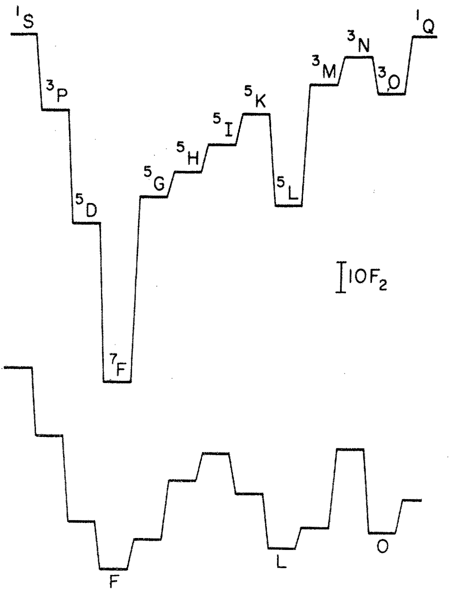

FIG. 1. The upper sequence of terms is calculated by diagonalizing the complete $4f^6$ matrices, assuming hydrogenic eigenfunctions. Only the lowest term with a given $L$ is represented. The lower sequence of terms is calculated in the approximation that (a) the character of the eigenfunctions of the terms in question is determined principally by the coupling $(I \times I)L$; and (b) within the $I$ term of $f^3$, tensors of rank 6 predominate.

to Racah.[8] For our purposes, it runs

$$(-1)^L \begin{Bmatrix} L & 6 & 6 \\ 6 & 6 & 6 \end{Bmatrix} \simeq \frac{P_L(\frac{1}{2})}{13}$$

for small $L$; but it does not work well for $L > 6$.

Application of these ideas can be made to a wide variety of allied problems. For example, the highest $S$, $D$, and $P$ terms of $f^4$ should result from the coupling $(P \times P)L$, since $P$ is the uppermost term of $f^2$ for which all $m_s = \frac{1}{2}$ or all $m_s = -\frac{1}{2}$. We should therefore expect the ordering $E_S > E_D > E_P$, which holds for $p^2$, to be satisfied for the highest terms of $f^4$. A detailed calculation[9] shows that this is indeed so. The chief advantage of this kind of approach is that it gives a broad understanding of relative term energies in certain circumstances; to obtain really accurate results a superposition of all possible basis states is required.

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# Atomic *g* Electrons*

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A scheme is presented for giving a complete classification of the states of the atomic configurations $g^N$. Repeated terms are separated by diagonalizing an operator $e$ that has, as its analog in the $f$ shell, the operator that classifies states according to the group $G_2$. Properties of $e$ that are typically group-theoretical in character are noted. Tables of fractional parentage coefficients and the energies of the terms of maximum multiplicity are given.

A glance at Charlotte Moore's compilation of atomic energy levels[1] reveals that single $g$ electrons have been observed in many atoms and ions. Theoretical preparations for $g^2$ were made as long ago as 1938 by Shortley and Fried.[2] Shudeman,[3] Karayianis,[4] and Wybourne[5] have counted and partially classified the states of $g^N$. The classification, as it stands at present, is inadequate because many like terms (i.e., terms with the same quantum numbers $S$ and $L$) are not separated by the groups used. It is the purpose of this article to give a method of uniquely specifying the states of the $g$ shell. Such a method is particularly valuable at a time when interest in super-heavy atoms and complex atomic configurations is increasing; but as will be seen from the subsequent discussion, it uncovers a theoretical problem that is of considerable interest in its own right.

