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The Group R_4 in Atomic-Structure Theory: The Hydrogenic R_4 versus the Mathematical R_4 and the Coulomb Interaction in $2s^m2p^n$ and $3s^m3p^n3d^r$ Configurations

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The rotation group in four dimensions R_4 is applied to the study of the $2s^m2p^n$ configurations of atoms. This Lie group is used in both the mathematical sense, describing the transformation properties of the angular parts of the 2s and 2p electrons, and in the more physical sense of an approximate symmetry group for the first-row atoms. The various states of each configuration are classified by means of R_4. By expressing the Coulomb interaction in terms of tensors, transforming according to irreducible representations of R_4, Coulomb and exchange integrals are evaluated group theoretically. The method is extended to $3s^m3p^n3d^r$ configurations. The states are classified by means of R_4 and Coulomb and exchange integrals are approximately evaluated.

The theory of groups has long played an important role in the quantum theory of atomic structure. The indistinguishability of electrons and the Pauli exclusion principle lead naturally to the introduction of the permutation group. The use of the three-dimensional rotation group in classifying states of definite angular momentum is of course well known. The group R_3 is not sufficiently large to explain the n^2-fold degeneracy of the nth level of hydrogen-like atoms, and in 1935 Fock[1] realized that the group R_4 would. He showed that, if the Fourier-transformed Hamiltonian is stereographically projected from three-dimensional p-space onto a four-dimensional sphere, the Hamiltonian exhibits four-dimensional rotation symmetry. It is this additional symmetry beyond R_3 which is responsible for the degeneracy of orbitals of the same principal quantum number. Each set of orbitals of a given principal quantum number when projected onto the four-dimensional sphere transforms according to one of the irreducible representations of R_4.

In his study of atomic spectra, Racah[2] found that in order to classify states of d^n and of f^n it is useful to introduce Lie groups larger than the R_3 describing the orbital angular momentum, and smaller than the SU_n describing the permutation symmetry and spin. These groups describe in more detail than does R_3 the transformation properties of the angular parts of the orbitals under consideration. Consequently such groups are able to provide the additional quantum numbers that can distinguish identical terms, e.g., the two ^2D states of d^3 are labeled by their seniority, a quantum number arising from R_5. These groups deal with the mathematical problems of the classification of states and will be called here "mathematical groups" as opposed to the "physical groups" such as the R_4 introduced by Fock.

In this paper we consider both descriptions of groups in an investigation of the application of R_4 to the study of the $2s^m2p^n$ configurations of atoms. We discuss the relationship between the two descriptions of groups. For the four 2s and 2p orbitals, the appropriate group for both the mathematical and physical descriptions is R_4, and the representations used in the analysis of atomic configurations are the same. The four 2s and 2p orbitals transform as the (10) representation of R_4. For any other principal quantum number the groups differ. In the case of the nine 3s, 3p, and 3d orbitals, the group used in the mathematical description is R_9, whereas the group used in the physical description remains R_4. The 3s, 3p, 3d orbitals transform as the (1000) representation of R_9 and according to the (20) representation of R_4.

We then investigate the $2s^m2p^n$ configurations and determine their transformation properties with respect to R_4. By means of the use of a model potential we are able to evaluate Coulomb and exchange integrals for 2s and 2p electrons by group-theoretical methods. Finally we evaluate Coulomb and exchange integrals for orbitals in the $n=3$ shell by an extension of the physical description of R_4 to the $3s^m3p^n3d^r$ configurations.

I. THE GROUPS RELEVANT TO THE STUDY OF $2s^m2p^n$

SU_n. If we consider any set of $2n$ spin orbitals, the indistinguishability of the electrons and the Pauli principle allow us to conclude that any m-electron wave function taken from these $2n$ spin orbitals must transform according to the $[1^m]$ representation of SU_{2n}.[3] This representation is usually symbolized by the Young diagram shown in Fig. 1. We now decompose SU_{2n} into $SU_n \times SU_2$, where × stands for the inner tensor product. Both factors contain the same electron coordinates. This decomposition is the familiar one into the space and spin parts of the wave function. For $2s^m2p^n$ configurations there are eight spin orbitals which transform according to irreducible representations of SU_8. Since we will be dealing exclusively with a spin-independent Hamiltonian, we make the decomposition into orbital and spin parts: $SU_8 \rightarrow SU_4 \times SU_2$ and need deal with the SU_4 part only. The allowed representations and their dimensions for an n-electron system $n=0,1,\ldots 4$ is shown in Table I. Note that the Pauli principle excludes space diagrams of more than two columns

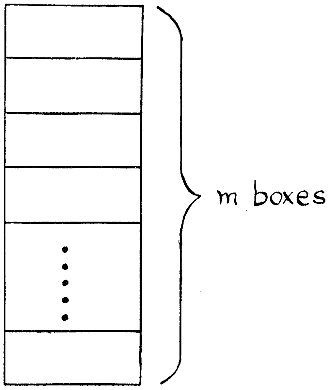

FIG. 1. Young diagram for an m-electron system.

TABLE I. Classification of Configurations $2s^m 2p^n$.

