $(p-g)$ linear relations, whereas $g$ of them are linearly independent.

A fundamental problem is now the construction of an orthonormal subset of order $g$ from the functions $\Theta_1, \Theta_2, \cdots, \Theta_p$. The solution is unique except for a unitary transformation, but the special choice is not exceedingly important if the subset is 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 first leave the question of approximate good quantum numbers aside and concentrate on the orthogonalization procedure. In constructing the subset of order $g$, we could either try to treat all the functions $\Theta_1, \Theta_2, \Theta_3, \cdots, \Theta_p$ in an equivalent way, or we could, orthogonalize them successively in order by means of the Schmidt process.[12] It should be observed 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 $\Theta_1$ and $\Theta_2$, defined by

$$\begin{aligned}\Theta_1&=O\phi_1=\phi_1c_{11}+\phi_2c_{21}+\phi_3c_{31}+\cdots,\\ \Theta_2&=O\phi_2=\phi_1c_{12}+\phi_2c_{22}+\phi_3c_{31}+\cdots,\end{aligned}\tag{42}$$

may be assumed to be linearly independent.[13] It is then possible to find two multipliers, $d_{12}$ and $d_{22}$, so that $\phi_1$ can be eliminated from the second expansion:

$$\begin{aligned}\Theta_1&=\phi_1c_{11}+\phi_2c_{21}+\phi_3c_{31}+\cdots,\\ \Theta_2'&=\Theta_1d_{12}+\Theta_2d_{22}=0+\phi_2c_{21}'+\phi_3c_{31}'+\cdots.\end{aligned}\tag{43}$$

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 $\Theta_2'$ must be orthogonal to $\Theta_1$, since we have

$$\begin{aligned}\int\Theta_1{}^*\Theta_2'(dx)&=\int(O\phi_1)^*O(\phi_1d_{12}+\phi_2d_{22})(dx)\\ &=\int\phi_1{}^*(\phi_2c_{21}'+\phi_3c_{31}'+\cdots)(dx)=0.\end{aligned}\tag{44}$$

The orthogonality is here accomplished simply be eliminating $\phi_1$ from the expansion of $\Theta_2'$.

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

$$\begin{aligned}\Theta_1&=O\phi_1=\phi_1c_{11}+\phi_2c_{21}+\phi_3c_{31}+\cdots,\\ \Theta_2&=O\phi_2=\phi_1c_{12}+\phi_2c_{21}+\phi_3c_{31}+\cdots,\\ \Theta_3&=O\phi_3=\phi_1c_{13}+\phi_2c_{23}+\phi_3c_{33}+\cdots,\end{aligned}\tag{45}$$

we can, by introducing convenient multipliers, eliminate $\phi_1$ from the second expansion and $\phi_1$ and $\phi_2$ from the third expansion:

$$\begin{aligned}\Theta_1&= &&\phi_1c_{11}+\phi_2c_{21}+\phi_3c_{31}+\cdots\\ \Theta_2'&=\Theta_1d_{12}+\Theta_2d_{22}= &&0+\phi_2c_{22}'+\phi_3c_{32}'+\cdots\\ \Theta_3'&=\Theta_1d_{13}+\Theta_2d_{23}+\Theta_3d_{33}= &&0+0+\phi_3c_{33}'+\cdots\end{aligned}\tag{46}$$

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

$$\begin{aligned}\Theta_1&=O\phi_1,\\ \Theta_2&=O(\phi_1d_{12}+\phi_2d_{22}),\\ \Theta_3&=O(\phi_1d_{13}+\phi_2d_{23}+\phi_3d_{33})\end{aligned}\tag{47}$$

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:

$$\begin{aligned}\int|\Theta_3'|^2(dx)&=\int|O(\phi_1d_{13}+\phi_2d_{23}+\phi_3d_{33})|^2(dx)\\ &=\int(\phi_1d_{13}+\phi_2d_{23}+\phi_3d_{33})^*\\ &\qquad\times(\phi_3c_{33}'+\phi_4c_{43}'+\cdots)(dx)\\ &=c_{33}'d_{33}{}^*.\end{aligned}\tag{49}$$

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

[13] If $\Theta_2$ happens to be proportional to $\Theta_1$, we will instead consider $\Theta_3, \Theta_4, \cdots$ etc. until we find a function which is not proportional to $\Theta_1$; this must be the case, since otherwise $g=1$.

The orthonormalization required is hereby concluded. It should be observed that the functions $\Theta_\nu$ 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 $\mathbf{c}$ of the projection operator $O$ with respect to the basis $\phi_1, \phi_2, \cdots, \phi_p$ is available, at least in principle. This matrix is definitely of essential theoretical interest, but, from the practical point of view of constructing wavefunctions, it is hardly worthwhile to evaluate the entire matrix. The simplest way of getting the complete matrix for $O$ is probably by repeated matrix multiplication according to (17) or (23), starting out from the complete matrix for $M^2$. If the latter is explicitly known, one can get all the eigenfunctions directly 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.

