SPATIAL EIGENFUNCTIONS OF THE SPIN-INDEPENDENT MANY-ELECTRON HAMILTONIAN

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SPATIAL EIGENFUNCTIONS OF THE SPIN-INDEPENDENT MANY-ELECTRON HAMILTONIAN (*)

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Résumé. — Les propriétés de symétrie des fonctions propres spatiales de l'hamiltonien à plusieurs électrons indépendant du spin sont étudiées, leurs valeurs propres et leurs dégénérescences sont discutées de même que les valeurs propres des fonctions d'ondes physiques correspondantes. Des exemples détaillés sont donnés principalement pour le problème à trois électrons de même que certaines propriétés de la structure des niveaux pour une configuration donnée ; on donne aussi le classement de ces niveaux et on généralise au problème à n électrons. On discute l'emploi de procédés de calcul de perturbations non symétriques pour obtenir les fonctions propres spatiales, et on considère les applications possibles de tels procédés.

Abstract. — The symmetry properties of the spatial eigenfunctions of the spin-independent many-electron Hamiltonian are examined and their eigenvalues and degeneracies are discussed along with eigenvalues of the corresponding physical wave functions. Detailed examples are given, mostly for the three-electron problem, with certain properties of the level structure of a given configuration and the ordering of such levels generalized to the many-electron problem. The use of non-symmetric perturbation theoretic procedures for calculating the spatial eigenfunctions is discussed and the potential utility of such procedures is considered.

I. **Introduction.** — The spin-independent Hamiltonian, H, for an arbitrary many-electron system has a spectrum of eigenvalues whose corresponding eigenfunctions are solutions to the equation

$$(H - E_i)\, \Phi_i(r) = 0 \qquad (1)$$

and are functions only of the spatial coordinates of the N-electrons, denoted symbolically by r. Because of the fact that electrons are indistinguishable, the Hamiltonian H is symmetric under all permutations of particle indices, and hence the eigenfunctions $\Phi_i(r)$ can be classified according to their transformation properties under the operations of the symmetric group, S_N. Thus, each eigenfunction can be associated to one of the irreductible representations, α, of S_N. If α is multi-dimensional, a transformation can be carried out among the corresponding multiply-degenerate set of eigenfunctions so that each eigenfunction can be associated with an individual row, λ, of the matrix for the irreducible representation, α, in any appropriate basis.

The set of functions $\Psi_i(r, \sigma)$ of the space and spin coordinates of the N-electrons (the latter denoted symbolically by σ) which are eigenfunctions of H, satisfying the Schrödinger equation

$$(H - E_i)\, \Psi_i(r, \sigma) = 0 \qquad (2)$$

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and which are antisymmetric under all permutations of particle indices are, according to the Pauli principle, all the « *allowed* » wave functions of the physical many-electron system. It is clear that the $\Psi_i(r, \sigma)$ must be constructed from linear combinations of products of degenerate $\Phi_i(r)$'s with functions of the spin-variables of the N-electrons. The explicit form of the wave function, $\Psi_i^{[\alpha]}(r, \sigma)$, which is denoted by two indices, i and α, indicating the i'th state belonging to the α'th representation, is given by [1]

$$\Psi_{i,m}^{[\alpha]} = \sum_{\lambda} \Phi_i^{[\alpha,\lambda]}(r)\, \chi_m^{[\tilde{\alpha},\lambda]}(\sigma) \qquad (3)$$

where the $\chi_m^{[\tilde{\alpha},\lambda]}$ are the unique functions of the spins of the N-electrons of total z-component m which transform like the conjugate row λ of the conjugate irreducible representation $\tilde{\alpha}$. This use of the conjugate irreducible representation for the spin function assures antisymmetry of the $\Psi_i^{[\alpha]}$ since, for example, if $\Phi_i^{[\alpha,\lambda]}$ is symmetric under the permutation P_{12}, the conjugate $\chi_m^{[\tilde{\alpha},\lambda]}$ will be antisymmetric under P_{12}. The wave function $\Psi_{i,m}^{[\alpha]}$ is an eigenfunction of total spin, S^2, since the operator S^2 is symmetric under all permutations of particle indices, and hence for a given α all the $\chi_m^{[\tilde{\alpha},\lambda]}(\sigma)$ have the same eigenvalue of total spin.

Despite the facts that the decomposition (3) was derived by Wigner in the early days of quantum mechanics and the theory of the symmetric group was

developed at the turn of the century, only with the recent work of Matsen [2] and the present author [3] has interest been focused on the spatial functions $\Phi_i^{[\alpha,\lambda]}$ themselves with the recognition that for spin-independent problems any one of the spatial functions gives the same information as the wave function $\Psi_{i,m}^{[\alpha]}$ itself. The history of the neglect of the spatial eigenfunctions — or even the extent of the knowledge of their behavior that not was reflected in the literature — is not at all trivial. It appears, however, that the immediate acceptance of the Slater determinant which enabled many-electron systems to be treated without group theory obviated the need for considering the spatial eigenfunctions themselves and led to a general lack of awareness of their properties. In fact the few authors who have explicitly considered the applications of the symmetric group to atomic and molecular systems have restricted themselves to procedures for constructing total wave functions, rather than recognizing the sufficiency for their purposes of one of the spatial functions. Thus Kotani's discussion [4] of the group theoretic treatment of Yamanouchi is used to describe wave functions ; Goddard's orbital procedures [5] for atomic and molecular calculations using various Young operators, which is more general than the Hartree-Fock procedure, always obtains wave functions ; and the methods of Pauncz [6], Harris [7] and others for evaluating matrix elements are always concerned with determinantal wave functions ; and none of these deals with the spatial parts alone even though necessarily identical results would be obtained. One cannot help but suspect — see for example the intricate studies of Arai [8] — that the sufficient nature of one of the spatial eigenfunctions was not altogether clear to these authors. Goscinski and Löwdin [9] have recently attempted to analyze the historical use of group theory in this construction of wave functions. Among the few scattered references using spatial functions alone are those of Delbrück [10], Wigner and Seitz [11], and Fock [12], all of which dealt with a single Young tableau [3*c*], and the recent studies of Kaplan [13], although it is claimed that Kotani discussed the spatial eigenfunctions at the Shelter Island meeting of 1951.

The present article is devoted to a study of the spatial eigenfunctions, Φ_i, and should serve to introduce the reader to the role played by symmetry in the ordering and in the degeneracies of the eigenvalues, E_i. Hopefully such a discussion will enable the recognition of the potential importance of procedures [2, 3] dealing directly with the spatial functions $\Phi_i(r)$ rather than with the total wave functions $\Psi_i(r, \sigma)$, as well as the difficulties involved in their utilization. This discussion, of necessity, considers all the $\Phi_i(r)$ without regard, in the first instance, to the physics, which constructs wave functions according to (3) and hence excludes certain $\Phi_i(r)$'s as being « *non-physical* » if they give only null wave functions $\Psi_i(r, \sigma)$. These « *non-physical* »eigenfunctions appear never to have been considered explicitly in the literature, and, of course, are of little interest except that they are to be carefully avoided when « *physical* » wave functions are being calculated.

The present article reviews the presumably well-known symmetry properties of the spatial eigenfunctions of H and, by presenting several simple examples and some interpretation, attempts to serve the pedagogic purpose of broadening the understanding of these functions and their behavior. Although much of the argument is based on properties of the permutation group, only the minimal and directly relevant aspects of the mathematical theory of groups are included here, the reader being referred to the many texts [14] on the subject for the justification of the various claims as needed.

In the next section a somewhat intuitive statement is presented of the symmetry properties and degeneracies of the eigenfunctions of an N-particle operator. Some details are given in Section III for the three-electron problem in order to illustrate the collection of eigenfunctions into configurations and the ordering of the eigenvalues within each configuration. Also in this Section is discussed the generalization to larger systems and the results of two new calculations of eigenvalues for « *non-physical* » spatial Φ_i's are indicated. The validity of perturbation theoretic procedures based on non-symmetric zeroth-order Φ_i's is discussed in Section IV along with some examples indicating their potential utility.

II. **Symmetry Properties.** — Since H is a operator symmetric in all the particle indices, i. e.

$$[H, \mathrm{P}] = 0 \qquad \mathrm{P} \in \mathrm{S}_N \tag{4}$$

where P is a permutation of the particle indices, it is easy to see that the eigenfunction Φ_i must possess certain symmetry properties. For example, it is possible to divide up the solutions into those which are symmetric under the transposition P_{12} and those which are antisymmetric under P_{12}. Similarly it is possible to specify simultaneously the symmetry under all the transpositions $\mathrm{P}_{n,n+1}$(n odd) since

$$[\mathrm{P}_{nm}, \mathrm{P}_{kl}] = 0 \qquad n, m \neq k, l \tag{5a}$$

but, since all transpositions do not, in fact, commute, i. e.

$$[\mathrm{P}_{nm}, \mathrm{P}_{nk}] \neq 0 \qquad m \neq k \tag{5b}$$

it is not possible, in general, to specify *simultaneously* the symmetry under all transpositions, no less under all permutations, P which can always be written as products of the P_{nm}. There are, however, two special classes of solutions for which all transpositions, *in effect*, commute. These are solutions which are either symmetric or antisymmetric under all P_{nm}, i. e. they satisfy

$$\mathrm{P}_{nm}\, \Phi_i = \pm\, \Phi_i \qquad \text{all } n, m$$

so that on such a Φ_i,

$$[P_{nm}, P_{nk}]\,\Phi_i = 0 \qquad \text{all } n, m, k\,.$$

Of course, the symmetry of the solutions can be simultaneously specified under *any* set of commuting operations, but the problem is that it is not at all obvious how to choose the maximal set of commuting operations, and it is at this point that one must have recourse to group theory. Notice that the choice of commuting operations is not unique — as, for example, it could include P_{12} or P_{13} but not both — which requires the existence of degenerate sets of eigenfunctions of H, since it must be possible to take linear combinations of eigenfunctions possessing symmetry under P_{12} to transform them into eigenfunctions possessing symmetry under P_{13} without changing the eigenvalues.

The group theoretic analysis of the permutation group — and the present discussion follows the analysis of Young — determines an arbitrary but well-defined *complete* set of commuting operations according to whose eigenvalues the functions $\Phi_i(r)$ can be classified. This analysis leads to the following two relatively simple statements :

1. Eigenfunctions of H can be classified as to the representation to which they belong. The number of representations for an N-electron system can be determined graphically as the number of Young diagrams, or the number of ways that N boxes can be lined up into rows and columns so that the number of boxes in any column decreases from left to right and the number of boxes in any row decreases from top to bottom. Eigenfunctions belonging to different representations are, in general, non-degenerate since there is no operation which is a function of the P's and hence commutes with H that can transform an eigenfunction belonging to one representation into an eigenfunction belonging to another.