Number of particles	Representation and dimension of SU_8	$SU_4 \times SU_2$	R_4	R_3	Configurations
1	$[1]$ (8)	$[1]\times[1]$ (4) (2)	(10) (4)	S (1)	s
				P (3)	p
2	$[1^2]$ (28)	$[2]\times[1^2]$ (10) (1)	(20) (9)	S (1)	s^2, p^2
				P (3)	sp
				D (5)	p^2
		$[1^2]\times[2]$ (6) (3)	(11) (3)	P (3)	p^2, sp
			(1−1) (3)	P (3)	p^2, sp
3	$[1^3]$ (56)	$[2,1]\times[2,1]$ (20) (2)	(21) (8)	P (3)	p^3, sp^2, s^2p
				D (5)	p^3, sp^2
			(2−1) (8)	P (3)	p^3, sp^2, s^2p
				D (5)	p^3, sp^2
			(10) (4)	S (1)	sp^2
				P (3)	p^3, sp^2, s^2p
		$[1^3]\times[3]$ (4) (4)	(10) (4)	S (1)	p^3
				P (3)	sp^2
4	$[1^4]$ (70)	$[2,1^2]\times[3,1]$ (15) (3)	(20) (9)	S (1)	sp^3
				P (3)	p^4, sp^3, s^2p^2
				D (5)	sp^3
			(11) (3)	P (3)	p^4, sp^3, s^2p^2
			(1−1) (3)	P (3)	p^4, sp^3, s^2p^2
		$[2,2]\times[2,2]$ (20) (1)	(20) (9)	S (1)	p^4, s^2p^2
				P (3)	sp^3
				D (5)	p^4, sp^3, s^2p^2
			(22) (5)	D (5)	p^4, sp^3, s^2p^2
			(2−2) (5)	D (5)	p^4, sp^3, s^2p^2
			(00) (1)	S (1)	p^4, s^2p^2
		$[1^4]\times[4]$ (1) (5)	(00) (1)	S (1)	p^4, s^2p^2

and spin diagrams of more than two rows.

R_3. The classification of states $s^m p^n$ with respect to this group (too familiar to warrant discussion) is also given in Table I.

R_4. We now want to consider a subgroup of SU_4 which contains R_3 as a subgroup. Such a group will connect representations of R_3 and provide additional classification labels for configurations of $2s^m 2p^n$. Thus sp and p^2 may both be ^3P; up to this point there are no group labels to distinguish them. R_4 is chosen as the intermediary group because in certain ways to be described below, all atoms are similar to the hydrogen atom.

The generators of R_4 commute with the Hamiltonian of the hydrogen atom. As we will see the six generators of R_4 can be expressed as the three components of the angular momentum vector and the three components of the Runge-Lenz vector. This latter vector is defined as

$$(2m)^{-1}(\vec{p}\times\vec{L})-(2m)^{-1}(\vec{L}\times\vec{p})-k\vec{r}/r\ ,$$

where m is the mass of the particle and $\vec{p}$ and $\vec{L}$ are the linear- and angular-momentum vectors respectively. It is this extra invariant vector that causes the degeneracy of the $2s$ and $2p$ orbitals. For the other first-row atoms, the $2s$ and $2p$ orbitals can be considered to be nearly degenerate. In addition for many problems the precise form of the radial parts of the orbitals has surprisingly little effect on the final result of a calculation.[3a] We are thus led to believe that hydrogen-like orbitals have considerable use for problems other than hydrogen, and that the group R_4 may in some sense be an approximate symmetry group for atoms other than hydrogen.

In addition to this physical motivation, the angular parts of the basic set of orbitals of the configurations $s^m p^n$, namely s, p_+, p_-, and p_0 transform according to the basic representation of R_4. To see this mathematically we consider the generators of R_4 treated as generalized Racah tensors. Upon studying the commutation relations of these tensors and the transformation properties of the wave functions, we will see that R_4 is the relevant group for $s^m p^n$ configurations. In fact we first obtain the generators for SU_4 and then exhibit a subset corresponding to the generators of R_4.

A. The Generators of R_4

Following Elliott[4] and Judd,[5] we define generalized one-electron Racah tensors $v_q^k(l, l')$ of rank k by means of their matrix elements

$$\langle l'''m_l'''|v_q^k(l,l')|l''m_l''\rangle = [k]^{1/2}[l]^{-1/2}(l''km_l''q|l''kl'''m_l''')\,\delta(l''',l)\delta(l',l'') \ , \tag{1}$$

where $[a] = 2a+1$ and $(l''km_l''q|l''kl'''m_l''')$ is a Clebsch-Gordan coefficient. The action of $v_q^k(l, l')$ on a single electron orbital is given by

$$v_q^k(l,l')\,|l''m_l''\rangle = \sum_{l'''m_l'''} \delta(l,l''')\delta(l',l'')(-1)^{l'''-m_l'''}[k]^{1/2} \times \begin{pmatrix} l''' & k & l'' \\ -m_l''' & q & m_l'' \end{pmatrix} |l'''m_l'''\rangle \ , \tag{2}$$

where $(:::)$ is a 3-j symbol, and the commutation relations for these tensors are

$$[v_{q_1}^{k_1}(l,l'),v_{q_2}^{k_2}(l'',l''')] = \sum_{k_3q_3} \{[k_1][k_2][k_3]\}^{1/2} \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & -q_3 \end{pmatrix} \times (-1)^{2l'''+l''-l'-q_3} \left[\delta(l',l'')(-1)^{k_1+k_2+k_3+l+l'+l''+l'''} \begin{Bmatrix} k_1 & k_2 & k_3 \\ l''' & l & l'' \end{Bmatrix} v_{q_3}^{k_3}(l''',l) - \delta(l,l''') \begin{Bmatrix} k_1 & k_2 & k_3 \\ l'' & l' & l \end{Bmatrix} v_{q_3}^{k_3}(l'',l') \right] , \tag{3}$$

where $\{:::\}$ is a 6-j symbol.

From these relations it follows that the group U_S, $s = 2(l+l'+1)$ is generated by the s^2 operators

$v_q^k(l, l)$, $v_q^k(l, l')$, $v_q^k(l', l)$ and $v_q^k(l', l')$;

and that R_S is generated by the operators

$v_q^k(l, l)$, k odd; $v_q^k(l', l')$, k odd; and $v_q^k(l, l') + v_q^k(l', l)$.