In constructing the wave functions by means of the projection operator $O$, the entire matrix $\mathbf{c}$ is not needed. It is sufficient to know a rectangular submatrix of order $p\times g$, provided that the $g$ 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 $g$ functions, where $g$ 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 wavefunctions describing the degenerate state.

The matrix elements of the energy, provided that $M^2$ commutes with the Hamiltonian $H_{\text{op}}$, are

$$\mathcal{H}_{\mu\nu}=\int\phi_\mu{}^*\mathcal{H}_{\text{op}}\phi_\nu(dx), \tag{50}$$

and using the expansion (39) we obtain

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

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

$$\int\Theta_\alpha{}^*\mathcal{H}_{\text{op}}\Theta_\beta(dx)=\int\phi_\alpha{}^*\mathcal{H}_{\text{op}}\Theta_\beta(dx)=\sum_\nu\mathcal{H}_{\alpha\nu}c_{\nu\beta}, \tag{52}$$

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

The nondiagonal matrix elements in (52) are usually fairly large, since the sum in the right-hand member contains the quantity $H_{\alpha\alpha}C_{\alpha\beta}$. If one goes over to the orthonormal subset $\Theta_1, \Theta_2', \Theta_3', \cdots$, the corresponding nondiagonal 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 $\phi_1, \phi_2, \phi_3, \cdots$ 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 $H_{\mu\nu}$, which depends only on the two-particle operators or higher interactions in $H_{\text{op}}$. Simplifying the nondiagonal elements of $H_{\text{op}}$ with respect to the set $\Theta_1, \Theta_2', \Theta_3', \cdots$ by means of the "turn-over rule" and (20), we obtain

$$\int\Theta_1{}^*\mathcal{H}_{\text{op}}\Theta_2'(dx)=\int\phi_1{}^*\mathcal{H}_{\text{op}}(\phi_2c_{22}'+\phi_3c_{32}'+\cdots)(dx)$$

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

The construction is such that one never gets a diagonal element $H_{\alpha\alpha}$ in the expansion in the right-hand member, which prevents the nondiagonal elements from becoming large.

## VII. A SPIN EXAMPLE

In order to give some illustrations of the projection operator formalism, we 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 $\alpha$ and $\beta$, 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 $\zeta_1$, $\zeta_2$, $\zeta_3$, and $\zeta_4$. According to the addition theorem, one has $S=2$ and $S=1$, and straightforward application of formula (32) gives then

$$O_{11}\alpha\alpha\alpha\beta=\tfrac{3}{4}\{\alpha\alpha\alpha\beta-\tfrac{1}{3}(\alpha\alpha\beta\alpha+\alpha\beta\alpha\alpha+\beta\alpha\alpha\alpha)\}, \tag{55}$$

$$O_{21}\alpha\alpha\alpha\beta=\tfrac{1}{4}(\alpha\alpha\alpha\beta+\alpha\alpha\beta\alpha+\alpha\beta\alpha\alpha+\beta\alpha\alpha\alpha). \tag{56}$$

The complete matrices of $O_{11}$ and $O_{21}$ have hence the form

$$O_{11}=\tfrac{1}{4}\times\begin{pmatrix} 3 & -1 & -1 & -1 \\ -1 & 3 & -1 & -1 \\ -1 & -1 & 3 & -1 \\ -1 & -1 & -1 & 3 \end{pmatrix};$$

$$O_{21}=\tfrac{1}{4}\times\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{pmatrix}. \tag{57}$$

We note that $O_{11}+O_{21}\equiv 1$, giving the "resolution of the identity" for this simple case. The case $S=2$ is nondegenerate ($g=1$) 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

$$\begin{array}{lcccc} & \phi_1 & \phi_2 & \phi_3 & \phi_4 \\ \hline \Theta_1= & \frac{3}{4} & -\frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} \\ \Theta_2'=\Theta_1\cdot\frac{1}{2}+\Theta_2\cdot\frac{3}{2}= & 0 & 1 & -\frac{1}{2} & -\frac{1}{2} \\ \Theta_3'=\Theta_1+\Theta_2+\Theta_3\cdot 2= & 0 & 0 & 1 & -1. \end{array} \tag{58}$$

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

$$\Theta_3'=\phi_3-\phi_4=\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha$$
$$=(\alpha\beta-\beta\alpha)\alpha\alpha=(S=0)\times(S=1). \tag{59}$$

It is hence the product of a pair singlet function and a pair triplet function and has the seniority $v=2$, whereas $\Theta_1'$ and $\Theta_2'$ both have the seniority $v=4$.

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 wavefunctions 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 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:

$$\begin{aligned} &\phi_1=(21\,|\,\bar{1}), &&\phi_2=(20\,|\,0), \\ &\phi_3=(2\bar{1}\,|\,1), &&\phi_4=(10\,|\,1), \\ &\phi_5=(2\bar{2}\,|\,2), &&\phi_6=(1\bar{1}\,|\,2), \end{aligned} \tag{60}$$

which span the subspace under consideration. The notation $(21\,|\,\bar{1})$ is an abbreviation for the Slater determinant

$$(21\,|\,\bar{1})\equiv(nd2\alpha,\ nd1\alpha,\ nd\bar{1}\beta), \tag{61}$$

where each one-electron function is characterized by four quantum numbers ($nlm_lm_s$).