2. Any function which is associated with a representation that has a Young diagram with other than a single column or a single row is one member of a set of degenerate eigenfunctions of H. The number of linearly independent degenerate solutions can be determined graphically being the number of ways the indices 1, 2, ..., N can be placed in the Young diagram such that their magnitude always increases from left to right and from top to bottom. Each way of fitting the particle indices into the Young diagrams is called a Young tableau and with each Young tableau is associated certain transformation properties. The phase « *transform according to a certain Young tableau* » can be expressed colloquially as « *possessing certain symmetries* ».

The representation to which a function is associated is denoted here by α and the tableau denoted by $[\alpha, \lambda]$, and of the several prescriptions for defining Young tableaux the one employed here is the « *orthogonal* » representation (see. e. g. Ref. 14*d* pp. 92). The set of Young tableaux can be defined by the set of projections, $D^{[\alpha]}_{\lambda\lambda}$ which are linear combinations of the N linearly independent permutations P, such that if $\Phi_i^{[\beta,\mu]}$ indicates a function transforming as $[\beta, \mu]$, the relation

$$D^{[\alpha]}_{\lambda\lambda}\,\Phi_i^{[\beta,\mu]} = \delta_{\alpha\beta}\,\delta_{\lambda\mu}\,\Phi_i^{[\alpha,\lambda]} \tag{6a}$$

holds. Thus $D^{[\alpha]}_{\lambda\lambda}$ projects an arbitrary function φ into a function transforming as $[\alpha, \lambda]$ or into zero if it has no component of $[\alpha, \lambda]$. The explicit form of these projections is usually obtained by a constructive technique [14, 6] building on the projections for the group S_{N-1}, although in certain few special cases general rules for obtaining these projections can be obtained. The particular notation used here has been introduced for simplicity and should not introduce any confusion when compared with the more standard notation. In particular it is convenient to use a single symbol α to signify the Young diagram usually indicated explicitly by a sequence of numbers also in square brackets, and also to use a symbol λ to denote the Young tableau which is usually not indicated explicitly. The spatial eigenfunctions $\Phi_i^{[\alpha,\lambda]}$ are thus denoted by their complete set of commuting « *observables* » and in ket notation would be given by $|\alpha\lambda i>$ where i refers to the i'th function of symmetry $[\alpha, \lambda]$.

Two degenerate eigenfunctions of H belonging to different tableaux, but *a fortiori*, to the same representation, are related by the « *off-diagonal* » operations $D^{[\alpha]}_{\lambda\mu}$ as

$$\Phi_i^{[\alpha,\lambda]} = D^{[\alpha]}_{\lambda\mu}\,\Phi_i^{[\alpha,\mu]}\,. \tag{6b}$$

In addition, the $D^{[\alpha]}_{\lambda\mu}$'s satisfy the following relations

$$D^{[\alpha]}_{\lambda\mu}\,D^{[\beta]}_{\kappa\nu} = \delta_{\alpha\beta}\,\delta_{\mu\kappa}\,D^{[\alpha]}_{\lambda\nu} \tag{7a}$$

and

$$D^{[\alpha]\dagger}_{\mu\nu} = D^{[\alpha]}_{\nu\mu}\,. \tag{7b}$$

The total number of D's, all of which are clearly linearly independent, is given by $\sum_\alpha f_\alpha^2$ with f_α the dimensionality of representation α, and this, in fact, equals N ! The set of D's provides, therefore, a set of operations in one-to-one correspondence with the set of permutations P, and thus spans the permutation space. The desired *complete* set of commuting operations, with which to classify the eigenfunctions of H, are the $D^{[\alpha]}_{\lambda\lambda}$, the ambiguity among the degenerate eigenfunctions belonging to the same representation being removed by the explicit choice of the λ's. There are thus no functions which have the same eigenvalues of H and the $D^{[\alpha]}_{\lambda\lambda}$ other than due to accidental degeneracies.

The relations (6) and (7) permit the wave functions of (3) to be written as

$$\Psi^{[\alpha]}_{i,m}(r,\sigma) = \sum_{\lambda} D^{[\alpha]}_{\lambda\mu} D^{[\alpha]}_{\lambda\mu} \Phi^{[\alpha,\mu]}_{i}(r)\, \chi^{[\tilde{\alpha},\mu]}_{m}(\sigma) \qquad (8)$$

in terms of a single spatial eigenfunction $\Phi^{[\alpha,\mu]}_{i}(r)$ for any μ and the spin function $\chi^{[\tilde{\alpha},\mu]}_{m}$ transforming as the conjugate tableau $[\tilde{\alpha}, \mu]$. Similarly, the expectation value of any symmetric spin-independent operator A is given by

$$\frac{<\Psi^{[\alpha]} \mid A \mid \Psi^{[\alpha]}>}{<\Psi^{[\alpha]} \mid \Psi^{[\alpha]}>} = \frac{<\Phi^{[\alpha,\mu]} \mid A \mid \Phi^{[\alpha,\mu]}>}{<\Phi^{[\alpha,\mu]} \mid \Phi^{[\alpha,\mu]}>} \qquad (9)$$

for any μ, dropping the subscripts m and i for simplicity. Thus it can be said that any of the $\Phi^{[\alpha,\mu]}$ provides all the information necessary for the specification of the physical state. Since a given Ψ_i is a linear combination of a set of $\Phi^{[\alpha,\mu]}_{i}\, \chi^{[\tilde{\alpha},\mu]}$ it will sometimes be easier to deal with one of the components $\Phi^{[\alpha,\mu]}_{i}$ directly [3] rather than with the composite $\Psi^{[\alpha]}_{i}$ itself, as will be discussed below.

Notice that the analog of the operations $D^{[\alpha]}_{\lambda\mu}$ for the eigenfunctions of a spherically symmetric Hamiltonian are easily derived in terms of the operations L^2, $L_{\pm}$ and L_z. The representations α correspond to the rotational quantum number L, and the degenerate tableaux $[\alpha, \lambda]$ to the specification of L and the azimuthal quantum number M where the dimensionality of α is $2L + 1$. For example, within the manifold of $L = 1$, the unnormalized operations would be

$$\begin{aligned} D^{[1]}_{11} &= (L_z + 1) L_z \\ D^{[1]}_{00} &= (L_z + 1)(L_z - 1) \\ D^{[1]}_{1,-1} &= L_z(L_z - 1) \end{aligned} \qquad (10)$$

and

$$\begin{aligned} D^{[1]}_{0,-1} &= L_+ L_z \\ D^{[1]}_{10} &= L_+(L_z + 1) \\ D^{[1]}_{1,-1} &= L^2_+ \end{aligned}$$

and similarly for $D^{[1]}_{MM'}$ with $M < M'$. The projector onto the $L = 1$ manifold is

$$0_{L=1} = \prod_{\substack{L'=0 \\ L' \neq 1}}^{\infty} [L^2_{0p} - L'(L' + 1)] \qquad (11)$$

and should be placed to the right of the operations $D^{[1]}_{\lambda\lambda}$ as defined above when the space of all functions (all L) is allowed. While the usual procedure would classify states as to their eigenvalue of L_z — analogous to classifying the eigenfunctions above as to their symmetry under the various P's — this type of projection operator procedure classifies states according to the single operator $D^{[\alpha]}_{\lambda\lambda}$ for which they have a non-zero eigenvalue. The two procedures are to be sure equivalent, but it is sometimes more convenient to consider the operations which will project a set of states rather than the matrices of physical operators, e. g. L_x, L_y and L_z using those states as a basis.

It is important to note that whereas most group theoretical discussions of the properties of the group S_N are concerned with the representation matrixes $\Gamma(P)$ for each permutation P — analogous to the matrices of L_x, L_y and L_z in the rotational symmetry case — the emphasis of the present discussion is on the symmetries of the basis functions, the Young tableaux, in terms of which these representations are defined. Recognition of the symmetry properties of the Young tableaux for a given representation is of great importance since it is these symmetries which serve « *to lift the permutation degeneracy* » of the eigenfunctions of H in an arbitrary but well-defined way. This permits the complete classification of all Φ_i according to their eigenvalues of the complete set of commuting operators H and $D^{[\alpha]}_{\lambda\lambda}$ (neglecting spatial degeneracies) which is after all precisely what group theory is intended to do.

In the orthogonal representation functions associated with a given Young tableau possess simple symmetry properties under a certain limited number of transpositions $P_{n,n+1}$: whenever the consecutive indices n, $n + 1$ are located in contiguous boxes in the tableau $[\alpha, \lambda]$, the function is either symmetric or antisymmetric under $P_{n,n+1}$, being symmetric when the indices are in the same row and antisymmetric when they are in the same column. Because the definition of the Young tableaux specifies that the numbers increase from left to right and from top to bottom, all the solutions $\Phi^{[\alpha,\lambda]}_{i}$ are described in terms of their symmetry or antisymmetry under P_{12} and only a few of them in terms of their symmetry under P_{13}. It is because of the arbitrariness of this description as mentioned above that such solutions must be degenerate and that they be related to each other by the transformation matrices $D^{[\alpha]}_{\lambda\mu}$. It is clear, for instance, that by taking linear combinations of the degenerate

$$\Phi^{[\alpha,\lambda]}_{i}$$

for fixed i and α transforming as the set of Young tableaux $[\alpha, \lambda]$ one must be able to construct a set of functions which are symmetric under the operation P_{13} instead of P_{12}, as would be obtained by applying P_{23} to the set $\Phi^{[\alpha,\lambda]}_{i}$. Thus one has the representation matrices $\Gamma(P)$ for every element P, of the group, such that, e. g.

$$P_{23}\, \Phi^{[\alpha,\lambda]}_{i} = \sum_{\mu} \Gamma^{[\alpha]}_{\lambda\mu}(P_{23})\, \Phi^{[\alpha,\mu]}_{i}. \qquad (12)$$

Similarly, it is clear that one can construct a set of functions which are all simultaneous eigenfunctions under any set of commuting transpositions such as $P_{n,n+1}$ (n odd) yet these are not the symmetries specified by the Young tableaux orthogonal representation. The Young tableaux thus choose certain symmetries under which a *complete* decomposition of the space can be obtained using the simple graphical

technique, but linear combinations of functions, which transform as the various tableaux, can be found to give any other set of symmetry properties as desired.

Consider now for purposes of illustration the group theoretic behaviour of systems of 2,3 and 4 electrons, whose Young diagrams are given in figure 1 and whose corresponding Young tableaux are given in figure 2.

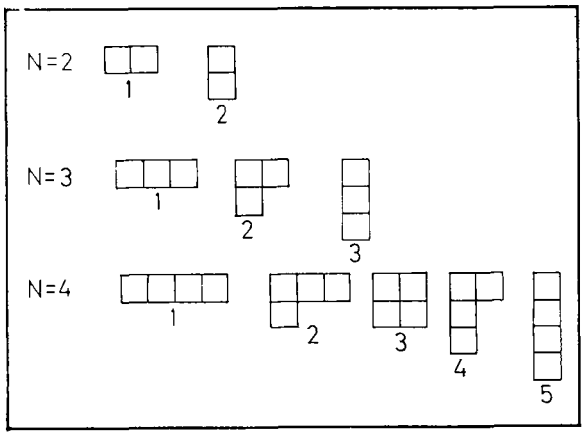

FIG. 1. — The Young diagrams for $N = 2$, 3 and 4.