Each v^k is of dimension $2k+1$ and $k \leqslant \max(l, l')$. Moreover as shown by Feneuille,[6] the tensor $v_q^k(l, l')$ transforms in the same way as $(-1)^{l'}|ll'kq\rangle$. If we consider the configurations s^mp^n; the sixteen operators $v^0(s, s)$, $v^0(p, p)$, $v^1(p, p)$, $v^2(p, p)$, $v^1(s, p)$, and $v^1(p, s)$ generate U_4; the six operators $v^1(p, p)v^1(s, p) + v^1(p, s)$ generate R_4; and the three operators $v^1(p, p)$ generate R_3. Thus the appropriate groups are U_4, R_4, and R_3 as claimed. It is essential to note that these groups have nothing whatever to do with any Hamiltonian; they are merely manifestations of the symmetry properties of the *angular* parts of the orbitals under consideration. Consequently they can not be expected to give any information about the energy spectra of the atomic system. It is for this reason that we designate the description of the orthogonal groups arising in this manner as the mathematical description, while designating the description of such groups as R_4 which commute with the Hamiltonian of the hydrogen atom as the physical description.

B. The Representations of R_4

The[7,8] six infinitesimal rotations in four dimensions J_{ij}, $i, j = 1, 2, 3, 4$ (the rotation in the ij plane) also constitute the generators of R_4. These generators obey the commutation relations

$$[J_{ij}, J_{kl}] = i\,(\delta_{il}J_{jk} + \delta_{jl}J_{ik} + \delta_{il}J_{kj} + \delta_{jk}J_{li}). \tag{4}$$

Upon introducing

$$\vec{\mathrm{L}} = \hat{i}\,J_{23} + \hat{j}\,J_{31} + \hat{k}\,J_{12} \tag{5a}$$

and

$$\vec{\mathrm{A}} = \hat{i}\,J_{14} + \hat{j}\,J_{24} + \hat{k}\,J_{34} \ , \tag{5b}$$

we find

$$\begin{aligned} [L_i, L_j] &= i\epsilon_{ijk}L_k, \\ [L_i, A_j] &= i\epsilon_{ijk}A_k, \\ [A_i, A_j] &= i\epsilon_{ijk}L_k. \end{aligned} \tag{6}$$

The six generators L_i and A_i, $i = 1, 2, 3$ have definite physical significance. When applied to the Kepler problem $\vec{L}$ is the angular momentum and $\vec{A}$ is proportional to the Runge-Lenz vector defined above. These vectors are the invariants of the Kepler problem, i.e., they commute with the Hamiltonian.

If we consider the linear combinations $\vec{M} = \frac{1}{2}(\vec{L} + \vec{A})$ and $\vec{N} = \frac{1}{2}(\vec{L} - \vec{A})$ we find

$$[M, N] = 0; \quad [M_i, M_j] = i\epsilon_{ijk} M_k; \quad [N_i, N_j] = i\epsilon_{ijk} N_k; \tag{7}$$

i.e. M and N each satisfy the commutation relations of angular momentum and the commutator between them is zero. Thus R_4 is isomorphic (locally) to the direct product of two three-dimensional rotation groups. Setting

$$M^2 \rightarrow j_1(j_1 + 1), \quad \text{and } N^2 \rightarrow j_2(j_2 + 1),$$

as in the ordinary theory of angular momentum and

$$p = j_1 + j_2, \quad q = j_1 - j_2, \quad \text{where } p \geqslant q,$$

we see that the representations of R_4 can be labeled by (p, q).

For the hydrogen atom, $\vec{L} \cdot \vec{A} = 0$, i.e., the Runge-Lenz vector is orthogonal to the angular-momentum vector. This relation implies that $q = 0$, and that solutions of the Laplace equation in four dimensions, which correspond to hydrogen eigenfunctions, belong to the $(p, 0)$ representation of R_4. If we use a scheme such that the R_3 quantum numbers label the rows of the R_4 representations, then $(p + 1, 0, L, M)$ is seen to correspond to the familiar $[NLM]$ notation for the hydrogen atom, where $N = p + 1$. For configurations containing more than one electron, it is not necessarily true that $q = 0$. Consequently we will use the $(pqlm)$ notation [often abbreviated to (pql) or even to (pq)] exclusively to label representations of R_4.

C. Branching Rules for $SU_4 \rightarrow R_4 \rightarrow R_3$ and Labels for Many-Electron States

In the construction of a many-electron state classified by means of irreducible representations of groups, it is convenient to begin with the largest group and determine the appropriate irreducible representations for a particular state. Then each particular representation can be decomposed into irreducible representations of a subgroup by restricting the original group to this subgroup. This process, the determination of the branching rules, enables us to make the desired classification. For the configuration $s^m p^n$ the branching rules $SU_4 \rightarrow R_4$ and $R_4 \rightarrow R_3$ are needed. The rules as stated in Littlewood[9] and described by Judd[5] can be applied to the $SU_4 \rightarrow R_4$ decomposition. In addition to these rules and dimensionality considerations, i.e., the sum of the dimensions of irreducible representations of the subgroup must equal the dimension of the parent representation, we make use of another property of R_4. For the case of $SU_{2p} \rightarrow R_{2p}$, p an integer, any representation of R_{2p} always appears in the decomposition of SU_{2p} with its conjugate. For example in R_4 if (p, q) appears in the decomposition of SU_4 so must $(p, -q)$.

The decomposition $R_4 \rightarrow R_3$ follows the rule

$$(p, q) \rightarrow (p), \quad (p - 1), \ldots, (|q|), \tag{8}$$

where (p_i) denotes the $2p_i + 1$ dimensional representation of R_3. This rule follows from the fact that R_4 is a semi-simple Lie group, not a simple group. A simple Lie group has no invariant subgroups; a semi-simple Lie group has no abelian (commutative) subgroups. In fact as seen previously $R_4 = R_3 \times R_3$. By expressing the character of R_4 in terms of products of characters of R_3, the desired branching rules can be derived. Table I gives the classification of all configurations $s^m p^n$ and incidentally the branching rules.

D. Mathematical versus Physical Description of the Lie Group

An examination of the branching rule $R_4 \rightarrow R_3$ makes very clear the relationship between R_4 labels and the principal quantum number N. The representation $(p, 0)$ can be labeled by $[N = p + 1, LM]$, because all $L \leqslant N$ appear in that representation. Thus when we use the (10) in (pq) notation or $[2LM]$ in $[NLM]$ notation, representation of R_4, we have placed the s and p electrons on an equal footing in the same representation, and we will be able to find relations between functions and integrals involving these types of orbitals.

