that the partially non-ionic character of the ground state will endow the molecule with a small component of orbital angular momentum precessing about the internuclear axis (this momentum being due to the hole in the $2p$ shell of the F atom, when it is in the neutral state). What is more important, it is not difficult to see that the currents induced by the rotation under these circumstances have just the type of space distribution that is most favorable to a strong field in the center,[11] so that the assumption made at the end of Section III about the connection between L_{n0} and H_{n0} is in this case well justified. It seems, therefore, that this model may give a satisfactory account of the data.

I wish to thank Dr. Rabi for attracting my attention to the large width of the resonance lines in LiF, CsF. Dr. Van Vleck kindly made available to me an early evaluation he had made independently by means of Hebb's formulae (unpublished). I am deeply indebted especially to Dr. Teller for his friendly interest and much helpful advice.

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Note on the Dirac Character Operators

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The Dirac character operators are evaluated for the classes of the symmetric group consisting of the triad, double interchange, tetrad, and pentad, and the corresponding group-theoretical primitive characters are listed for comparison. It is also shown that the evaluation of these and similar character operators is all that is required for the solution of the standard molecular problems in the spirit of Dirac's original program which avoids appeal to formal group theory.

I. INTRODUCTION

SOME years ago Dirac[1] established the remarkable exchange-spin identity

$$\mathbf{P}_{ij} = -\tfrac{1}{2}(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j), \tag{1}$$

which expresses the simple interchanges of electron orbits in terms of the associated vector-spin operators. In the discussion of the classification of multiplets he introduced the character (class) operators

$$\chi_c = \frac{1}{n_c}\sum_{\text{class}} \mathbf{P}_c, \tag{2}$$

defined as the average of all similar permutations, and showed that the *almost* exclusive states are characterized by the different sets of eigenvalues of these operators. These operators commute with all permutations so that in an irreducible representation of the symmetric group their matrices are scalar (Schur's lemma),[2] and it follows that the eigenvalues of the χ's are simply the corresponding primitive group characters divided by the dimension of the representation;[3] *viz.*,

$$\chi'[2^{\alpha_2}\cdots n^{\alpha_n}] = [2^{\alpha_2}\cdots n^{\alpha_n}]/[I], \tag{3}$$

where $\{2^{\alpha_2}\cdots n^{\alpha_n}\}$ is the usual group exponent notation (omitting unary cycles) for the partition[4] of n defining the class of permutations, and the square brackets indicate the associated primitive characters; $[I]$ being that of the unit class. From the result (1) and the expression

$$\sum_{i<j}(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j) = \tfrac{1}{2}[4\mathbf{S}(\mathbf{S}+1)-3n] = \mathfrak{y} \tag{4}$$

[1] Cf. P. A. M. Dirac, *Quantum Mechanics* (Clarendon Press, Oxford, 1935).

[2] Cf. F. D. Murnaghan, *Theory of Group Representations* (The Johns Hopkins University Press, Baltimore, 1938).

[3] This may be easily seen by operating on a degenerate set of eigenstates (symbolic $|>$'s) with the χ's and taking the spur, the degree of degeneracy being, of course, the dimension of the representation.

[4] $\alpha_1+2\alpha_2+\cdots n\alpha_n = n$.

defining the spin magnitude variable **S**, Dirac obtains the character variable of the class of interchanges in the form

$$\chi[2]=\frac{2}{n(n-1)}\sum_{i<j}\mathbf{P}_{ij}$$
$$=-\frac{2}{2n(n-1)}\sum_{i<j}(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j) \quad \text{(A)}$$
$$=-\frac{2}{2n(n-1)}\left\{\frac{n(n-1)}{2}+\mathfrak{y}\right\},$$

so that the exclusive sets of states are defined by the eigenvalues of **S**.[5]

For many purposes this result is essentially all that is required as regards group theory, e.g., the calculation of atomic term energies (without resolution of coincident terms).[6]

II.

It is not our purpose to consider here the details of these calculations for the atomic case and the modifications required in the case of coincident orbits. These may be found in the references of the preceding footnote. We wish to consider here the evaluation of some of the character variables of higher order, which is per se not entirely trivial; and moreover these more general variables are essentially all that is required in order to solve the 4–8 electron problems,[7] for example, in accord with Dirac's original program of avoiding appeal to formal group theory.

The characters considered here as examples are $\chi[3]$, $\chi[2^2]$, $\chi[4]$, $\chi[5]$, and we may merely list some easily verified aids to computation, *viz.*,

$$\mathfrak{y}^2=\frac{3n(n-1)}{2}+2(n-3)\mathfrak{y}$$
$$+\sum_{i<j}\sum_{\substack{k<l\\ \neq i,j}}(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)(\boldsymbol{\sigma}_k\cdot\boldsymbol{\sigma}_l), \quad \text{(5a)}$$

$$(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_k)=(\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_k)+i\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j\times\boldsymbol{\sigma}_k, \quad \text{(5b)}[8]$$

$$(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_k)+(\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_i)(\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_k)$$
$$=(\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_k)+(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_k), \quad \text{(5c)}$$

$$(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_k)+(\boldsymbol{\sigma}_k\cdot\boldsymbol{\sigma}_j)(\boldsymbol{\sigma}_k\cdot\boldsymbol{\sigma}_i)$$
$$=(\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_k)+(\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_i), \quad \text{(5d)}$$

and as a special case of these when $j=k$,

$$(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)^2=3-2(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j). \quad \text{(5e)}$$