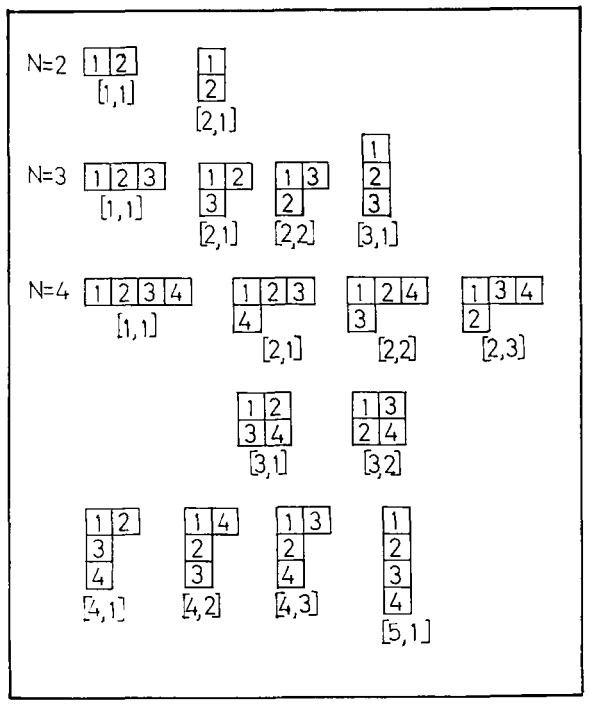

FIG. 2. — The Young tableaux for $N = 2$, 3 and 4.

For $N = 2$ all the eigenfunctions of H can be classified as being either symmetric (the set of functions being denoted as $\Phi_i^{[1,1]}$) or antisymmetric (the set of functions being denoted as $\Phi_i^{[2,1]}$) under P_{12} there being no commuting operators available to specify the system other than P_{12} and H. The single permutation P_{12} therefore corresponds to the operators L^2 and L_z in the rotational symmetry case according to which all eigenfunctions of H can be classified. The projection operators associated with the two tableaux are easily seen to be

$$D_{11}^{[1]} = 2^{-1/2}(1 + P_{12}) \tag{13a}$$

$$D_{11}^{[2]} = 2^{-1/2}(1 - P_{12}) \tag{13b}$$

which clearly satisfy (6*a*). There is no way of using permutation operators to project a function belonging to the tableau [1, 1] onto a function belonging to the tableau [2, 1] for the simple reason that there is no inverse of the $D_{11}^{[\alpha]}$'s, i. e. there is no way to unsymmetrize or to un-antisymmetrize a function by using the operators of the permutation group [15]. This explains why eigenfunctions of H belonging to the symmetric representation [1] are, in general, not degenerate with eigenfunctions belonging to the antisymmetric representation. As both representations are one-dimensional there is, of course, no degeneracy other than due to spatial symmetry among functions belonging to one of these representations. The same argument as to the inability to un-symmetrize a function generalizes to larger systems and explains why there are no transformations $D_{\lambda,\mu}^{[\alpha,\beta]}$ which take a function belonging to one representation and transform it into a function belonging to a different representation. It is, of course, true that even in the special cases when functions belonging to different representations are degenerate, e. g. if $H = \sum_{i=1}^{N} h(i)$, there is no way to transform the functions from one representation to another.

Wave functions $\Psi_{i,m}^{[\alpha]}$ can be constructed according to (3) as

$$\Psi_{i,m}^{[1]}(r, \sigma) = \Phi_i^{[1,1]}(r)\, \chi_m^{[2,1]}(\sigma) \tag{14a}$$

and

$$\Psi_{i,m}^{[2]}(r, \sigma) = \Phi_i^{[2,1]}(r)\, \chi_m^{[1,1]}(\sigma) \tag{14b}$$

where the $\chi_m^{[\alpha,\lambda]}(\sigma)$ are the *unique* functions of the spin variables with $S_z = m$ which transform according to the λ'th tableau of the α' th representation, representation [2] being conjugate to representation [1]. The spin functions are the well-known eigenfunctions of S^2 and S_z,

$$\chi_0^{[2,1]} = 2^{-1/2}(\alpha\beta - \beta\alpha)$$

$$\chi_{1,0,-1}^{[1,1]} = \begin{cases} \alpha\alpha \\ 2^{-1/2}(\alpha\beta + \beta\alpha) \\ \beta\beta \end{cases} \tag{15}$$

where the particles are labelled consecutively. As spin-space is so restricted that these four functions span it completely — as distinguished from ordinary space which requires the two infinite sets $\Phi_i^{[1,1]}$ and $\Phi_i^{[2,1]}$ to completely span it — the spin-dependence of wave functions is given simply and uniquely by the

specification o $f\alpha$ and m, or equivalently by S^2 and m since each representation for which there is a non-vanishing spin-function can be associated with a particular value of S^2. The set of solutions $\Psi_{i,0}^{[1]}$ are therefore called singlets, due to the lack of degeneracy of the spin eigenfunction in representation [2, 1], and the set of solutions $\Psi_{i,0}^{[2]}$ are called triplets due to the triple-degeneracy of the spin-eigenfunctions $\chi_m^{[1,1]}$ which leads to a triple degeneracy in the $\Psi_{i,m}^{[2]}$. The fact that both the representations [1] and [2] are one-dimensional implies that according to (3) the space and spin-variables of any eigenfunction of a spin-independent two-electron Hamiltonian are always separable, as shown explicitly in (14). The same will hold for any N for the states of « *highest multiplicity* » as the totally symmetric representation, whose Young diagram is a single row, will always be one-dimensional.

The difficulties of the general many-particle problem occur in virtually all their generality in the three particle problem, and for this reason one is justified in devoting considerable attention, in the remaining part of the present article, to this the simplest of all many-particle problems. For three electrons there is no obvious set of commuting operators, the choice of either P_{12}, P_{13} or P_{23} to go along with H being completely arbitrary yet being insufficient to completely define the solutions. This is analogous to the case of the hydrogen atom for which one can choose arbitrarily among L_x, L_y and L_z to define an axis of quantization but for which L^2 is necessary as well as H in order to provide a complete set of commuting operators to define the « *symmetry* » of the eigenfunctions. The Young tableau prescription implicitly takes P_{12} as one of the commuting operators, i. e. « *quantizes* » the system according to parity under P_{12}, although under no other single permutation, since, as can be seen from figure 2, every tableau describes a function which is either symmetric or antisymmetric under P_{12}. The choice of the remaining operators — or quantizations — is in general quite complicated, and the usual set of commuting operators does not explicitly include P_{12} but rather uses the set of projection operators $D_{\lambda\lambda}^{[\alpha]}$ which satisfy (6*a*) and which, by definition specify the symmetries of the Young tableaux. Note that one of these projections could be eliminated as being redundant in the sense that any function which all the remaining $D_{\lambda\lambda}^{[\alpha]}$ project onto zero must transform as the missing $D_{\lambda\lambda}^{[\alpha]}$. Notice also that if symmetry under P_{12} alone were taken, there would be two pairs of incompletely defined symmetries, the tableaux [1, 1] and [2, 1] being both symmetric under P_{12} and the tableaux [2, 2] and [3, 1] being both antisymmetric. The symmetry could therefore be completely defined by adding the symmetrizer $\mathcal{S}$, which is actually $D_{11}^{[1]}$, and the antisymmetriser $\mathcal{A}$, which is actually $D_{11}^{[3]}$, to P_{12} to make a complete set of commuting operations, or equivalently by adding $D_{11}^{[2]}$ and $D_{22}^{[2]}$ to P_{12}. Such, of course, is not the way one treats the problem in general, but it is useful to be aware of the various ways by which one can specify the symmetries of the $\Phi_i^{[\alpha,\lambda]}$.

The set of projections which are used to define the Young tableaux for $N = 3$, and which satisfy (6*a*) are [16]

$$D_{11}^{[1]} \equiv \mathcal{S} \tag{16a}$$

$$D_{11}^{[2]} = 3^{-1}(1 + P_{12} - \tfrac{1}{2}P_{23} - \tfrac{1}{2}P_{13} - \tfrac{1}{2}P_{132} - \tfrac{1}{2}P_{123}) \tag{16b}$$

$$D_{22}^{[2]} = 3^{-1}(1 - P_{12} + \tfrac{1}{2}P_{23} + \tfrac{1}{2}P_{13} - \tfrac{1}{2}P_{132} - \tfrac{1}{2}P_{123}) \tag{16c}$$

and

$$D_{11}^{[3]} \equiv \mathcal{A} \tag{16d}$$

although they also could have been written in terms of products of transpositions P_{nm}. The operators which transform the $\Phi_i^{[2,1]}$ to $\Phi_i^{[2,2]}$ and *vice versa*, satisfying (6*d*) are

$$D_{12}^{[2]} = (2\sqrt{3})^{-1}(P_{23} - P_{13} - P_{132} + P_{123}) \tag{17a}$$

and

$$D_{21}^{[2]} = (2\sqrt{3})^{-1}(P_{23} - P_{13} + P_{132} - P_{123}). \tag{17b}$$

Just as for the two-electron case there is no way to project a function from one representation to another using permutation operators which serves as a reminder of the tautological statement : since functions belonging to different representations are, in general, non-degenerate, there can be no operator which commutes with H that transforms an eigenfunction (or for that matter any function) belonging to one representation into an eigenfunction (or linear combination of eigenfunctions) belonging to a different representation.

The wave functions of the three-electron system can be constructed using (3) out of the degenerate pairs of eigenfunctions $\Phi_i^{[2,\lambda]}$ as

$$\Psi_{i,m}^{[2]}(r, \sigma) = \Phi_i^{[2,1]}(r)\,\chi_m^{[2,2]}(\sigma) + \Phi_i^{[2,2]}(r)\,\chi_m^{[2,1]}(\sigma) \tag{18a}$$

and out of the non-degenerate eigenfunctions $\Phi_i^{[3,1]}$ as

$$\Psi_{i,m}^{[3]}(r, \sigma) = \Phi_i^{[3,1]}(r)\,\chi_m^{[1,1]}(\sigma) \tag{18b}$$

where the $\chi_m^{[\alpha,\lambda]}(\sigma)$ are the *unique* functions of the variables transforming as the appropriate tableaux of the appropriate conjugate representation of the permutation group. Typical spin functions are

$$\chi_{3/2}^{[1,1]} = \alpha\alpha\alpha \tag{19a}$$

$$\chi_{1/2}^{[2,1]} = 6^{-1/2}(2\,\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) \tag{19b}$$

and

$$\chi_{1/2}^{[2,2]} = 2^{-1/2}(\alpha\beta - \beta\alpha)\,\alpha\,. \tag{19c}$$

Since the $\chi_m^{[1,1]}$ and $\chi_m^{[2,\lambda]}$ are each quadruply-degenerate and doubly-degenerate respectively, the wave functions $\Psi_{i,m}^{[2]}$ are called doublets and the $\Psi_{i,m}^{[3]}$ are called quartets, where once again the multiplicity is equivalently given by $2S + 1$ where S is the eigenvalue associated with the particular representation. Because of the fact that spin-space for spin $-\frac{1}{2}$ particles is only two-dimensional, there is no spin function that transforms according to representation [3], as it would have to be anti-symmetric in three particle indices which is clearly not possible. For this reason the functions $\chi_m^{[3,1]}(\sigma)$ are non-existent, or can be said to vanish identically, and hence the entire set of spatial functions $\Phi_i^{[1,1]}(r)$ can never be used to construct wave functions. Notice also that the two degenerate solutions $\Phi_i^{[2,1]}$ and $\Phi_i^{[2,2]}$ are *both* required in the construction of the single wave function $\Psi_{i,m}^{[2]}$ so that even though there are degenerate pairs of spatial eigenfunctions of H there are no degenerate wave functions of given value of m.