The connection between the physical and mathematical descriptions of R_4 is also clarified. The mathematical description (Racah) depends solely on the angular parts of the orbitals and of course on the permutation properties. The generators, expressed as tensor operators, have no dynamical significance. Thus R_4 would be a useful group for any set of s and p electrons. Each of these sets is characterized by the basic representation (10).

The generators in the physical description, on the other hand, are functions of the basic dynamical variables, position and momentum. Here the fact that we are dealing with $2s$, $2p$ rather than say $3s, 3p$ is essential. The $2s$ and $2p$ electrons completely fill the (10) representation of R_4, i.e. the representation corresponding to $n = 2$. If for example $n = 3$, there would not be enough orbitals, using s and p orbitals alone, to fill the representation (20), since the dimension of the (20) representation is nine. It is necessary in this case to consider all $n = 3$ orbitals $3s$, $3p$, and $3d$. Since for both the physical and the mathematical descriptions the same representation of R_4 is used for the $2s$ and $2p$ electrons and since in both cases the rows of the representations are labeled by the R_3 quantum numbers, the classification of configurations will yield the same results irrespective of the model of the group used. It is clear that it is only for the $2s^m 2p^n$ configurations that the group used as well as the relevant representations coincide.

II. CONSTRUCTION OF WAVE FUNCTIONS OF $2s^m 2p^n$ TRANSFORMING ACCORDING TO R_4

We will show the construction of the wave functions using both the mathematical and physical descriptions of R_4. These wave functions are needed in the discussion of the Coulomb interaction which is given in the following section and also in the evaluation of energy-level separations and near degeneracy correlation energies. These properties will be discussed in a subsequent paper. For the sake of clarity, in the remainder of this paper we will denote the mathematical and physical versions of R_4 as $R_4{}^m$ and $R_4{}^p$ respectively.

A. Mathematical

We have seen that $v_q{}^1(p,p)$ and $v_q{}^1(s,p)+v_q{}^1(p,s)$; $q=0, +1, -1$, are the six generators of R_4. The essential property of these generators is that matrix elements of any generator between two states transforming according to different representations of R_4 vanish. Upon examination of the branching rules for two-electron states we see that s^2S and p^2S have components in both the (00) and the (20) representations of $R_4{}^m$. The D state is unique. It is p^2D and therefore must be the (202) state. The three P states, p^2P, spP, and psP transform like linear combinations of (111), (1 − 1 1) and (201). The (111) and (1 − 1 1) states have zero coupling with the (202) state for the reason mentioned above, and thus we may determine the (111) and (1 − 1 1) states by means of the equations

$$\langle (ap^2+b\,sp+c\,ps)(111)| \times [V_0{}^1(s,p)+V_0{}^1(p,s)]\,|p^2(202)\rangle = 0\,, \tag{9}$$

$$\langle (a'p^2+b'\,sp+c'ps)(1-1\,1)| \times [V_0{}^1(s,p)+V_0{}^1(p,s)]\,|p^2(202)\rangle = 0\,, \tag{10}$$

where $V_0{}^1=\sum_i (V_0{}^1)_i$; i is summed over the number of particles. The (201) state is easily found using the fact that it must be orthogonal to (111) and (1 − 1 1). Finally we determine the linear combination of s^2S and p^2S transforming according to (00) by means of the relation

$$\langle (a''\,s^2+b''\,p^2)(000)|[V_0{}^1(s,p)+V_0{}^1(p,s)] \times |(ap^2+b\,sp+c\,ps)(111)\rangle = 0, \tag{11}$$

and the linear combination of s^2 and p^2S transforming according to (20) follows by orthogonality. The linear combinations for each of these states is shown in Table II.

The $R_4{}^m$ symmetric wave functions for states with more than two electrons are found in the same manner. These cases are somewhat more complicated, and either coefficients of fractional parentage or expansions in Slater determinants must be used. The one-electron operators, of course, remain the same. For these cases Racah's formulas[10] for matrix elements of one-electron operators making use of the coefficients of fractional parentage are invaluable.

TABLE II. Two-electron wave functions transforming according to irreducible representations of R_4 for $2s$, $2p$.

$(00)S$	$=$	$\frac{1}{2}\,\|2s^2\,S\rangle$	$-$	$(\sqrt{3}/2)\,\|2p^2\,S\rangle$		
$(20)S$	$=$	$(\sqrt{3}/2)\,\|2s^2S\rangle$	$+$	$\frac{1}{2}\,\|2p^2\,S\rangle$		
$(11)P$	$=$	$\frac{1}{2}(\sqrt{2}\,\|2p^2\,P\rangle$	$-$	$\|2s2p\,P\rangle$	$+$	$\|2p2s\,P\rangle)$
$(1-1)P$	$=$	$\frac{1}{2}(\sqrt{2}\,\|2p^2\,P\rangle$	$+$	$\|2s2p\,P\rangle$	$-$	$\|2p2s\,P\rangle)$
$(20)P$	$=$	$(1/\sqrt{2})\,\|2s2p\,P\rangle$	$+$	$(1/\sqrt{2})\,\|2p2s\,P\rangle$		
$(20)D$	$=$	$\|2p^2D\rangle$				

B. Physical

We have seen that the correspondence between the orbitals with principal quantum number two and the $(10LM)$ representation of $R_4{}^p$ is very close. Let us now investigate this correspondence in more detail. Following Fock and Shibuya-Wulfman,[11] let us take the Fourier transform of the position-space wave function:

$$\hat{\psi}(\vec{p}) = (2\pi)^{-3/2}\int \exp(i\vec{p}\cdot\vec{r})\psi(\vec{r})\,d^3r\,. \tag{12}$$