The class $\{3\}$. Here one readily obtains

$$\chi[3]=\frac{3}{4n(n-1)(n-2)}$$
$$\times\sum_{i=1}^{n-2}\sum_{j>i}^{n}\sum_{\substack{k>i\\ \neq j}}\{(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)(1+\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_k)\} \quad \text{(B)}$$
$$=\frac{3}{4n(n-1)(n-2)}$$
$$\times\left\{\frac{n(n-1)(n-2)}{3}+2(n-2)\mathfrak{y}\right\},$$

and we leave the result in unsimplified form here, as in later cases, to show more clearly the origin of the various terms in the final expression.

The class $\{2^2\}$.

$$\chi[2^2]=\frac{8}{4n(n-1)(n-2)(n-3)}\sum_{i=1}^{n-3}\sum_{j>i}\sum_{\substack{k>i\\ \neq j}}\sum_{\substack{l>k\\ \neq j}}$$
$$\times\{(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)(1+\boldsymbol{\sigma}_k\cdot\boldsymbol{\sigma}_l)\}$$
$$=\frac{8}{4n(n-1)(n-2)(n-3)}$$
$$\left\{\frac{n(n-1)(n-2)(n-3)}{8}+\frac{\mathfrak{y}^2}{2}\right.$$
$$\left.+\frac{(n-3)(n-4)}{2}\mathfrak{y}-\frac{3n(n-1)}{4}\right\}. \quad \text{(C)}$$

The class $\{4\}$.

$$\chi[4]=\frac{-4}{8n(n-1)(n-2)(n-3)}\sum_{i}^{n-3}\sum_{j>i}\sum_{\substack{k>i\\ \neq j}}\sum_{\substack{l>i\\ \neq j,k}}$$
$$\times\{(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_k)(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_l)\}$$
$$=\frac{-4}{8n(n-1)(n-2)(n-3)}$$
$$\left\{\frac{n(n-1)(n-2)(n-3)}{4}+\mathfrak{y}^2\right.$$
$$\left.+(n-3)(3n-8)\mathfrak{y}-\tfrac{3}{2}n(n-1)\right\}. \quad \text{(D)}$$

[5] Equivalently, the eigenvalues of **S** define the permissible eigenvalues of the χ, and hence the particular irreducible representations allowed by the exclusion principle.

[6] Cf. P. A. M. Dirac, see reference 1; J. H. Van Vleck, Phys. Rev. **45**, 405 (1934); R. Serber, Phys. Rev. **45**, 461 (1934).

[7] Including non-orthogonality correction, if desired.

[8] Dirac, see reference 1.

The class $\{5\}$.

$$\chi[5]=\frac{5}{16n(n-1)(n-2)(n-3)(n-4)}\times\sum_{i}^{n-4}\sum_{j>i}\sum_{\substack{k>i\\ \neq j}}\sum_{\substack{l>i\\ \neq j,k}}\sum_{\substack{m>i\\ \neq j,k,l}}\{(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_k)(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_l)(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_m)\}$$

$$=\frac{5}{16n(n-1)(n-2)(n-3)(n-4)}\times\left\{\frac{n(n-1)(n-2)(n-3)(n-4)}{5}+4(n-4)\mathfrak{y}^2+4(n-3)(n-4)^2\mathfrak{y}-6n(n-1)(n-4)\right\}. \quad (E)$$

These may be compared with the corresponding group-theoretical results

$$[2]=-\binom{n-2}{k}+\binom{n-2}{k-1}-\binom{n-2}{k-2}+\binom{n-2}{k-3}, \quad (A')$$

$$[3]=\binom{n-3}{k}-\binom{n-3}{k-1}+\binom{n-3}{k-3}-\binom{n-3}{k-4}, \quad (B')$$

$$[2^2]=\binom{n-4}{k}-\binom{n-4}{k-1}+2\binom{n-4}{k-2}-2\binom{n-4}{k-3}+\binom{n-4}{k-4}-\binom{n-4}{k-5}, \quad (C')$$

$$[4]=-\binom{n-4}{k}+\binom{n-4}{k-1}-\binom{n-4}{k-4}+\binom{n-4}{k-5}, \quad (D')$$

$$[5]=\binom{n-5}{k}-\binom{n-5}{k-1}+\binom{n-5}{k-5}-\binom{n-5}{k-6}, \quad (E')$$

$$k=\frac{n}{2}-S,$$

$$[I]=\binom{n}{k}-\binom{n}{k-1}$$

$=$dimension of representation.