The scheme we choose to adopt for defining the states of the $g$ shell is based on a separation of the electrons according to their spin orientations, $m_S$. All those electrons with spin up are considered to lie in a space $A$; all those with spin down in a space $B$. A state of $g^N$ is defined by writing

$$|([\lambda_A]\,\tau_A L_A \times [\lambda_B]\,\tau_B L_B) L M_L\rangle\,, \qquad (1)$$

as has been described in detail elsewhere.[6] The tableaux $[\lambda_A]$ and $[\lambda_B]$ are both of the type $[11\ldots1]$; the number ($\alpha$ or $\beta$) of symbols 1 gives the number of electrons in each space. Evidently

$$N=\alpha+\beta\,, \quad M_S=\tfrac{1}{2}(\alpha-\beta)\,.$$

Because of the alignments of the spins in the $A$ space, only those $L_A$ values occur that correspond to the terms of maximum multiplicity in $g^\alpha$. There are several duplications. The distinguishing symbol $\tau_A$ is required to separate a pair of $F$ terms when $\alpha=3$ or 6, and the pairs $D$, $G$, and $I$ when $\alpha=4$ or 5. Similar remarks apply to the $B$ space.

A direct way to give meaning to the symbols $\tau_A$ and $\tau_B$ is to construct coefficients of fractional parentage (cfp) for the terms of maximum multiplicity in $g^3$ and $g^4$. If we use the scheme (1), there is no need to construct any other cfp, since we can always exploit the electron-hole symmetry in the $A$ space or in the $B$ space when necessary. However, it is highly desirable to have some systematic procedure for constructing the cfp of the duplicated terms. In the case of the $f$ shell, the classification through the group $G_2$ is equivalent to diagonalizing the scalar two-body operator

$$e' = \sum_{i>j}\left[(\underline{v}_i^{(1)}\cdot\underline{v}_j^{(1)}) - 2(\underline{v}_i^{(3)}\cdot\underline{v}_j^{(3)}) + (\underline{v}_i^{(5)}\cdot\underline{v}_j^{(5)})\right]\,,$$

where $\underline{v}^{(k)}$ is a single-electron tensor operator with reduced matrix element $(2k+1)^{1/2}$. The operator $e'$ transforms according to the representations (111) of $R_7$ and (00) of $G_2$.[7] Although there is no analog of the group $G_2$ in the case of $g$ electrons, we can nevertheless construct an operator that is scalar and transforms according to the representation (1111) of $R_9$. It is

$$e = \sum_{i>j}\left[11(\underline{v}_i^{(1)}\cdot\underline{v}_j^{(1)}) - 14(\underline{v}_i^{(3)}\cdot\underline{v}_j^{(3)}) - 5(\underline{v}_i^{(5)}\cdot\underline{v}_j^{(5)}) + 8(\underline{v}_i^{(7)}\cdot\underline{v}_j^{(7)})\right]\,.$$

Any operator belonging to (1111) must have vanishing matrix elements for the singlets of $g^2$, and this condition enables the coefficients in the above expression for $e$ to be obtained.

The procedure of Redmond[8] is the most convenient for calculating the required cfp. The results are set out in Tables I and II. All duplicated terms can be separated by diagonalizing $e$, and the eigenvalues $\langle e\rangle$ are included in the tables. What is especially remarkable is the frequent occurrence of repeated eigenvalues. For example, in $g^4$ we find $\langle e\rangle=15$ four times and $\langle e\rangle=-9$ four

TABLE I. Coefficients of fractional parentage for $g^3$.