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

$$O_{22}=\tfrac{1}{42}\times\begin{pmatrix} 15 & -15 & 9 & 3\sqrt{6} & -3 & -6 \\ -15 & 15 & -9 & -3\sqrt{6} & 3 & 6 \\ 9 & -9 & 11 & -\sqrt{6} & -13 & 2 \\ 3\sqrt{6} & -3\sqrt{6} & -\sqrt{6} & 12 & 5\sqrt{6} & -4\sqrt{6} \\ -3 & 3 & -13 & 5\sqrt{6} & 23 & -10 \\ -6 & 6 & 2 & -4\sqrt{6} & -10 & 8 \end{pmatrix}. \tag{62}$$

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 $O\phi_2$ is proportional to $O\phi_1$ and that the projection of $\phi_2$ thus should be omitted. As basic subset, we will instead choose the following functions

$$\begin{array}{rcccccc}
 & \phi_1 & \phi_2 & \phi_3 & \phi_4 & \phi_5 & \phi_6 \\
\hline
O_{22}\phi_6= & \frac{1}{42}\times(-6 & 6 & 2 & -4\sqrt{6} & -10 & 8) \\
O_{22}(3\phi_6+4\phi_1)= & 1\times(\ \ 1 & -1 & 1 & 0 & -1 & 0),
\end{array} \qquad (63)$$

where $\phi_6$ has been eliminated in the second function. In order to find 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

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

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

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

$$=\{(20\mid 0)+(2\bar{2}\mid 2)-(21\mid \bar{1})-(2\bar{1}\mid 1)\}/5, \qquad (65)$$

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. With decreasing seniority, the number of projected determinants increases, 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 nonorthogonality problem connected with these functions is not yet fully solved.

The projection operator method for deriving wavefunctions 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.

## IX. DISCUSSION: FURTHER DEVELOPMENTS

Since the results in this paper were first preliminarily reported in our technical note No. 12 in 1958, there has been a considerable development along this line of approach. The general theory of normal constants of motion in quantum mechanics and their projection operators have been discussed by the author.[14] The theory is here based on the use of the concept of "scalar product," but it has later been realized that this concept is unnecessary and that all the fundamental theorems are characteristic for a theory based solely on linear algebra. These generalizations are discussed in a forthcoming paper. A series of powerful theorems seems to be common to both quantum theory and group algebra, and it is essentially these theorems which provide the simple treatment of angular momenta for many-particle systems discussed here.

The connection between the successive and symmetric treatment of angular momenta has been studied. The Clebsch–Gordan coefficients have been derived by means of projection operator technique.[15] For the case of the spin, the connection between the product projection operators and the Young tableaux projection operators has been treated by McIntosh.[16] The spin projection operators and the associated spin eigenfunctions have further been considered by Percus and Rotenberg[17] and by Pauncz.[18] A study of the Racah coefficients by means of the projection operator technique is now also under way.

The atomic wavefunctions of pure angular momentum for the configurations $p^n$ and $d^n$ have been studied in some detail.[19] The atomic configurations $d^n$ have been treated by Abate[20] and by Rotenberg,[21] and the corresponding eigenfunctions have here been evaluated by means of electronic computers. Applications to nuclear structure have been carried out by Calasis[22] and to diatomic molecules by Cooley.[23]

The use of the "component analysis" of a given trial function by means of the projection operator tech-

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nique is of particular importance in connection with the correlation problem in many-body quantum theory. In the conventional Hartree–Fock procedure, one usually assumes that the basic Slater determinant shall have the symmetry of the system without realizing that this condition is really a constraint on the variational procedure.[24] This leads to a symmetry dilemma in the Hartree–Fock scheme. If the symmetry constraint is removed, the total energy of the system will go down, but at the same time the basic Slater determinant $D$ will become a mixture between various symmetry types. Since these symmetry types do not interact with respect to the Hamiltonian, one of the symmetry components will necessarily have a lower energy than the original determinant, and this symmetry component can now be selected by means of a proper projection operator.[14] The corresponding wavefunction $\Psi = OD$ will have the correct symmetry and a lower energy than the original Slater determinant, but it is clear that a still further lowering can be obtained by another optimization of the one-particle functions involved. This leads to the so-called "extended" Hartree–Fock scheme.[25,26]

This approach contains the method for treating correlation effects by using "different orbitals for different spins" as a special case. The treatment of a spin-projected Slater determinant is a comparatively complicated problem which is greatly simplified by the existence of the so-called "pairing theorem".[26] The spin-mixture contained in a single Slater determinant has been analyzed by Ohno and Sasaki.[27] The first-order density matrix, the natural-spin orbitals and their occupation numbers as well as the spin density for a spin-projected Slater determinant has been obtained by Harriman.[28]

Energy calculations according to this approach have been carried out by means of the so-called alternant molecular orbital method, and particularly the results obtained for conjugated systems and the infinite linear chain are very encouraging.[29] In the investigations by Pauncz and de Heer, remarkably good results have been obtained not only for ground state but also for the excited states of various spin multiplicity.[30]

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