These are obtained from the general expression given by Wigner,[9] namely, that within the restriction imposed by the exclusion principle the primitive character of the class of permutations of ρ cycles, with cycle lengths $\lambda_1, \lambda_2, \cdots \lambda_\rho$ is the coefficient of x^k in

$$(-)^{n-\rho}(1-x)(1+x^{\lambda_1})(1+x^{\lambda_2})\cdots(1+x^{\lambda_\rho}). \quad (6)$$

It does not appear to be possible to obtain a corresponding general result from the present primitive method because of the requirement of explicit resolution into products of interchanges, although the signature $(-)^{n-\rho}$ is a trivial consequence of the relation (1) and a cycle of length λ is resolvable into a product of $\lambda-1$ interchanges.

The application of the results (A–E) to the afore-mentioned molecular problems derives basically from Dirac's result that the average eigenvalue of $\mathbf{V}$ (for the states of a given multiplicity) is given by

$$\langle V'\rangle=\sum_P\langle P\alpha|\mathbf{V}|\alpha\rangle\chi'[P]=\sum_P V_P\chi'[P], \quad (7)$$

where $\mathbf{V}=\sum_P V_P\mathbf{P}$ represents the perturbation energy *or* the Hamiltonian, depending on the choice of the unperturbed functions $\langle x|P\alpha\rangle=\Pi_j\langle x_j'|P\alpha_j\rangle$ over which the matrix of $\mathbf{V}$ is defined. Correspondingly, as Dirac notes, the average eigenvalue of any function of $\mathbf{V}$ may be evaluated in similar fashion. Hence we need only evaluate the iterated quantities $\mathbf{V}$, $\mathbf{V}^2$, $\mathbf{V}^3$, $\cdots$ etc., the number of iterations depending on the number of states of a given multiplicity involved, and substitute the appropriate character eigenvalues as obtained from (A–E) to calculate the levels for various multiplicities. Thus, with (A) alone London's equation for 4 electrons follows in trivial fashion from the evaluation of $\langle V'\rangle$, $\langle V^{2\prime}\rangle$, and the generalization, including non-

[9] E. P. Wigner, *Gruppentheorie* (F. Vieweg und Sohn, Braunschweig, 1931), pp. 149, 196.

orthogonality correction, may be readily obtained by using the results (A–D). The calculations for the 6- and 8-electron problems are, of course, more tedious, but proceed along similar lines[10] after calculation of the additional requisite character operators for the higher order classes.

In this more physical approach the presence of additional elements of (space) symmetry in a given problem is also recognized by noting that **V** commutes with a certain *subgroup* of the symmetric group involved, the character operators of which therefore furnish additional commuting constants of the motion whose values may be simultaneously assigned, leading to a further significant classification of energy levels and a simplification of the problem. Group-theoretically this, of course, corresponds to recognizing that the rotation-reflection group of **V** (under which **V** is invariant) in such cases is realizable in terms of an appropriate subgroup of the symmetric group, i.e., with which it is abstractly identical. Thus, one finds *six* additional commuting constants of the motion in the 6-electron problem with hexagonal symmetry, *five* for octahedral symmetry, *ten* in the 8-electron problem with (extended) cubic symmetry, etc.[11] Needless to say, the more formal treatment, as given by Serber, is in many respects simpler since it is guided by the more definite prescription of group theory proper, but the present viewpoint shows again that following Dirac's program the formal group methods can, in effect, be avoided.

[10] This method may be compared with the equivalent treatment given by R. Serber, J. Chem. Phys. **2**, 697 (1934), along more matrical (group-theoretical) lines, which comparison also serves to show the relation between the symbolic and formal group methods. It may be mentioned that the iterations in the latter method give sums of eigenvalues rather than averages, for obvious reasons. Cf. Eq. (3).

[11] R. Serber, see reference 10.

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On the Rydberg-Ritz Formula in Quantum Mechanics

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A derivation is given of the Rydberg-Ritz formula for series spectra. Simple expressions are obtained for the Rydberg and Ritz coefficients. It is shown that the Ritz coefficient is proportional to the difference between the radial period of the electron and the period of the hypothetical orbit, with the same energy which would exist if the atomic core were to contract to zero radius.

The derivation necessitates a study of the confluent hypergeometric function. An expansion in powers of the energy is obtained for this function. The coefficients in the expansion are found to be simple combinations of Bessel functions.

Calculations of the Rydberg and Ritz coefficients are carried out for the *S* series of Na, K, and Cs and show satisfactory agreement with observation. The comparison with experiment yields information concerning the relative accuracy of different types of central fields employed to approximate the effect of the atomic core upon the valence electron. It is concluded that the Hartree-Fock field is not a convenient starting point for this purpose.

1. INTRODUCTION

IT is known that in many cases the terms of series spectra obey the empirical Rydberg-Ritz formula,

$$E=-\frac{1}{2}\frac{1}{(\mathbf{n}+\alpha+\beta E)^2}, \qquad (1.1)$$

where E is the energy expressed in atomic units, n is the principal quantum number, and α and β are the Rydberg and Ritz coefficients, respectively. For a given atom these coefficients depend only upon l, the azimuthal quantum number.

Bohr, considering the electron as moving in the static central field arising from the nucleus and the core electrons, gave an ingenious derivation of (1.1) on the basis of the old quantum