The argument for four electrons is exactly analogous to that for $N = 3$ with the doubly-degenerate $\Phi_i^{[3,1]}$ and $\Phi_i^{[3,2]}$ being used to construct a singlet wave function $\Psi_{i,m}^{[3]}$, the triply degenerate $\Phi_i^{[4,\lambda]}$ being used to construct a triplet wave function $\Psi_{i,m}^{[4]}$ — note that the designation triplet is due to the degeneracy of m, and not the degeneracy of the $\Phi_i^{[4,\lambda]}$ — and the non-degenerate $\Phi_i^{[5,1]}$ being used to construct a quintet wave function $\Psi_i^{[5]}$. There is no non-vanishing $\Psi_i^{[1]}$ or $\Psi_i^{[2]}$ since there are no spin functions transforming as the tableaux $[4, \lambda]$ and [5, 1] as they have more than two rows and therefore require antisymmetry in three or more particle indices.

This completes a simplified and rather intuitive examination of the symmetry properties of the spatial eigenfunctions and wave functions of the N-electron system. It remains to examine the functional form of the spatial eigenfunctions as will be done in the next section. While clearly these spatial eigenfunctions will be very complicated functions of the $3N$ variables, it is nevertheless possible to collect these functions into « *configurations* » according to their approximate « *orbital* » structure. This serves the very important purpose of introducing some order, albeit in an approximate manner, into what would otherwise be a hopeless jumble of uncorrelated eigenfunctions and eigenvalues.

III. The $\Phi_i(r)$ and their Eigenvalues. — A. THE THREE-ELECTRON PROBLEM. — In order to appreciate the detailed behaviour of the set of eigenfunctions $\Phi_i(r)$ of a many-electron Hamiltonian, it is illustrative to consider the spatial eigenfunctions of the Li atom Hamiltonian

$$H = \sum_{i=1}^{3} \left(-\frac{1}{2}\nabla_i^2 - \frac{3}{r_i} \right) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \qquad (20)$$

which are simple enough to allow presentation of some of their detailed behaviour, yet show the complexities of the general many-electron problem.

As the first step, which permits the classification of the solutions $\Phi_i(r)$ into « *configurations* », as in atomic spectroscopy, consider the solutions to the simpler Hamiltonian [17-19].

$$H_0 = \sum_{i=1}^{3} h_0(i) = \sum_{i=1}^{3} \left(-\frac{1}{2}\nabla_i^2 - \frac{3}{r_i} \right). \qquad (21)$$

This hydrogen-like Hamiltonian can be taken as the zeroth-order Hamiltonian in a perturbation theoretic scheme which writes

$$H(\lambda) = H_0 + \lambda H_1 \qquad (22)$$

and solves for the eigenfunctions as a function of λ, where H ($\lambda = 1$) equals the H of (21). The eigenfunctions of H_0 are obtained from the hydrogen-like eigenfunctions $u_k(i)$, generally called « *orbitals* », satisfying

$$[h_0(i) - e_k]\, u_k(i) = 0 \qquad (23)$$

as

$$U_{klm}(123) = u_k(1)\, u_l(2)\, u_m(3) \qquad (24)$$

with the corresponding eigenvalue

$$E_{klm} = e_k + e_l + e_m \qquad (25)$$

where the indices k, l and m can be continuous as well as discrete.

The eigenfunctions U_{klm} can be grouped into configurations according to the degeneracies of H_0 such that each configuration contains all the U_{klm}'s which have the same indices k, l and m occurring in any order and hence have the same energy $E_{klm} = E_{imk}$, etc. Thus a configuration will contain one solution if all the particles are in the same orbital, i. e. $k = l = m$, will contain three solutions if two particles are in one orbital and one in a second orbital, i. e. $k = l \neq m$, and will contain six solutions if all particles are in different orbitals, i. e. $k \neq l \neq m$. The grouping into configurations of eigenfunctions of H, itself, as distinguished from those of H_0, is of necessity dependent on the relatively arbitrary choice of any H_0 which is the sum of one-electron operators, such as that of (21), since otherwise there is no definition of orbitals. Despite the potential ambiguity involved, such descriptions have been immensely useful in atomic spectroscopy, and will play a similar role in the classification of spatial eigenfunctions of H. The configurations of spatial eigenfunctions will contain more eigenfunctions than the « *physical configurations* » of spectroscopy, since no solutions will be excluded by the Pauli principle and since degenerate spatial multiplets belonging to the same representation will appear separately rather than as combined according to (3) into a single wave function.

The grouping of eigenfunctions of H_0 into confi-

gurations rs also necessary when perturbation theoretic calculations are to be performed since one must always lift the first-order degeneracy due to H_1 by diagonalizing the first-order secular equation, before one can use a perturbation procedure. This diagonalization is, in fact, equivalent to combining the functions U_{klm} into functions which transform as one of the irreducible representations as it divides the secular determinant into blocks along the diagonal one for each non-degenerate set of solutions belonging to the appropriate representations. Within each block, i. e. among the solutions belonging to a degenerate representation, one is then able to take appropriate linear combinations to choose functions that transform as the various Young tableaux. One could also have done the reverse and chosen the linear combinations of all the degenerate wave functions which transform as the various Young tableaux and which would also reduce the secular determinant to a series of diagonal blocks that must then be diagonalized. This procedure is more generally useful and can be applied best to CI calculations in which the set of determinants can be replaced by the smaller number of linearly independent $D^{[\alpha]}_{\lambda\lambda} U_{klm}$'s within a restricted basis.

Consider the three lowest s-state orbitals, 1s, 2s, and 3s, denoted respectively as u, v and w, and three typical configurations which can be constructed using them. The lowest eigenvalue of H_0 is 3 e_u and the single eigenfunction belonging to the corresponding configuration u^3 is the non-degenerate

$$\Phi^{[1,1]}_{1,0} = u(1)\, u(2)\, u(3) \qquad (26)$$

which transforms as the totally symmetric representation [1]. The subscript zero indicates that this is a zeroth-order solution, or an eigenfunction of H_0, and not the desired exact eigenfunction of H, while the subscript 1 labels this particular eigenfunction, the first eigenfunction belonging to the tableau [1, 1]. Notice that there is only one function belonging to u^3 since there is only one function of energy 3 e_u, but also that there is no possibility that a function transforming as representations [2] or [3] belong to u^3 since there is no way to construct from the three orbitals u a non-vanishing function antisymmetric in two or more particle indices. The fact that there is only one eigenfunction in this configuration, or only one eigenvalue in the vicinity of 3 e_u implies that an *approximation* to the exact eigenfunction need possess *no* symmetry whatsoever for it to be associated with this solution, there being no other nearly-degenerate solution with which it could be confused.

The next higher eigenvalue of H_0 is $2e_u + e_v$ and is triply degenerate with the corresponding eigenfunctions

$$u(1)u(2)v(3),\ u(1)v(2)u(3) \text{ and } v(1)u(2)u(3) \qquad (27)$$

belonging to the configuration u^2 v. As there are non-vanishing « *off-diagonal matrix elements* », e. g. $\mu = \langle uuv | H_1 | uvu \rangle \neq 0$, the perturbation *partially* lifts the degeneracy, and the correct zeroth-order solutions are found by diagonalizing

$$\begin{vmatrix} E_0+\nu-W & \mu & \mu \\ \mu & E_0+\nu-W & \mu \\ \mu & \mu & E_0+\nu-W \end{vmatrix} = 0 \qquad (28)$$

where $E_0 = 2e_u + e_v$ and $\nu = \langle uuv | H_1 | uuv \rangle$. There is one non-degenerate solution

$$W^{[1]} = E_0 + \mu + 2\nu$$

which has equal coefficients for each of the U's, i. e. $C_1 = C_2 = C_3$; and there are two degenerate solutions of $W^{[2]} = E_0 + \mu - \nu$, both of which have coefficients satisfying

$$C_1 + C_2 + C_3 = 0 \qquad (29)$$

and any function satisfying this condition can be used as a zeroth-order solution in a perturbation theoretic calculation. The non-degenerate symmetric solution is therefore

$$\Phi^{[1,1]}_{2,0} = 3^{-1/2}(uuv + uvu + vuu) \qquad (30a)$$

labelling the particles in order, and the two degenerate solutions can be taken as transforming according to the $[2, \lambda]$ using (16*b*, *c*) as

$$\Phi^{[2,1]}_{1,0} = 6^{-1/2}(2\,uuv - uvu - vuu) \qquad (30b)$$

and

$$\Phi^{[2,2]}_{1,0} = 2^{-1/2}(uvu - vuu) \qquad (30c)$$

which clearly satisfy (29). Since the exchange integral μ is necessarily positive, the first-order energy eigenvalue $W^{[1]}$ of the totally symmetric solution is necessarily greater than the $W^{[2]}$ of the « *less symmetric* » or « *partially antisymmetric* » doubly-degenerate solutions. This observation, when generalized to many-electron systems below, plays an important role in determining the ordering of the eigenvalues within a given term.

It should be noted that there is no function belonging to configuration u^2v that transforms according to representation [3] it not being possible to construct a non-null function of the orbitals which is antisymmetric in all particle indices. This incidentally implies that due to the simple nature of the set of Young tableaux for $N = 3$, antisymmetry under the single transposition P_{12} and an energy in the vicinity of $2e_u + e_v$ uniquely determines a (spherically-symmetric) function to be an approximation to $\Phi^{[2,2]}$. Thus a perturbation theoretic procedure based on any such approximate function possessing only this symmetry yet *not* transforming as [2,2] will converge to $\Phi_1{}^{[2,2]}$ if it converges at all. Similarly, a CI-type calculation using functions all of which are antisymmetric under

P_{12} will give all the solutions belonging to [2,2] and [3,1]. As the representations [2] and [3] provide all the physical wave functions of the three-electron system — being doublets and quartets respectively — this will determine all the physical eigenvalues based on a secular equation of considerably reduced size than that for all the $\Phi_i(r)$.

Notice again that while all three of these Φ_0's are degenerate eigenfunctions of H_0, the perturbation H_1 serves to split them into two non-degenerate representations one of which is two-dimensional and hence doubly degenerate due to symmetry. This degeneracy, therefore, remains unlifted to all orders of perturbation theory which is why the symmetries of the individual Young tableaux are necessary in order to specify the eigenfunctions completely.

