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Atomic Term Patterns*

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The electrostatic energies of terms of complex configurations can sometimes be understood better by separating the electrons according to their spin orientation and then coupling the two parts. The method is illustrated in detail for the low terms of f^6 .

Although traditional atomic-shell theory rests on the separation of the spin and orbital spaces, a number of advantages accrue if the electrons of a configuration are separated according to their spin orientation, $m_s.^{1,2}$ The purpose of this note is to point out that this alternative approach leads to a better understanding of the relative energies of the low-lying terms of $4f^6$.

The energies of the lowest S term, the lowest P term, the lowest D term, etc., as found by Gruber and Conway³ for 4f hydrogenic eigenfunctions are plotted out (in units of the Slater integral F_2) in the upper part of Fig. 1. The total spin S varies from term to term; but all terms possess components for which $M_S = 0$. To achieve this value of M_S in f^6 , we must have $m_S = \frac{1}{2}$ for three electrons, and $m_s = -\frac{1}{2}$ for the remaining three. Each triple must have as its principal component the ${}^{4}I$ term of f^{3} , since this is the lowest term of f^3 for which all m_S are equal. In this approximation, the 13 terms of Fig. 1 result from the coupling $(I \times I)L$, in which $0 \le L \le 12$. If we expand the Coulomb interaction between the electrons as scalar products of spherical harmonics Y_{ka} , Eq. (7.1.6) of Edmonds⁴ tells us that the relative energies of the terms $(I \times I)L$ are given by

$$\sum_{k} (-1)^{L} \left\{ \begin{array}{c} L & 6 & 6 \\ k & 6 & 6 \end{array} \right\} ({}^{4}I || C^{(k)} || {}^{4}I)^{2}F^{(k)} ,$$

in which $\underline{C}^{(k)} = [4\pi/(2k+1)]^2 \underline{Y}_k$, and $F^{(k)}$ is a

Slater integral. Now, the reduced matrix elements of $\underline{C}^{(k)}$ for the 4I term of f^{3} possess an interesting property: The one for which k = 6 is much larger than the ones for which k = 2 or 4. Dropping the constant term (k = 0), and using the tables of Nielson and Koster⁵ for the reduced matrix elements, we find that the relative energies E_L of the terms $(I \times I)L$ are given approximately by

$$E_{L} = \frac{419900}{11} (-1)^{L} \left\{ \begin{array}{c} L & 6 & 6 \\ 6 & 6 & 6 \end{array} \right\} F_{6} ,$$

where $F^{(6)} = 7361.64F_6$. The 6-*j* symbols can be readily evaluated, and the energies E_L are plotted out in the lower part of Fig. 1. The relation F_6 = $(175/11583)F_2$, which is appropriate to 4f hydrogenic eigenfunctions,⁷ is used to scale correctly the upper and lower parts of Fig. 1.

The correspondence between the upper and lower parts of Fig. 1 is striking. The differences $E_{L+1}-E_L$ are correctly predicted in all cases except one (for which L = 6). This relation between terms of different L is not at all apparent in the conventional approach, which would lead us to think of the term energies in the upper part of Fig. 1 merely as the lowest eigenvalues of thirteen independent matrices. (There are, for example, six ${}^{3}P$ terms in f^{6} .) The rapid descent from ${}^{1}S$ to ${}^{7}F$ can be understood in even more basic terms by using an asymptotic formula due

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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

$$(-1)^{L} \left\{ \begin{array}{c} L & 6 & 6 \\ 6 & 6 & 6 \end{array} \right\} \simeq \frac{P_{L}^{\left(\frac{1}{2}\right)}}{13}$$

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 calculation⁹ 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 levels¹ 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 Wybourne⁵ 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