Then making the stereographic transformation from p-space to a four-sphere, we have

$$\begin{aligned} &\xi^2+\eta^2+\zeta^2+\chi^2=1\,,\\ &\xi = 2p_0p_x/(p_0{}^2+p^2) = \sin\alpha\,\sin\theta\,\cos\varphi\\ &\eta = 2p_0p_y/(p_0{}^2+p^2) = \sin\alpha\,\sin\theta\,\sin\varphi\\ &\zeta = 2p_0p_z/(p_0{}^2+p^2) = \sin\alpha\,\cos\theta\\ &\chi = (p_0{}^2-p^2)/(p_0{}^2+p^2) = \cos\alpha. \end{aligned} \tag{13}$$

It can be shown that

$$\psi(\alpha,\theta,\varphi) = (\pi/\sqrt{8})p_0{}^{-5/2}(p_0{}^2+p^2)\hat{\psi}(p),\qquad Z/p_0=n\,, \tag{14}$$

and that this $\psi(\alpha,\theta,\varphi)$ is precisely $\psi_{nlm}(\alpha,\theta,\varphi)$, the four-dimensional spherical harmonic and the representation $(n-1, 0lm)$ of R_4. Thus in the transformed space, the hydrogen orbitals can be identified with the representation of R_4. One note of caution: the four-sphere (in terms of p) is of radius $p_0=(-2E)^{1/2}$. Thus in order to remain on the same four-sphere we must restrict attention to hydrogen functions with the same principal quantum number.

Now we are able to determine the linear combinations of, for example, $2s^2S$ and $2p^2S$, that transform according to irreducible representations of R_4. If

$$(00)\,S = a\,2s^2\,S + b\,2p^2\,S\,,$$

then since $2s=(1000)$ and $2p_m=(101m)$,

$$a = \langle (0000)|(1000)(1000)\rangle$$

and $b = \langle (0000) | \sqrt{3}[(1011)(101-1)$

$$- (1010)(1010) + (101-1)(1011)] \rangle ,$$

where the matrix elements are the Clebsch-Gordan coefficients for the group R_4. Biedenharn[7] has derived a formula for these coefficients making use of the fact that $R_4 = R_3 \times R_3$.

$$\begin{aligned} &\langle p'q'l'm'; pqlm | p'q'pq; PQLM \rangle \\ &= (-1)^{l+l'-L}[(P+Q+1)(P-Q+1)(2l+1) \\ &\times (2l'+1)\langle l'm'lm | ll'LM \rangle] \\ &\times \chi \begin{Bmatrix} \frac{1}{2}(p+q) & \frac{1}{2}(p'+q') & \frac{1}{2}(P+Q) \\ \frac{1}{2}(p-q) & \frac{1}{2}(p'-q') & \frac{1}{2}(P-Q) \\ l & l' & L \end{Bmatrix} \end{aligned} \tag{15}$$

where $\langle l'm'lm | ll'LM \rangle$ is the ordinary R_3 Clebsch-Gordan coefficient and $\chi\{\vdots\vdots\vdots\}$ is the Wigner $9-j$ coefficient.[12] Tables of χ coefficients for half-integral values of the parameters are given by Smith and Stevenson.[13] In addition for the great majority of cases we consider, the $9-j$ symbol has at least one zero and it can be immediately reduced to the more familiar $6-j$ symbol by means of the formula

$$\chi \begin{Bmatrix} a & b & e \\ c & d & h \\ f & g & 0 \end{Bmatrix} = \frac{(-1)^{b+c+e+f}}{\{[e][f]\}^{1/2}} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} \delta_{eh}\delta_{fg} . \tag{16}$$

Using Biedenharn's formula we obtain $a = \frac{1}{2}$, $b = -\sqrt{3}/2$ exactly as we did using the generalized Racah tensors. The coefficients obtained by means of $R_4{}^p$ are identical to those obtained by means of $R_4{}^m$. The result is a consequence of the discussion at the end of the previous section dealing with the relationship between $R_4{}^m$ and $R_4{}^p$. As for the case of the Racah tensors, this method can be extended to obtain the R_4 symmetric wave functions with more than two electrons.

III. THE MODEL POTENTIAL FOR THE COULOMB INTERACTION

Our next concern is the determination of Coulomb and exchange integrals for the $2s$ and $2p$ orbitals group theoretically. To attain this end we write the $G = \sum_{i>j} 1/r_{ij}$ potential in the form $\sum_i a_i D_i$, where the a_i are real constants, and where each D_i is a linear combination of products of two one-electron tensors. These one-electron tensors are in the form of four-dimensional spherical harmonics. Each product contributing to the same D_i transforms according to the same irreducible representation of R_4. For electrons of principal quantum number two there are five independent parameters which determine all the possible Coulomb and exchange integrals. These are the F and G parameters[14] $F_0(2s, 2s)$, $F_0(2p, 2p)$, $F_2(2p, 2p)$, $F_0(2s, 2p)$, and $G_1(2s, 2p)$. All the Coulomb and exchange integrals are linear combinations of these parameters with coefficients determined by R_3. We will show that for $n = 2$ there are three different a_i and that the contributions to the integrals from the D_i are determined completely by R_4. Thus we can obtain all five necessary F and G parameters from a knowledge of three constants.