| | | | $g^2$ | | | |
|---|---|---|---|---|---|---|
| $g^3$ | $\langle e\rangle$ | $D$[a] | $^3P$ | $^3F$ | $^3H$ | $^3K$ |
| $^4P$ | −29 | $27^{\frac{1}{2}}$ | 0 | $14^{\frac{1}{2}}$ | $13^{\frac{1}{2}}$ | 0 |
| $^4F$ | 11 | $126^{\frac{1}{2}}$ | 7 | $12^{\frac{1}{2}}$ | $33^{\frac{1}{2}}$ | $32^{\frac{1}{2}}$ |
| $^4F'$ | −24 | $6006^{\frac{1}{2}}$ | 0 | −52 | $2816^{\frac{1}{2}}$ | $-486^{\frac{1}{2}}$ |
| $^4G$ | −9 | $2970^{\frac{1}{2}}$ | $363^{\frac{1}{2}}$ | $-1372^{\frac{1}{2}}$ | $-275^{\frac{1}{2}}$ | $960^{\frac{1}{2}}$ |
| $^4H$ | 11 | $6435^{\frac{1}{2}}$ | $-1859^{\frac{1}{2}}$ | $546^{\frac{1}{2}}$ | $1650^{\frac{1}{2}}$ | $2380^{\frac{1}{2}}$ |
| $^4I$ | −9 | $429^{\frac{1}{2}}$ | 0 | $52^{\frac{1}{2}}$ | $-275^{\frac{1}{2}}$ | $102^{\frac{1}{2}}$ |
| $^4K$ | −2 | $3861^{\frac{1}{2}}$ | 0 | $1105^{\frac{1}{2}}$ | $-704^{\frac{1}{2}}$ | $-2052^{\frac{1}{2}}$ |
| $^4M$ | 15 | $13^{\frac{1}{2}}$ | 0 | 0 | $3^{\frac{1}{2}}$ | $-10^{\frac{1}{2}}$ |

[a] The number $D$ is a common divisor for all entries standing to the right.

TABLE II. Coefficients of fractional parentage for $g^4$.

| $g^4$ | $\langle e \rangle$ | $D$[a] | $g^3$ |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | $^4P$ | $^4F$ | $^4F'$ | $^4G$ | $^4H$ | $^4I$ | $^4K$ | $^4M$ |
| $^5S$ | $-18$ | $1$ | $0$ | $0$ | $0$ | $1$ | $0$ | $0$ | $0$ | $0$ |
| $^5D$ | $-33$ | $1120^{\frac{1}{2}}$ | $0$ | $-3$ | $-572^{\frac{1}{2}}$ | $175^{\frac{1}{2}}$ | $0$ | $364^{\frac{1}{2}}$ | $0$ | $0$ |
| $^5D'$ | $15$ | $5280^{\frac{1}{2}}$ | $0$ | $1573^{\frac{1}{2}}$ | $44^{\frac{1}{2}}$ | $819^{\frac{1}{2}}$ | $-2816^{\frac{1}{2}}$ | $-28^{\frac{1}{2}}$ | $0$ | $0$ |
| $^5F$ | $-9$ | $1848^{\frac{1}{2}}$ | $231^{\frac{1}{2}}$ | $-275^{\frac{1}{2}}$ | $-208^{\frac{1}{2}}$ | $-315^{\frac{1}{2}}$ | $-385^{\frac{1}{2}}$ | $-26^{\frac{1}{2}}$ | $408^{\frac{1}{2}}$ | $0$ |
| $^5G$ | $2$ | $558558^{\frac{1}{2}}$ | $0$ | $148720^{\frac{1}{2}}$ | $-47385^{\frac{1}{2}}$ | $-13104^{\frac{1}{2}}$ | $-137984^{\frac{1}{2}}$ | $131040^{\frac{1}{2}}$ | $80325^{\frac{1}{2}}$ | $0$ |
| $^5G'$ | $-29$ | $40920^{\frac{1}{2}}$ | $10571^{\frac{1}{2}}$ | $-33^{\frac{1}{2}}$ | $-5616^{\frac{1}{2}}$ | $1365^{\frac{1}{2}}$ | $-165^{\frac{1}{2}}$ | $-13650^{\frac{1}{2}}$ | $9520^{\frac{1}{2}}$ | $0$ |
| $^5H$ | $-9$ | $17160^{\frac{1}{2}}$ | $2028^{\frac{1}{2}}$ | $-1144^{\frac{1}{2}}$ | $2888^{\frac{1}{2}}$ | $-4680^{\frac{1}{2}}$ | $-1760^{\frac{1}{2}}$ | $-325^{\frac{1}{2}}$ | $60^{\frac{1}{2}}$ | $-4275^{\frac{1}{2}}$ |
| $^5I$ | $-9$ | $112112^{\frac{1}{2}}$ | $0$ | $1001^{\frac{1}{2}}$ | $-4732^{\frac{1}{2}}$ | $-22295^{\frac{1}{2}}$ | $10780^{\frac{1}{2}}$ | $24752^{\frac{1}{2}}$ | $48552^{\frac{1}{2}}$ | $0$ |
| $^5I'$ | $15$ | $583440^{\frac{1}{2}}$ | $0$ | $206635^{\frac{1}{2}}$ | $5780^{\frac{1}{2}}$ | $-33813^{\frac{1}{2}}$ | $-89012^{\frac{1}{2}}$ | $-70720^{\frac{1}{2}}$ | $27000^{\frac{1}{2}}$ | $150480^{\frac{1}{2}}$ |
| $^5K$ | $-9$ | $240240^{\frac{1}{2}}$ | $0$ | $1144^{\frac{1}{2}}$ | $41472^{\frac{1}{2}}$ | $22932^{\frac{1}{2}}$ | $2618^{\frac{1}{2}}$ | $-63869^{\frac{1}{2}}$ | $57000^{\frac{1}{2}}$ | $51205^{\frac{1}{2}}$ |
| $^5L$ | $15$ | $194480^{\frac{1}{2}}$ | $0$ | $0$ | $0$ | $16796^{\frac{1}{2}}$ | $-63954^{\frac{1}{2}}$ | $9945^{\frac{1}{2}}$ | $-33000^{\frac{1}{2}}$ | $-70785^{\frac{1}{2}}$ |
| $^5N$ | $15$ | $2856^{\frac{1}{2}}$ | $0$ | $0$ | $0$ | $0$ | $0$ | $425^{\frac{1}{2}}$ | $660^{\frac{1}{2}}$ | $-1771^{\frac{1}{2}}$ |