The third possible type of configuration for the three-electron problem locates each electron in a different orbital and is denoted by uvw. For the energy eigenvalue $e_u + e_v + e_w$ there are six degenerate eigenfunctions of H_0

$$\text{uvw, vwu, wuv, vuw, uwv and wvu .} \qquad (31)$$

The secular equation gives the six eigenvalues : the non-degenerate

$$W^{[1]} = e_u + e_v + e_w + Q^{[1]} \qquad (32a)$$

and

$$W^{[3]} = e_u + e_v + e_w + Q^{[3]} \qquad (32b)$$

and the two doubly-degenerate

$$W_1^{[2]} = e_u + e_v + e_w + Q_1^{[2]} \qquad (32c)$$

and

$$W_2^{[2]} = e_u + e_v + e_w + Q_2^{[2]} \qquad (32d)$$

where the representations to which the solutions belong are indicated in brackets. The energies are given schematically, and can be expressed in terms of the three distinct off-diagonal matrix elements

$$a = < \text{uvw} \mid H_1 \mid \text{uwv} >$$

$$b = < \text{uvw} \mid H_1 \mid \text{wvu} >$$

and

$$c = < \text{uvw} \mid H_1 \mid \text{vuw} > .$$

There are thus two degenerate pairs of solutions which belong to representation [2] and one solution which belongs to each of the representations [1] and [3]. These solutions can be given schematically as

$$\Phi_{3,0}^{[1,1]} = \text{Su(1) v(2) w(3)} \qquad (33a)$$

$$\Phi_{2,0}^{[2,1]} = D_{11}^{[2]}\,\text{uvw} + a_1\, D_{11}^{[2]}\,\text{uwv} \qquad (33b)$$

$$\Phi_{2,0}^{[2,2]} = D_{22}^{[2]}\,\text{uvw} + a_2\, D_{22}^{[2]}\,\text{uwv} \qquad (33c)$$

$$\Phi_{3,0}^{[2,1]} = D_{11}^{[2]}\,\text{uvw} + a_3\, D_{11}^{[2]}\,\text{uwv} \qquad (33d)$$

$$\Phi_{3,0}^{[2,2]} = D_{22}^{[2]}\,\text{uvw} + a_4\, D_{22}^{[2]}\,\text{uwv} \qquad (33e)$$

$$\Phi_{1,0}^{[3,1]} = \text{Au(1) v(2) w(3)} \qquad (33f)$$

where the numbering of the subscripts corresponds to the ordering of the energies of the solutions belonging to a given representation, and where the constants a_i are obtained from the appropriate secular equation [20]. Since in general the integrals $a, b, c > 0$ the ordering of the eigenvalues is

$$W^{[1]} > W_1^{[2]},\ W_2^{[2]} > W^{[3]}$$

and the totally symmetric solution has the highest first-order eigenvalue of the configuration. The lowest eigenvalue of the configuration corresponds to the totally antisymmetric solution, and the solutions of intermediate symmetry have intermediate values for the eigenvalues.

Notice that for the uvw, which could be called the configuration of maximally open shell, there exist solutions which transform as *each* of the four tableaux for $N = 3$ as distinguished from the configurations u^2 v and u^3 discussed above for which certain more antisymmetric representations had only null solutions. Notice also that while it is true that any linear combination of $\Phi_{2,0}^{[2,1]}$ and $\Phi_{3,0}^{[2,1]}$ would transform according to the tableau [2,1], it would not diagonalize the secular determinant. However *either* of the two pairs of functions $\Phi_i^{[2,\lambda]}$ can serve as « *basis functions* » for the orthogonal representation of the Young tableaux.

The wave functions belonging to the physical or spectroscopic configuration uvw are two doublets from $\Phi_{2,0}^{[2,\lambda]}$ and $\Phi_{3,0}^{[2,\lambda]}$ and one quartet from $\Phi_{1,0}^{[3,1]}$ with the quartet of lower energy than the doublets. Again the $\Phi_{3,0}^{[1,1]}$ cannot be used to construct a wave function.

The term levels of the approximate spatial eigenfunctions of H and of the corresponding approximate wave functions can now be summarized. In configuration u^3 there is one eigenfunction, whose eigenvalue is in the vicinity of 3 e_u, and no wave function ; in configuration u^2 v there are three eigenfunctions two of which are degenerate, and one doublet wave function, all of eigenvalue in the vicinity of $2\,e_u + e_v$; and in configuration uvw of eigenvalues in the vicinity of $e_u + e_v + e_w$ there are six eigenfunctions, two pairs of which are degenerate, and three non-degenerate wave functions, two of which are doublets and one of which is a quartet.

B. GENERALIZATION TO N-ELECTRONS. — The extension of the results just described to the N-electron problem leads to the following general statements :

(1) The eigenfunctions $\Phi_i(r)$ of the N-electron Hamiltonian can usually be collected into « *configurations* » corresponding to the « *orbital occupancy* » in the eigenfunctions of an approximate separable H_0.

(2) The number of different eigenvalues belonging to a given configuration is in general less than the

number of irreducible representations of S_N since, unless all the orbitals are « *singly occupied* », solutions belonging to certain of the « *more antisymmetric* » representations are excluded. The degeneracy of each eigenvalue remains, of course, the same as the dimensionality of the representation to which it belongs.

(3) The ordering of eigenvalues within a configuration is generally such that the totally symmetric eigenfunction, which occurs in all configurations has the highest eigenvalue, and the antisymmetric eigenfunction, when it occurs, has the lowest. The eigenvalue decreases through the configuration as the « *symmetry* » of the solution decreases, or the « *antisymmetry* » increases, where the « *symmetry* » of a representation is associated roughly with the length of the various rows or columns respectively in the corresponding Young diagrams. There are, to be sure, ambiguities in such a statement for solutions of systems of large N whose Young diagrams are neither mostly long columns or mostly long rows, but these can be resolved by merely diagonalizing the appropriate secular equation. The argument is exactly the same as Hund's rule — for a recent discussion see Matsen [2] — only applied to *all* the spatial functions $\Phi_i(r)$ within a configuration instead of being restricted to those functions out of which wave functions can be constructed.

These statements define the structure of the general configuration $a^\alpha b^\beta c^\gamma \ldots$ which is described as having α, β, γ, ... electrons respectively placed in orbitals a, b, c, ... where the orbitals are some approximate and not necessarily orthogonal functions. The explicit symmetries (and implicitly, the degeneracies) of the solutions belonging to a given configuration can be deduced, in many cases by considering the number of linearly independent functions, and the *allowed* symmetries with which they can be associated. This can be illustrated by the four-electron case, whose configurations are a^4, a^3b, a^2b^2, a^2bc and $abcd$ with 1, 4, 6, 12 and 24 linearly independent solutions respectively. Referring to the Young diagram of figure 1 and tableaux of figure 2 it is seen that the solution a^4 can only belong to representation [1], which is already symmetric ; the solutions in $a^3\,b$ can only belong to representations [1] and [2] since [3] would require simultaneous antisymmetry in two disjoint pairs of particles and [4] and [5] would require antisymmetry in three and four particles respectively, all of which are impossible ; representation [2] is triply-degenerate and thus the four $a^3\,b$ functions are divided uniquely into one set of [2] solutions and one [1] solution. The solutions in the configuration $a^2\,b^2$ can transform as [1], [2] and [3] and the six solutions are uniquely divided into one set each of (triply-degenerate) [2] and (doubly-degenerate) [3] solutions and one [1] solution. The solutions in the configuration $a^2\,bc$ can transform as any diagram except [5] and the division of the 12 functions is, in fact, anbiguous with one [1] and one pair of [3] solutions and either 2 sets of [2] solutions and one set of [4] solutions or *vice versa*. The first of these is the correct result which can be shown explicitly, or could have been guessed since the three particle antisymmetry of [4] should be constructed in fewer ways from $a^2\,bc$ functions than can the three particle symmetry of [2]. The pair of [2] solutions have to be diagonalized among themselves (if H_0 is symmetric) as indicated for the three-electron problem in Eq. (32, 33). The configuration *abcd* with 24 linearly-independent functions can be assigned symmetries — all of which are allowed — by recognizing that 24 linearly-independent linear combinations of these functions can be generated from $a(1)\,b(2)\,c(3)\,d(4)$ by projecting with the 24 linearly-independent operations $D^{[\alpha]}_{\lambda\mu}$ which span the four-particle permutation space. This gives immediately f_α linearly-independent functions transforming as each of the tableaux $[\alpha,\ \lambda]$ where f_α is the dimension of the representation α, which must be diagonalized among explicitly. Thus there is 1 function each of representation [1] and [5], 3 sets of triply-degenerate solutions for each of [2] and [5] ; and two sets of doubly-degenerate solutions [3].

This type of analysis should be useful in considering the energy levels of partially-filled d- and f-shells and mixed shells where it must be remembered that the simple configurations discussed here will be zeroth-order degenerate and must be mixed together in a super-configuration. Thus, for example, the atomic d^4 configuration would give rise to 5 a^4 « *configurations* », 20 $a^3\,b$ « *configurations* », etc., all of which are zeroth-order degenerate. The division into angular momentum eigenfunctions follows in the usual manner except that again the non-physical solutions (e. g. $L = 8$ for d^4) are also obtained. There might, however, turn out to be some advantage in the generality of dealing with all the spatial eigenfunctions simultaneously. In particular, the elegant methods developed to deal with these problems since the early work of Racah might be directly applied to the non-restricted set of all solutions within a given configuration.

Notice that the description in terms of configurations does not require that the approximate eigenfunctions of H are given explicitly in terms of these orbitals, but rather that these are in some sense a limiting case of the approximate eigenfunctions. For example a^α represents symbolically α electrons in « a-like » orbitals, a_1, a_2, ..., a_α, which might be 1s-orbitals of different screening parameters, all of which reduce to a itself when the parameters are taken as equal.

The ordering of the eigenvalues within a given configuration is of particular importance since this is what usually determines the symmetry of the solution to which a perturbation expansion will converge. The only configurations which will give rise to physical wave functions must contain solutions belonging to representations possessing only two columns, and hence are of the form $a^2b^2 \ldots n^2m \ldots yz$ with no orbital more than doubly occupied. The spatial

eigenfunctions of the lowest eigenvalue within the configuration will, by Hund's rule, be those corresponding to the wave function of highest multiplicity, i. e. whose representation has the largest possible first column with all the remaining functions including those belonging to tableaux with more than two columns being of higher eigenvalue. The representation with the largest possible first column is not usually the totally antisymmetric function since only if all the orbitals are singly occupied is there such a solution within the configuration. Thus since the spatial function of lowest symmetry or highest antisymmetry — analogous to the highest multiplicity for wave functions — has the lowest eigenvalue within a configuration, the lowest eigenvalue in

$$a^2\, b^2 \ldots z^2 ,$$

with all orbitals paired, gives the energy of a singlet wave function, the lowest eigenvalue in $a^2\, b^2 \ldots y^2\, z$ gives the energy of a doublet wave function and the lowest eigenvalue in $a^2\, b^2 \ldots x^2\, yz$ gives the energy of a triplet, etc.