The number of different a_i necessary is simply the number of different irreducible representations of R_4 that contribute to the Coulomb interaction. We use the Wigner-Eckart theorem applied to R_4 to determine which representations of R_4 contribute to G. In R_4 the Wigner-Eckart theorem states that

$$\langle \gamma''p''q''l''m'' | A_{LM}{}^{PQ} | \gamma pqlm \rangle = \langle \gamma''p''q'' \| A^{PQ} \| \gamma pq \rangle \langle pqlm;\ PQLM | pqPQ; p''q''l''m'' \rangle , \tag{17}$$

where the second factor on the right-hand side is the R_4 Clebsch-Gordan coefficient and where γ, γ'' are any additional quantum numbers needed to specify the states.[7]

We first note that since G is spherically symmetric, $L = 0$. Since a 9-j symbol is zero if any column does not obey the triangle inequalities

$$a + b \geqslant c, \quad a + c \geqslant b, \quad b + c \geqslant a,$$

any possible nonzero R_4 contribution to G must have $\frac{1}{2}(P+Q) = \frac{1}{2}(P-Q)$, that is, $Q = 0$. By considering all possible R_4 representations on each side of the matrix element, making use of Table II, and by employing the well-known symmetry properties of the 9-j symbol, we can determine the possible R_4 representations contributing to G. Some of the possible matrix elements are

$$\langle (20) | A_1 | (20) \rangle, \quad \langle (20) | A_2 | (00) \rangle, \quad \langle (00) | A_3 | (00) \rangle, \quad \langle (111) | A_4 | (201) \rangle .$$

We find that A_1 is (000) or (200) or (400); A_2 must be (200); A_3 is (000) and A_4 must be (200). Consequently the Coulomb operator is of the form

$$G = a_1(000) + a_2(200) + a_3(400). \tag{18}$$

We must now determine the proper combination of products of four-dimensional spherical harmonics that contribute to each of these three irreducible representations of R_4. To accomplish this end we begin by expressing the Coulomb interaction in terms of equivalent operators in the form of tensors. Making use of the transformation properties of these tensors, we translate the expression into the representations of the physical description of the group R_4. We drop the parameters involving the radial parameters, since these are already included in the transformation properties of the four-dimensional spherical harmonics.

We now express G in terms of the equivalent operator

$$\begin{aligned}\textstyle\sum_{i>j} & F_0(2s,2s)v_i{}^0(s,s)\cdot v_j{}^0(s,s)+3F_0(2p,2p)v_i{}^0(p,p)\cdot v_j{}^0(p,p)\\ &+6F_2(2p,2p)v_i{}^2(p,p)\cdot v_j{}^2(p,p)+\sqrt{3}F_0(2s,2p)[v_i{}^0(s,s)\cdot v_j{}^0(p,p)\\ &+v_i{}^0(p,p)\cdot v_j{}^0(s,s)]+G_1(2s,2p)\{[v_i{}^1(s,p)-v_i{}^1(p,s)]\cdot[v_j{}^1(s,p)-v_j{}^1(p,s)]\}\,. \end{aligned}\tag{19}$$

Let us now determine the transformation properties of the v^k tensors. We have already noted that $v_q{}^k(l_1,l_2)$ transforms like $(-1)^{l_2}|l_1l_2kq\rangle$. We can find the transformation properties of $|l_1l_2kq\rangle$ in terms of R_4 irreducible representations in one of two ways. We can solve the set of simultaneous equations expressing the irreducible representations of R_4 in terms of the s^mp^n configurations (Table II), for the s^mp^n configurations themselves. Or we can use methods analogous to those outlined in the preceding section. Explicitly the Clebsch-Gordan coefficient

$$\langle(p'''q''')|l_1(pq),l_2(p'q')\rangle$$

is the coefficient of the representation $(p'''q''')$ for the configuration $|l_1l_2kq\rangle$.

The Coulomb interaction is now in the form of linear combinations of products of four-dimensional spherical harmonics. For example $v^0(s,s)\cdot v^0(s,s)$ becomes

$$\tfrac{1}{4}(00)(00)+\sqrt{3}/4[(00)(20)+(20)(00)]+\tfrac{3}{4}(20)(20)\,.\tag{20}$$

Analogous expressions are derived for each of the other terms of Eq. (19). This expression (20) has components in the (000), (200), and (400) representations. Using the Clebsch-Gordan coefficients again we determine the fraction of $v^0(s,s)\cdot v^0(s,s)$ in each of the (000), (200), and (400) representations. Thus the $(200)\circ(200)$ part of $v^0(s,s)\cdot v^0(s,s)$ is decomposed into

$$\tfrac{1}{3}(00)+(\sqrt{3}/3)(20)+(\sqrt{5}/3)(40)\,.\tag{21}$$

This procedure is carried out for the other terms contributing to $v^0(s,s)\cdot v^0(s,s)$ as well as for the other terms constituting the Coulomb interaction. All such products transforming as (000) have coefficient a_1, those transforming as (200) have coefficient a_2 and similarly for (400). We have thus been able to cast the Coulomb interaction into the desired form. For example the term derived from $v^0(s,s)\cdot v^0(s,s)$ and thus the value of $1/r_{12}$ for the integral $\langle 2s2s|1/r_{12}|2s2s\rangle$ is

$$\begin{aligned}& a_1[\tfrac{1}{4}(00)(00)+\tfrac{1}{4}(20)(20)]\\ &\quad+a_2[(\sqrt{3}/4)(00)(20)+(\sqrt{3}/4)(20)(00)+(\sqrt{3}/4)(20)(20)]+a_3(\sqrt{5}/4)(20)(20)\,.\end{aligned}\tag{22}$$

Matrix elements for various configurations can now be evaluated. We must deal with linear combinations of matrix elements of the form

$$\begin{aligned}& a_i\langle(pqlm)(p'q'l'm')|(PQLM)\cdot(P'Q'L'M')|(p''q''l''m'')(p'''q'''l'''m''')\rangle\\ &\quad=a_i\langle(pqlm)|(PQLM)|(p''q''l''m'')\rangle\langle(p'q'l'm')|(P'Q'L'M')|(p'''q'''l'''m''')\rangle\,,\end{aligned}\tag{23}$$

where $i=1$, 2, or 3 depending on whether we are dealing with the (000), (200), or (400) component of $(PQLM)\cdot(P'Q'L'M')$. These expressions can be evaluated by means of the Shibuya-Wulfman expression for the decomposition of the product of two four-dimensional spherical harmonics having the same arguments.