[a] The number $D$ is a common divisor for all entries standing to the right.

times. Repetitions of this kind are characteristic of eigenfunctions belonging to a common irreducible representation of a group; and yet a detailed study has failed to uncover any group which is a subgroup of $R_9$ and which, at the same time, possesses as a subgroup the rotation group $R_3$ in ordinary three-dimensional space.[9] At the moment, the reason for the repeated eigenvalues is obscure. It would be very interesting to see whether analogous repetitions occur for $h$ electrons.

The tables of cfp have been used to calculate the energies of the terms of maximum multiplicity for the $g$ shell. Although there are five Slater integrals $F_k (k=0,2,4,6,$ and $8)$, the relative energies of these terms depend on only two linear combinations of these quantities, namely[6]

$$Y=3(5F_2+10F_4-3F_6-68F_8)$$

and $Z=3(7F_2-35F_4+27F_6+17F_8)$.

If the radial eigenfunction $R$ is strongly peaked at a certain radial distance $a$ [i.e., if $R \sim \delta(r-a)$], then $Z<0$; as the function broadens out, $Z$ passes through zero and becomes positive. The zero corresponds quite closely to hydrogenic $5g$ eigenfunctions.[10] To simplify the analysis, it is convenient to set $Z=0$. All spacings (for terms of maximum multiplicity) involve just one quantity, $Y$. The term schemes can thus be drawn out subject to a single scaling factor; this is done in Fig. 1. The actual numerical values are collected in Table III.

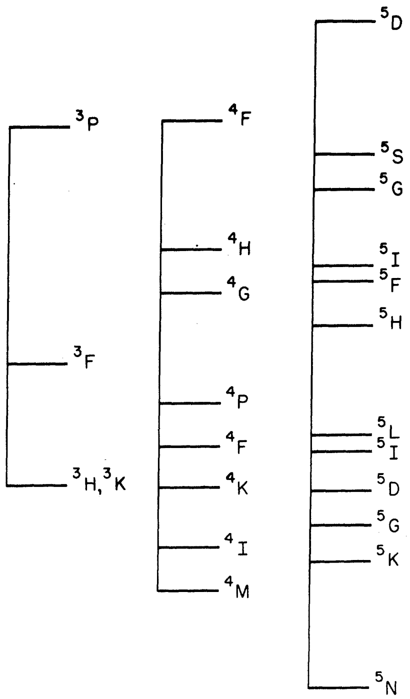

FIG. 1. Relative energies of the terms of maximum multiplicity for $g^2$, $g^3$, and $g^4$. The assumption for $g^2$ that $E(^3H)=E(^3K)$ corresponds closely to the situation for a hydrogenic $5g$ eigenfunction. As is made clear in Table III, the term patterns for other $g^N$ configurations are simply related to the ones drawn out here.