The above analysis, which is a straightforward generalization of Hund's rule to all the spatial eigenfunctions, presumes that the first-order energies of an approximate orbital description give an ordering of levels which corresponds *precisely* to the ordering of exact energies. Such is, of course, not always the case and even Hund's rule for spectroscopic states is known to break down in certain instances. Nevertheless, the number of exceptions is relatively few, and as long as one is aware of the fact that the « *rule* » is not infallible, this analysis can often be used to provide a rather reliable indication of the multiplicity of non-degenerate eigenvalues and their ordering within a particular configuration of a many-electron system.

Recently Amos and Burrows have considered the set of spatial eigenfunction for the four π-electron problem of butadiene in which the many « *configurations* » are not separated in energy sufficiently to be treated separately and they are all mixed together in what is called « *complete configuration interaction* ». This calculation is instructive in that Hund's rule is not satisfied, the lowest solution being totally symmetric (of representation [1]), as is to be expected when many configurations have very similar energies so that there is strong mixing among them. (For this case the orbitals a, b, c and d are 2 p_π-orbitals on different atoms, and so e. g. the different configurations a^2bc, a^2cd, b^2cd, etc., have the same energy.)

C. Two Calculations. — The energy difference between the different physical states belonging to the same configuration are known experimentally to be relatively small. For example the difference between the energies of ^{1}S and ^{3}S He (1s2s) is 0.029 36 a. u. and the Z-expansions of these energies are [21]

$$E(^1\mathrm{S}) = -\frac{5}{8}Z^2 + \frac{169}{729}Z - 0.114\,48 + 0.009\,42\,Z^{-1} + \theta(Z^{-2})$$
$$= -2.146\,12 + \theta(Z^{-2})$$

$$E(^3\mathrm{S}) = -\frac{5}{8}Z^2 + \frac{137}{729}Z - 0.047\,41 - 0.004\,87\,Z^{-1} + \theta(Z^{-2})$$
$$= -2.173\,99 + \theta(Z^{-2})$$

as compared with the exact $-2.145\,97$ and $-2.175\,33$ respectively with the triplet of lower energy than the singlet. Analogous results have been obtained for several other configurations. For two electron systems, the state of higher multiplicity does appear to be lower in energy, following Hund's rule which assumes that the term linear in Z dominates, the « *exchange integral* » being necessarily positive. Notice, however, that the contribution in Z^0 for the singlet state is considerably larger in magnitude than that for the triplet state, and the difference between the two is actually *greater* than the difference in the total energies. This indicates immediately that one must be cautious in assuming the significance of the ordering obtained from the result linear in Z, and for some states of higher l, Hund's rule is indeed not obeyed.

For systems containing more than two electrons the spectroscopic analysis is much more complex, at least for the multiply excited states, and the situation is somewhat less clear although it appears that this regularity, or Hund's rule, is often satisfied. The eigenvalues of H corresponding to the spatial functions $\Phi_i(r)$ are, however, not only those of the physical states of particular multiplicity, but also those whose eigenfunctions cannot be used to construct wave functions. These, in effect, have lower « *multiplicity* » than the singlet state and so by extension of Hund's rule described above are expected to lie above the physical energy levels.

In order to gain some insight into the actual location of these non-physical or in some sense « *spurious* » eigenvalues, and make the first step into the serious investigation of the validity of these remarks, calculations are presented here on the totally symmetric eigenfunctions of the $1s^2\ 2s$ and $1s^2\ 2p$ terms of Li. Chisholm and Dalgarno [17], and Seung-Hui and Wilson [18] have calculated the energy of the physical wave function ^{2}S Li ($1s^2\ 2s$) denoted as $\Psi^{[2]}(1s^2\ 2s)$ in the Z-expansion through order Z^0 and Z^{-1} respectively ; and Chisholm, Dalgarno and Innes [22] have calculated the energy of ^{2}P Li ($1s^2\ 2p$) denoted as $\Psi^{[2]}(1s^2\ 2p)$ through order Z^0. The calculations for the « *energy* » of the symmetric eigenfunctions, $\Phi^{[1,1]}(1s^2\ 2s)$ and $\Phi^{[1,1]}(1s^2\ 2p)$ require precisely the same integrals involved in the calculation of the physical energies ; they merely enter with different signs and coefficients. Thus, for example, using

the M_i defined by Chisholm and Dalgarno [17], the energy of the symmetric solution is easily derived to be

$$E[\Phi^{[1,1]}(1\,s^2\,2\,s)] = \\ = 2\,e_u + e_v + [uu \mid uu] + 2[uv \mid uv] + \\ + 2[uv \mid vu] + E_2(1\,s^2) + 2\,E_2(1\,s\,2\,s\,{}^1S) \\ + 4(M_1 + M_2) + 2(M_3 + M_4 + M_5) + \theta(Z^{-1}) \tag{34}$$

with [uv |uv] and [uv |vu] the 1 s 2 s Coulomb and exchange integrals respectively. This compares with the eigenvalue of the degenerate $\Phi^{[2,\lambda]}$'s which give the physical wave function,

$$E[\Phi^{[2,\lambda]}(1\,s^2\,2\,s)] = 2\,e_u + e_v + [uu \mid uu] + 2[uv \mid uv] - \\ - [uv \mid vu] + E_2(1\,s^2) + \tfrac{1}{2}\,E_2(1\,s\,2\,s\,{}^1S) \\ + \tfrac{3}{2}\,E_2(1\,s\,2\,s\,{}^3S) + 4\,M_1 - 2\,M_2 - M_3 - M_4 \\ + \tfrac{1}{2}\,M_5 + \tfrac{3}{2}\,M_6 + \theta(Z^{-1})\,. \tag{35}$$

When the values from Ref. (17) are substituted into (34), the series

$$E[\Phi^{[1,1]}(1\,s^2\,2\,s)] = -\,1{,}125\,Z^2 \\ + 1.088\,65\,Z - 0.597\,6 + \theta(Z^{-1}) \\ = -\,7.456\,7 + \theta(Z^{-1}) \tag{36}$$

is obtained for the symmetric solution which compares with

$$E[\Phi^{[2,\lambda]}(1\,s^2\,2\,s)] = -\,1.125\,Z^2 + 1.022\,81\,Z - \\ - 0.480\,3 + \theta(Z^{-1}) \\ = -\,7.464\,7 + \theta(Z^{-1}) \tag{37}$$

for the physical state. As can be seen, the difference linear in Z of 3[uv | vu] is all but cancelled off by the second term which shows the possible breakdown of the generalized Hund's rule in such a case. Both of these series have, of course, not yet converged to a significant extent to determine the ordering unambiguously, although it is clear that they are very nearly degenerate if percentage of the eigenvalue itself is taken as a criterion of degeneracy.

The same calculation performed for the two eigenfunctions in the 1 s^2 2 p configuration gives

$$E[\Phi^{[1,1]}(1\,s^2\,2\,p)] = \\ = -\,1.125\,Z^2 + 1.144\,74\,Z - 0.762\,6 + \theta(Z^{-1}) \\ = -\,7.453\,4 + \theta(Z^{-1}) \tag{38}$$

which compares with

$$E[\Phi^{[2,\lambda]}(1\,s^2\,2\,p)] = \\ = -\,1.125\,Z^2 + 1.093\,53\,Z - 0.527\,2 + \theta(Z^{-1}) \\ = -\,7.371\,6 + \theta(Z^{-1}) \tag{39}$$

of Chisholm *et al.* [22]. Here the approximate « *spurious* » eigenvalue is even *lower* in energy than the physical one, but again convergence has not been approached. This illustrates the fact that to evaluate such splittings second-order perturbation theory in the Z-expansion is not sufficient. More accurate techniques are, however, available (see e. g. Ref. 19) so that for example one should be able to calculate pair-corrections to non-hydrogenic orbitals to first or even infinite order, with which one should obtain reasonable values for many such splittings. For large N, this might still not be sufficient in order to calculate the small differences between the very many representations of « *intermediate symmetry* », i. e. whose Young diagrams are relatively square, and many orders of perturbation theory will have to be used. Notice that while it is among these intermediate levels that the generalized Hund's rule is most apt to break down, these are all levels which are of no actual interest in physical systems since their Young diagrams contain more than two columns so that the eigenfunctions cannot be used in the construction of wave functions.

IV. **Procedures based on Non-Symmetric H_0's.** — A. THEORY. — The conventional type of perturbation theoretic calculation of a spatial eigenfunction $\Phi_i(r)$ would utilize a zeroth-order function such as those of Section III which transforms as one of the Young tableaux and which is an eigenfunction of an H_0 which possesses the full symmetry of H itself, i. e.

$$[H_0, P] = 0 \qquad P \in S_N \tag{40}$$

Once $\Phi_{i,0}$ is associated with a Young tableau, the symmetry of H assures that the exact Φ_i defined by

$$\Phi_i = \Phi_{i,0} + \lambda\Phi_{i,1} + \lambda^2\,\Phi_{i,2} + \cdots \tag{41}$$

will also transform as the same Young tableau.

The nature of a perturbation theoretic expansion, however, nowhere requires that the zeroth-order solution possess all the symmetries of the exact solution. While it is often convenient to include all such symmetries in the zeroth-order, and hence in all orders, it is also sometimes convenient not to include all such symmetries in the zeroth-order, and in other words start a calculation using a « *broken symmetry* » which is « *repaired* » as the accuracy is increased. Such is, for example, the case in some Hartree-Fock calculations on non-spherical nuclei, and in the standard procedure for specifying the spin or angular momentum component in atomic calculations by applying a small magnetic field later allowed to approach zero. In calculations of atomic and molecular wave functions the advantage of using non-symmetric zeroth-order solutions lies in the simplification it affords of the algebraic manipulations involved [3]. At the same time, however, such a procedure suffers from the defect that it can lead to potential ambiguities in the results and that care must be taken to examine

carefully the nature of the solution in each case. The techniques of using these non-symmetric zeroth-order solutions have been described previously [3] and the present discussion is intended to place that treatment in the context of the above discussion on the symmetry properties of the $\Phi_i(r)$ as well as to illustrate further the potential convergence and the effect of near-degeneracies on the particular perturbation expansion employed.

Consider a function $\Phi_{i,0}(r)$ possessing *no* symmetry properties, such that it is a non-degenerate eigenfunction of H_0 for which of necessity

$$[\mathrm{P}, H_0] \neq 0 \qquad \mathrm{P} \in \mathrm{S}_N \tag{42}$$

(as otherwise there will usually be other degenerate eigenfunctions) and solve for the perturbation theoretic corrections using the expansion (41). If the expansion converges to an eigenfunction of H it *must* converge to a function $\Phi_i^{[\alpha,\lambda]}(r)$ which transforms according to one of the irreducible representations, α, for λ in an unspecified basis, merely because all such representations are non-degenerate except for accidental degeneracies. Two parts of the question of convergence must however be treated with great care and are (a) the actual convergence of the expansion ; and (b) the convergence to an eigenfunction belonging to the *appropriate* representation, α. It is also desirable, although less important, to know the explicit tableau $[\alpha, \lambda]$ according to which the solution transforms.