$$\begin{aligned}\psi_{n'l'm'}(\Omega)\psi_{nlm}(\Omega)=&\sum_{NLM}(i)^{l+l'-L}[n'nN(2l'+1)(2l+1)]^{\frac{1}{2}}\\ &\times\langle l'lm'm|l'lLM\rangle\,\chi\left\{\begin{matrix}\frac{1}{2}(n'-1) & \frac{1}{2}(n-1) & \frac{1}{2}(N-1)\\ \frac{1}{2}(n'-1) & \frac{1}{2}(n-1) & \frac{1}{2}(N-1)\\ l' & l & L\end{matrix}\right\}\psi_{NLM}(\Omega)\,.\end{aligned}\tag{24}$$

The coefficients a_1, a_2, a_3 are determined by using three calculated integrals over hydrogen orbitals. Hydrogen orbitals are used in order to test the accuracy of the R_4 model in yielding the Coulomb integrals between two hydrogen orbitals. This calculation of course does not refer to any actual system, not even the H^- ion. But it is used here only for a mathematical test in reproducing the fictitious F and G integrals with hydrogen orbitals. We compare the values of the F and G parameters calculated by means of $R_4{}^p$ with those calculated by actual integration over hydrogen orbitals. By solving three simultaneous linear equations a_1, a_2, and a_3 are found and from these the values of $F_0(2s,2p)$ and $G_1(2s,2p)$ can be determined.

TABLE III. Coulomb and exchange integrals (principal quantum number = 2).

	Hydrogen Orbitals[a]		Hartree-Fock orbitals for boron[b]	
	Exact	R_4	Exact	R_4
$F^0(2s,2s)$	0.150 39	fitted	0.460 26	fitted
$F^0(2p,2p)$	0.181 64	fitted	0.417 71	fitted
$F^2(2p,2p)$	0.087 90	fitted	0.189 75	fitted
$F^0(2s,2p)$	0.162 11	0.173	0.437 36	0.461
$G^1(2s,2p)$	0.087 90	0.075	0.273 29	0.277

[a] See text.

[b] E. Clementi, IBM J. Res. Develop. 9, 2 (1965).

This type of calculation of Coulomb integrals has also been done for the Hartree-Fock self-consistent-field orbitals of boron to show the applicability of the method to an actual atom. Table III gives the results of these calculations. In each case we note the good agreement for the $F_0(2s,2p)$ and $G_1(2s,2p)$. All other Coulomb and exchange integrals are easily obtained by using the c_k and a_k coefficients as tabulated in, for example, Ref. 14.

This method for calculating Coulomb and exchange integrals using $R_4{}^p$ is based on the fact that, although hydrogen and Hartree-Fock orbitals are quite different from each other, orbitals of each type transform among themselves in approximately the same manner. That is, if the values of a particular property using one set of orbitals is known, then given a proper "scale," the values of that property using the other set can be determined. In our calculation, the evaluation of the parameters a, b, and c determine the scale. It is for this reason that we can expect $R_4{}^p$ to give good values for Coulomb and exchange integrals of Hartree-Fock orbitals even though the theory is based on hydrogenic ones. The R_4 calculations using hydrogen orbitals do not agree exactly with hydrogen Coulomb and exchange integrals, because the R_4 calculation assumes that $\vec{L}\cdot\vec{A}=0$, i.e. $q=0$. For many-electron wave functions, q is not necessarily equal to zero as we see from Table II.

IV. EXTENSION TO $3s$, $3p$, $3d$ ORBITALS

For the $n=3$ level of orbitals the groups used in the mathematical and physical descriptions no longer coincide. As previously mentioned the group used in the mathematical description is R_9, whereas the one used in the physical description remains R_4. We apply exactly the same methods here as we did for the $n=2$ case. The two-electron R_4-symmetric wave functions are determined and are given in Table IV. The Coulomb interaction is written in terms of equivalent operators and since the group is still R_4, we use exactly the same method to derive the model potential in terms of four-dimensional spherical harmonics. Let us note that for the $n=3$ case there are five parameters corresponding to the (000), (200), (400), (600), and (800) representations of R_4 that contribute to G. Since there are fourteen F and G parameters, the $n=3$ case, in which the number

TABLE IV. Two electron wave functions transforming according to irreducible representations of R_4 for $3s, 3p, 3d$.