TABLE III. Relative energies of terms of maximum multiplicity for $g^N$ in units of $Y/12$.

| Configuration | $L$ | Energy |
|---|---|---|
| $g^2, g^7, g^{11}, g^{16}$ | $P$ | 1001 |
| | $F$ | 221 |
| | $H, K$ | $-175$ |
| $g^3, g^6, g^{12}, g^{15}$ | $P$ | 91 |
| | $F$ | $485 \pm 286\,276^{\frac{1}{2}}$ |
| | $G$ | 455 |
| | $H$ | 595 |
| | $I$ | $-381$ |
| | $K$ | $-185$ |
| | $M$ | $-525$ |
| $g^4, g^5, g^{13}, g^{14}$ | $S$ | 910 |
| | $D$ | $576 \pm 592\,036^{\frac{1}{2}}$ |
| | $F$ | 494 |
| | $G$ | $240 \pm 303\,300^{\frac{1}{2}}$ |
| | $H$ | 350 |
| | $I$ | $240 \pm 91\,396^{\frac{1}{2}}$ |
| | $K$ | $-430$ |
| | $L$ | $-14$ |
| | $N$ | $-850$ |

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[10] A hydrogenic $5g$ eigenfunction gives a small negative value to $Z$, not a positive value as stated in Ref. 6.

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# Photo-Ionization of the Hydrogen Molecule

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One-center wave functions are employed to investigate the photo-ionization of the hydrogen molecule from its ground state $X(1s\sigma\,{}^1\Sigma_g{}^+)$, from 700 to 300 Å. It is assumed that the residual ion is left in its ground state, and the free electron is in a $p\sigma$ or $p\pi$ orbital. Using the one-center wave functions for $H_2{}^+$ for the internuclear distance equal to $1.4a_0$, the free-electron wave functions are obtained by solving the integrodifferential equations in exchange and polarized-orbital approximations. The oscillator strengths obtained in the polarized-orbital approximation are found to be in satisfactory agreement with the experimental data.

## I. INTRODUCTION

Recently the author[1–3] has employed one-center wave functions for the hydrogen molecule to investigate the direct and the exchange excitation of the molecule due to electron bombardment. For these bound-bound transitions, satisfactory agreement between the theory and the experiment has been obtained. Hence it seems interesting to extend the use of one-center wave functions to the investigation of the bound-free transitions.

In 1960, Shimizu[4] investigated the photo-ionization of the hydrogen molecule. He employed two-center wave functions for $H_2$ and $H_2{}^+$. However, the free electron was represented by a plane wave, which is not likely to be a good approximation. Flannery and Öpik,[5] in 1965, reinvestigated the problem, again employing two-center wave functions for $H_2$ and $H_2{}^+$. To obtain the wave function of the free electron, they considered its motion in the field of two positive charges, each of half a unit, separated by a distance. Thus, the solution of the continuum orbital was obtained for a one-electron system. The use of these solutions in the computation of the matrix elements of the photo-ionization cross section completely ignores the effects of the departure of the static field from the two-point charge field, of the exchange of the free electron with the bound electron, and of the polarization of the bound-electron orbital by the free electron. One-center wave functions provide an easy means of studying all the above-mentioned effects which are found to be of significance in atomic systems.

Recently, Temkin and Vasavada[6] have analyzed the electron-molecule scattering problem in spherical coordinates. In addition, they have generalized the method of polarized orbitals to treat the electron scattering from diatomic molecules, with specific application to $H_2{}^+$. The chief idea of their method is the utilization of a single-center expansion for the target system. Their