If the eigenvalues of H are « *sufficiently* » non-degenerate — although there is apparently no *a priori* way to determine when this will be the case — then the perturbation theoretic procedure will usually pick out a particular eigenfunction belonging to one of the non-degenerate representations, α and λ will converge to it. In general this converges in such a way that the continuous curves as functions of the perturbation parameter λ, do not cross unless the orbital symmetries of the solutions differ. Were the $\Phi_{i,0}$, to possess *all* the symmetries of H, i. e. transform as a particular Young tableau or linear combination thereof, then there would be, in general, only one solution in the vicinity of $E_0 + E_1$ possessing that symmetry, and to which the $\Phi_{i,0}$ would obviously converge. For the non-symmetric $\Phi_{i,0}$ such an argument does not obtain and one has to know the ordering of both the approximate eigenvalues and the exact eigenvalues which, by virtue of the non-crossing rule, permits a determination of the solution to which a given expansion will converge. In calculations for ground state wave functions there will, hopefully, be no ambiguity as to the Young tableau involved. There the perturbation expansion should introduce in all but exceptional circumstances the symmetry of the desired Young tableau as a necessary consequence of its convergence.

Consider as an example the three-electron problem discussed at length above, and in order to restrict the problem somewhat, choose as H_0 an operator which is symmetric under the transposition P_{12} but which has no symmetry under P_{13}. Such an H_0 would be the Hartree-Hamiltonian described in Ref. 3*b* for calculations on the ground state of Li in which electrons 1 and 2 are in the field of a 2s-electron and a single 1s electron, i. e.,

$$h_a(i) = -\frac{1}{2}\nabla_i^2 - \frac{3}{r_i} + [-a \mid -a] + [-b \mid -b] \qquad i = 1, 2 \tag{43a}$$

and electron 3 is in the field of two 1s-electrons, i. e.

$$h_b(3) = -\frac{1}{2}\nabla_3^2 - \frac{3}{r_3} + 2[-a \mid -a] \tag{43b}$$

with

$$H_0 = h_a(1) + h_a(2) + h_b(3)\,. \tag{44}$$

The orbitals a and b are defined as the lowest and second lowest eigenfunctions respectively of the equations

$$[h_a(i) - e_k^a]\, a_k(i) = 0 \tag{45a}$$

and

$$[h_b(i) - e_k^b]\, b_k(i) = 0 \tag{45b}$$

i. e. $a \equiv a_1$ or the 1s function and $b \equiv b_2$ or the 2s function. This definition of H_0 is specifically designed for Hartree-type self-consistency in calculating $\Phi(r)$ for the ground-state of Li. However it does have a spectrum of eigenvalues which can be used for calculation of other functions and, in order of increasing eigenvalue, these are given by

$$a(1)\, a(2)\, b_1(3) \equiv a_1(1)\, a_1(2)\, b_1(3) \tag{46a}$$

of energy $2\, e_1^a + e_1^b$,

$$a(1)\, a(2)\, b(3) \equiv a_1(1)\, a_1(2)\, b_2(3) \tag{46b}$$

of higher eigenvalue $2\, e_1^a + e_2^b$, which is the Hartree Φ_0, and the two degenerate functions

$$a_2(1)\, a_1(2)\, b_1(3) \tag{46c}$$

and

$$a_1(1)\, a_2(2)\, b_1(3) \tag{46d}$$

of eigenvalue $e_1^a + e_2^a + e_1^b$. This last eigenvalue is, by the definition of H_0, always of higher energy than that of the previous function (46*b*). The orbital eigenvalues have been calculated by J. M. Schulman [23] and are -2.49, -1.23, -0.18 and -0.32 for e_1^a, e_1^b, e_2^a and e_2^b respectively, and the energies of the four states are thus -6.21, -5.16, and -4.04 (doubly-degenerate). These four functions can now be used in perturbation theoretic calculations to obtain the lowest four solutions $\Phi_1^{[1,1]}$, $\Phi_2^{[1,1]}$, $\Phi_1^{[2,1]}$ and $\Phi_1^{[2,2]}$ to the symmetric problem using the notation of Section III above.

Clearly if $\Phi_{1,0}^{[1,1]}$ is taken as (46*a*) this should provide convergence to $\Phi_1^{[1,1]}$ as there is no other solution in the vicinity of the desired eigenvalue. Furthermore, although (46*a*) is not symmetric under P_{13}, there is a significant overlap of orbital b_1 with orbital a so that $P_{13}\ aab_1$ is not terribly different from aab, itself, with $< aab_1 \mid P_{13}\, aab_1 > = < a \mid b_1 >^2$.

The treatment of the next three solutions is straightforward once one remembers the usual perturbation theoretic argument which prohibits crossing of energy levels as a function of the perturbation parameter, λ, unless the matrix elements of the perturbation connecting the states vanish. The latter is not the case here since there is no P_{13} and P_{23} symmetry to the problem until the perturbation is fully « *switched on* », i. e. $\lambda = 1$, and the behaviour of the solutions is that sketched in figure 3. Since (46*b*) is symmetric under P_{12} and is of next lowest eigenvalue it is clearly to be taken as $\Phi_{1,0}^{[2,1]}$ and when the perturbation expansion

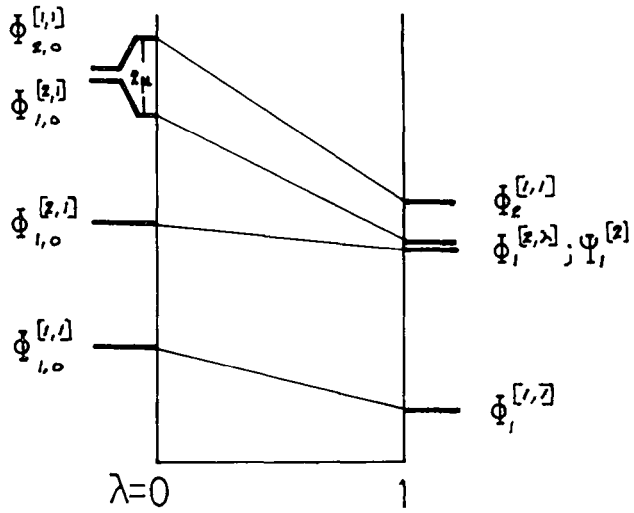

FIG. 3. — The likely convergence of non-symmetric Φ_0's for the three electron system.

is carried out it is expected to converge to $\Phi_1^{[2,1]}$ the lowest remaining eigenfunction that is symmetric under P_{12}. Now, the remaining two exact solutions differ in P_{12} symmetry, $\Phi_1^{[2,2]}$ which is degenerate with $\Phi_1^{[2,1]}$ being antisymmetric and $\Phi_2^{[1,1]}$ being symmetric. As the two remaining approximate solutions are degenerate in zeroth-order, they must be diagonalized before perturbation theory can be applied which leads to the immediate choice of (unnormalized)

$$\Phi_{1,0}^{[2,2]} = [a_2(1)\, a_1(2) - a_1(1)\, a_2(2)]\, b_1(3) \qquad (47a)$$

and

$$\Phi_{2,0}^{[1,1]} = [a_2(1)\, a_1(2) + a_1(1)\, a_2(2)]\, b_1(3) \qquad (47b)$$

and the convergence should be as indicated in figure 3.

Notice that the use of non-symmetric eigenfunctions and the convergence of figure 3 are predicated on the (reasonable) assumption that there exists a one-to-one correspondence between eigenfunctions of H_0 and eigenfunctions of H. This, however, requires that a single H_0 is used to generate all the $\Phi_{i,0}$'s which is not the case when projected $\Phi_{i,0}$'s are used. It also assumes that the assignment of configurations is equally valid for H_0 as for H, and thus, for example, assumes that the lowest approximate $1s^2$ 3s state is higher in energy than the highest approximate $1s^2$ 2s solution.

As a last remark it should be noted that in exceptional cases perturbation theory might appear to converge to a sum of functions belonging to different representations which are nearly degenerate in energy. When this occurs, the energy so obtained should be sufficiently close to that of the solution desired that no further correction is necessary for most purposes. The desired eigenfunction itself can be simply projected out of the « converged » solution with $D_{\lambda\lambda}^{[\alpha]}$, it always being easier to do the projection at the end of the calculation as with these non-symmetric methods, than at the beginning of calculations as with usual determinantal methods. If $D_{\lambda\lambda}^{[\alpha]}\ \Phi_i$ actually is close to zero, or equivalently if for normalized Φ_i, $< \Phi_i \mid D_{\lambda\lambda}^{[\alpha]}\ \Phi_i > \ll 1$, then the solution contains no component of the desired symmetry, and the procedure for non-symmetric $\Phi_{i,0}$'s breaks down. It is, of course, only a matter of convenience whether one tests for this breakdown of the procedure by projections with $D_{\lambda\lambda}^{[\alpha]}$, or by anti-symmetrizing the product $\Phi_i^{[\alpha,\lambda]}(r)\, \chi_m^{[\tilde{\alpha},\lambda]}(\sigma)$. It is likely that the procedure should not often fail but it is also satisfying to know that such an ultimate test of its validity can be performed in so straightforward a manner.

B. USEFUL NON-SYMMETRIC H_0'S. — Although, in principle, any arbitrary non-symmetric H_0 can be used in developing a perturbation theoretic expansion for the $\Phi_i(r)$, in practice it is desirable and almost necessary that the choice of H_0 be restricted to those possessing certain partial symmetries as well as other properties. These restrictions on H_0 serve to assure that the solution Φ_i will possess the correct symmetry properties as they enable a relatively simple collection of the eigenfunctions into configurations, permit the general determination of the lowest eigenvalue within that configuration, and associate the solution with a standard Young tableau which has a correspondingly simple spin function, rather than the more general linear combination of such tableaux and corresponding spin-functions.

Procedures based on non-symmetric H_0's have been argued to be of particular utility under either of the following two conditions : [3*b*, *c*] (1) $\Phi_{i,0}$ is symmetric under a sufficient number of transpositions such that only one Young tableau of less than three columns can possess such symmetries ; or

(2) $\Phi_{i,0}$ is antisymmetric under a sufficient number of transpositions such that only one Young tableau of fixed maximum column length can possess such symmetry.