$$\begin{aligned}
(000)S &= \tfrac{1}{3}|3s^2\rangle - (\sqrt{3}/3)\,|3p^2\rangle + (\sqrt{5}/3)\,|3d^2\rangle\\
(200)S &= (\sqrt{3}/3)\,|3s^2\rangle - \tfrac{1}{2}|3p^2\rangle - (\sqrt{15}/6)\,|3d^2\rangle\\
(400)S &= (\sqrt{5}/3)\,|3s^2\rangle + (\sqrt{15}/6)\,|3p^2\rangle + \tfrac{1}{6}|3d^2\rangle\\
(201)P &= (\sqrt{3}/6)\,|3s3p\rangle + (\sqrt{3}/6)\,|3p3s\rangle - (\sqrt{15}/6)\,|3p3d\rangle - (\sqrt{15}/6)\,|3d3p\rangle\\
(401)P &= (\sqrt{15}/6)\,|3s3p\rangle + (\sqrt{15}/6)\,|3p3s\rangle + (\sqrt{3}/6)\,|3p3d\rangle + (\sqrt{3}/6)\,|3d3p\rangle\\
(111)P &= -\tfrac{1}{3}|3s3p\rangle + \tfrac{1}{3}|3p3s\rangle + (\sqrt{5}/6)\,|3p3d\rangle - (\sqrt{5}/6)\,|3d3p\rangle + (\sqrt{3}/6)\,|3p^2\rangle + (\sqrt{15}/6)\,|3d^2\rangle\\
(1-1\ 1)P &= +\tfrac{1}{3}|3s3p\rangle - \tfrac{1}{3}|3p3s\rangle - (\sqrt{5}/6)\,|3p3d\rangle + (\sqrt{5}/6)\,|3d3p\rangle + (\sqrt{3}/6)\,|3p^2\rangle + (\sqrt{15}/6)\,|3d^2\rangle\\
(311)P &= -(\sqrt{5}/6)\,|3s3p\rangle + (\sqrt{5}/6)\,|3p3s\rangle - \tfrac{1}{3}|3p3d\rangle + \tfrac{1}{3}|3d3p\rangle + (\sqrt{15}/6)\,|3p^2\rangle - (\sqrt{3}/6)\,|3d^2\rangle\\
(3-1\ 1)P &= (\sqrt{5}/6)\,|3s3p\rangle - (\sqrt{5}/6)\,|3p3s\rangle + \tfrac{1}{3}|3p3d\rangle - \tfrac{1}{3}|3d3p\rangle + (\sqrt{15}/6)\,|3p^2\rangle - (\sqrt{3}/6)\,|3d^2\rangle\\
(202)D &= \tfrac{1}{2}|3p^2\rangle - (\sqrt{21}/6)\,|3d^2\rangle - (\sqrt{3}/6)\,|3s3d\rangle - (\sqrt{3}/6)\,|3d3s\rangle\\
(402)D &= (\sqrt{21}/6)\,|3p^2\rangle + \tfrac{1}{6}|3d^2\rangle + (\sqrt{7}/6)\,|3s3d\rangle + (\sqrt{7}/6)\,|3d3s\rangle\\
(222)D &= -(\sqrt{3}/6)\,|3p^2\rangle - (\sqrt{7}/6)\,|3d^2\rangle + \tfrac{1}{3}|3s3d\rangle + \tfrac{1}{3}|3d3s\rangle + \tfrac{1}{2}|3p3d\rangle - \tfrac{1}{2}|3d3p\rangle\\
(2-2\ 2)D &= -(\sqrt{3}/6)\,|3p^2\rangle - (\sqrt{7}/6)\,|3d^2\rangle + \tfrac{1}{3}|3s3d\rangle + \tfrac{1}{3}|3d3s\rangle - \tfrac{1}{2}|3p3d\rangle + \tfrac{1}{2}|3d3p\rangle\\
(312)D &= \tfrac{1}{2}|3s3d\rangle - \tfrac{1}{2}|3d3s\rangle + \tfrac{1}{2}|3p3d\rangle + \tfrac{1}{2}|3d3p\rangle\\
(3-1\ 2)D &= -\tfrac{1}{2}|3s3d\rangle + \tfrac{1}{2}|3d3s\rangle + \tfrac{1}{2}|3p3d\rangle + \tfrac{1}{2}|3d3p\rangle\\
(313)F &= (1/\sqrt{2})\,|3d^2\rangle + \tfrac{1}{2}|3p3d\rangle - \tfrac{1}{2}|3d3p\rangle\\
(3-1\ 3)F &= (1/\sqrt{2})\,|3d^2\rangle - \tfrac{1}{2}|3p3d\rangle + \tfrac{1}{2}|3d3p\rangle\\
(403)F &= (1/\sqrt{2})\,|3p3d\rangle + (1/\sqrt{2})\,|3d3p\rangle\\
(404)G &= |3d^2\rangle
\end{aligned}$$

of parameters is reduced to five provides a more stringent test of the model potential. These calculations for the $n = 3$ case were carried out in the same manner as those for the $n = 2$ case. The results of the calculation for both hydrogen ($Z = 1$) orbitals and for the Hartree-Fock orbitals of magnesium are given in Table V. The Hartree-Fock orbitals of magnesium were obtained from the work of McKoy and Sinanoḡlu.[15] They used the actual 3*s* orbital and virtual 3*p* and 3*d* orbitals in the study of near-degeneracy correlation effects in second-row atoms.

V. CONCLUSION

A discussion of and the relationship between the physical and mathematical description of Lie groups for atomic systems has been given. We determined the transformation properties for states having $2s^m 2p^n$ configurations using both descriptions. Using a model potential for the Coulomb interaction we obtained Coulomb and exchange integrals group theoretically. The method was extended to $3s^m 3p^n 3d^r$ configurations. The states were classified according to R_4 and Coulomb and exchange integrals were evaluated. The good agreement with the actual value of these integrals indicates that R_4 does have relevance as an approximate symmetry for atoms having a greater number of electrons than hydrogen.

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TABLE V. Coulomb and exchange integrals (principal quantum number = 3).

	Hydrogen Orbitals[a]		Hartree-Fock orbitals for magnesium[b]	
	Exact	R_4	Exact	R_4
$F^0(3s, 3s)$	0.066 325	fitted	0.280 326	fitted
$F^0(3s, 3p)$	0.068 750	fitted	0.254 942	fitted
$F^0(3s, 3d)$	0.073 089	fitted	0.268 379	fitted
$F^0(3p, 3p)$	0.071 865	fitted	0.235 970	fitted
$F^2(3p, 3p)$	0.035 987	0.046	0.123 456	0.135
$F^0(3p, 3d)$	0.076 930	0.076	0.246 005	0.243
$F^2(3p, 3d)$	0.036 132	0.032	0.128 257	0.131
$F^0(3d, 3d)$	0.086 046	fitted	0.258 023	fitted
$F^2(3d, 3d)$	0.045 421	0.040	0.136 202	0.116
$F^4(3d, 3d)$	0.029 622	0.028	0.088 828	0.081
$G^1(3s, 3p)$	0.042 292	0.031	0.170 336	0.163
$G^2(3s, 3d)$	0.022 774	0.018	0.140 433	0.141
$G^1(3p, 3d)$	0.034 179	0.030	0.166 871	0.172
$G^3(3p, 3d)$	0.024 052 1	0.019	0.100 961	0.100

[a] See text.

[b] These are the actual 3*s* and the virtual 3*p* and 3*d* used by V. McKoy and O. Sinanoḡlu, Modern Quantum Chemistry (Academic Press, Inc., New York 1965), Vol. 2, p. 23, in the study of near degeneracy correlation effects of second-row atoms.

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