The first of these conditions allows for solutions of most closed-shell and slightly open-shell atoms and molecules since it enables the desired solution to be the allowed solution of lowest energy to which the perturbation expansion must, of necessity, converge, if it does converge. The second of these conditions allows for alternant molecular orbital treatments for both closed and partially open shell molecules since the number of different orbitals is limited by the maximum column size, no solution exists within that configuration of longer column. This therefore excludes solutions of « *higher antisymmetry* » on the grounds of their not existing within the given configuration whereas the first condition excludes solutions of « *higher symmetry* », as they will be, according to the generalized Hund's rule, of high energy, and perturbation theory will generally take the lowest eigenfunction of H_0 into the lowest eigenfunction of H. In terms of Young tableaux a sufficient set of transposition symmetries would be those under $P_{n,n+1}$ (n odd) corresponding to the tableau [1, 1] of figure 4 and which are possessed by no tableau or linear combination of tableaux of less than three columns [3*b*]. A sufficient set of antisymmetries would be those under $\mathcal{A}_{1,2\ldots N/2}$ and under $\mathcal{A}_{(N/2+1),\ldots,N}$, corresponding to the tableau [1, 2] of figure 4. Although these same antisymmetries are also possessed by the tableau [2, 1] of figure 4, if the orbitals of the first $N/2$ electrons are related to the orbitals of the second $N/2$ electrons such that the solution belongs to a limiting term $a^2\ b^2\ c^2$, ..., there is no solution belonging to this configuration transforming as this totally antisymmetric tableau.

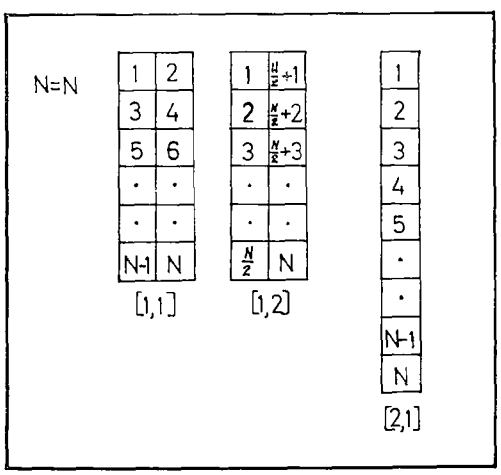

FIG. 4. — Some illustrative Young tableaux for $N = N$.

The Hartree-like procedure [3*b*] for singlet states which satisfies the first of these two conditions looks for an expression which will converge to a solution belonging to the tableau [1, 1] of figure 4, and in order to do this takes H_0 to be a sum of one electron operators symmetric under $P_{n,n+1}$ (n odd), i. e.

$$H_0 = h_a(1) + h_a(2) + h_b(3) + h_b(4) + \cdots . \quad (48)$$

The non-degenerate eigenfunction Φ_0 is defined as

$$\Phi_0 = a(1)\, a(2)\, b(3)\, b(4) \ldots \quad (49)$$

where $a \equiv a_1$ the lowest or 1s eigenfunction of h_a satisfying

$$(h_a - e_i^a)\, a_i = 0 \quad (50a)$$

and $b \equiv b_2$, the second lowest or 2 s eigenfunction of h_b satisfying

$$(h_b - e_i^b)\, b_i = 0\,, \quad \text{etc.} \quad (50b)$$

It is important that H_0 not possess higher symmetry than under $P_{n,n+1}$ (n odd) since otherwise Φ_0 of (48) would not be a non-degenerate eigenfunction of H_0 and the first order secular equation would have to be diagonalized. It is also important that H_0 be symmetric under $P_{n,n+1}$ (n odd) since this greatly restricts the possible tableaux to which the converged exact solution can belong to a certain subset (or linear combination thereof) of all the tableaux.

The Hartree choice of the one electron Hamiltonian which defines the one-electron orbitals to be screened by all other occupied orbitals can be seen to give the relationship between the corresponding eigenfunctions,

$$e_1^a < e_1^b\,; \quad e_2^b < e_2^c\,; \quad \text{etc.} \quad (51)$$

As $|\, e_1^a\,| > |\, e_2^b\,| > |\, e_3^c\,|$, etc. this relationship can be seen to imply that the eigenvalue of Φ_0 of(49)

$$E_0 = 2(e_1^a + e_2^b + e_3^c + \cdots) \quad (52)$$

should be the lowest eigenvalue of H_0 within the configuration $a^2\ b^2\ c^2$ ... Since the eigenfunctions of H_0 and H are in a one-to-one correspondence, the non-crossing rule assures that the Φ_0 of (49) corresponding to this E_0 will converge by (41) to the eigenfunction of H within this configuration belonging to the lowest eigenvalue, i. e. to the desired $\Phi^{[1,1]}$, exactly as sketched in figure 3 for the three-electron example.

In a similar way, the procedure which calculates wave functions for alternant hydrocarbons [3*c*] introduces a sufficient set of restrictions into the non-symmetric H_0 to enable the appropriate and well-defined perturbation theoretic solution to be obtained, even though such was not the purpose of the original argument. For example, for singlet systems, H_0 is taken to be symmetric under permutation of the first $N/2$ indices and under the last $N/2$ indices, i. e.

$$H_0 = \sum_{i=1}^{N/2} h(i) + \sum_{i=(N/2)+1}^{N} \bar{h}(i)\,. \quad (53)$$

The zeroth-order solution, that approximating the result of Alternant Molecular Orbital (AMO) theory, is

$$\mathcal{A}_{N/2}\, a(1)\, b(2) \ldots \mathcal{A}_{N/2}\, \bar{a}\left(\frac{N}{2}+1\right) \bar{b}\left(\frac{N}{2}+2\right) \ldots \quad (54)$$

where $a, b, \ldots$ and $\bar{a}, \bar{b}, \ldots$ are the lowest $N/2$ eigenfunctions of h and $\bar{h}$ respectively and $\mathcal{A}_{N/2}$ antisymmetrizes with respect to the appropriate $N/2$ indices. Since the eigenvalue spectra of h and $\bar{h}$ are similar — for benzene they are the same, as h and $\bar{h}$ are related by a 60° rotation about the six-fold symmetry axis — there is no solution belonging to the same term that is totally antisymmetric. This, along with antisymmetry in the two sets of $N/2$ indices, implies that convergence of the perturbation expansion *must* lead to the solution belonging to the representation with two equal columns, and transforming as the tableau [1, 2] of figure 4. This is so merely because there exists no solution within that configuration transforming as the only other possible tableau, the totally antisymmetric [2, 1].

There are, of course, other possible choices of H_0's which are symmetry-restricted yet which are not totally symmetric, and which may be of utility in computations of wave functions ; some of these have been given in Ref. 4*c* to describe excited states in alternant systems, and others can be generated as desired for particular problems. Again, it should be emphasized that symmetry and other restrictions are not *necessary*, but are only *convenient* as they enable simple recognition of the particular state to which the expansion will converge.

To appreciate this point, it is of interest to recall the original argument on the non-symmetrical wave function for the two-electron problem of the hydrogen molecule [3*a*] as the result for two electrons is so easily visualized. All eigenfunctions of the two-electron Hamiltonian are either even or odd under P_{12} and therefore, if perturbation theory converges, it must converge to a function which is either even or odd under P_{12}, there being in general no degenerate solutions other than those due to spatial symmetry. The eigenvalue spectrum of the non-symmetric Hamiltonian

$$H_0 = h_A(1) + h_B(2) \quad (55)$$

where h_A and h_B are the hydrogen-atom Hamiltonians located on centers A and B, can be worked out in a straightforward manner, and the convergence of the different perturbative solutions can be worked out in a manner analogous to that of figure 3 with only the additional complication of the nuclear symmetry to take into account. The lowest eigenvalue is clearly non-degenerate so that perturbation theory on the zeroth-order function

$$\Phi_0 = \pi^{-1} \exp -(r_{1A} + r_{2B}) \quad (56)$$

must converge to the exact eigenfunction of ground-state molecule, symmetric under P_{12}, if it converges at all. It is, however, only because of the simplicity of the two-electron two-center problem that it is possible to classify the eigenfunctions of this H_0 which contains no symmetry whatsoever, and to discuss the behaviour of the perturbation theoretic solutions in an *a priori* manner. It is clear that, in general, such an analysis is not possible for many-electron problems, and the utility of such « *totally non-symmetric* » H_0's must be limited in practice, if not, as pointed out above, in principle.

The extension of these ideas to large molecular systems is obvious and would involve choosing as a Φ_0 a simple product constructed from arbitrarily-determined localized orbitals $a, b, c, \ldots$ and where an approximation to Φ could be found by minimizing the small coefficients, $\alpha, \beta, \ldots$ in

$$\tilde{\Phi} = (1 + \alpha r_{12} + \beta r_{23} + \cdots)\, a(1)\, a(2)\, b(3)\, b(4) \ldots \quad (57)$$

This would provide an approximation to all the desired physical properties even though it would surely be a linear combination of many nearly-degenerate spatial eigenfunctions, with the advantage that the orbitals could be chosen « *physically* ». The parameters can be varied freely as long as the variational space is not too large as within the context of a perturbation solution Φ must describe a function belonging to the same configuration $a^2\, b^2 \ldots$ as Φ_0 itself.

V. **Concluding Remarks.** — In the study of spatial eigenfunctions of H presented here the simplifying assumption has been made that the exact Hamiltonian is spin-independent, this assumption being necessary for the definition of the problem. In general, of course, any real Hamiltonian contains spin-dependent terms, the most important being that of the spin-orbit interaction, and which become increasingly significant as $Z\alpha$ approaches 1. For the most part, however, such effects can be treated using perturbation theory, and the corrections to ψ given by (3) can be obtained in a straightforward, if intricate, manner following Wigner [1]. Also, in attempting to keep the discussion as simple and transparent as possible, the problem has been restricted to s-state solutions in which there is no additional degeneracy due to non-vanishing components of angular momentum. When configurations with orbitals of $l \neq 0$ are included certain linear combinations of orbital products are necessary in order that the individual $\Phi_{i,0}$'s be eigenfunctions of total L^2. The procedure for obtaining these, however, is exactly the same as for obtaining Ψ_0's which are eigenfunctions of L^2, and can be worked out as necessary. In other words the various algebraic problems which are encountered in dealing with open-shell problems can, in principle, be worked out using the formalism of the spatial eigenfunctions of the spin-independent Hamiltonian. This has not been done here since the purpose of the present study was to illustrate in

the simplest possible way the behaviour of the spatial eigenfunctions rather that to develop them for immediate applicability to the variety of problems of atomic and molecular spectroscopy and atomic collision theory.

Two methods for obtaining approximate, but accurate, spatial eigenfunctions have been considered explicitly since there is some likelihood that these procedures will prove quite useful in future calculations. The non-symmetric procedures [3] should prove useful in simplifying the algebra for calculations on medium size atoms and molecules, and even when the Hund's rule arguments fail and the perturbation solution converges to an « *undesired* » state the zeroth-order solution plus first-order corrections should provide energies and expectation values very close to those of the desired state. These procedures are, to be sure, essentially untried relative to the traditional methods used in atomic and molecular calculations, and their utility in a wide variety of problems remains to be convincingly demonstrated. It is hoped, however, that the present article will lead to a more widespread understanding of the behavior of the spatial eigenfunctions, which in turn might lead to a greater exploitation of their potential. If such exploitation can indeed be realized, then it will be possible to claim that these procedures provide useful alternatives to the determinantal methods used in virtually all of atomic and molecular physics.

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