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The Calculation of Matrix Elements for Lewis Electronic Structures of Molecules

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Starting from the discovery by Rumer that the eigenfunctions corresponding to different distributions of valence bonds in a molecule can be represented by plane diagrams which provide information regarding their mutual linear independence, a very simple graphical method is developed for calculating the coefficients of the integrals occurring in the matrix elements involved in Slater's treatment of the electronic structure of molecules.

IN his valuable paper[1] on *Molecular Energy Levels and Valence Bonds* Slater developed a method for formulating approximate eigenfunctions for molecules and for constructing the corresponding secular equation. This method has been successfully applied by a number of investigators in the discussion of general valence theory and of the structure of individual simple molecules, its application to more complex molecules having been retarded in part by the laborious nature of the calculation of the coefficients of the various exchange integrals in the matrix elements. It is shown in the following paragraphs that these coefficients can be easily calculated by a simple procedure involving the use of plane diagrams similar to those introduced by Rumer[2] in his recent discussion of the linear independence of electronic structures.

SINGLET STATES WITH SPIN DEGENERACY ONLY

For a system involving N electrons, Slater constructed the function

$$\Psi = \frac{1}{(N!)^{\frac{1}{2}}} \sum_{P''} (-1)^{P''} P'' A(1) B(2) \cdots E(N),$$

which is completely antisymmetric in the electrons (satisfying Pauli's principle). Here A, $B \cdots E$ are one-electron spin-orbit functions, and the symbol P'' represents the $N!$ permutations of the functions $A \cdots E$ among the electrons, the coefficient being -1 for odd, $+1$ for even permutations. For two such functions Ψ and Ψ' the matrix element corresponding to a dynamical quantity F is

$$(1/N!) \int \{\sum_{P''} (-1)^{P''} P'' A(1) \cdots E(N)\} F\{\sum_{P'} (-1)^{P'} P' A'(1) \cdots E'(N)\} dv,$$

which reduces to

$$\int A(1) \cdots E(N) F\{\sum_{P} (-1)^{P} P A'(1) \cdots E'(N)\} dv,$$

with $P' = P'' P$, in case that F is completely symmetric in the electrons. This may be written as

$$\sum_{P} (-1)^{P} (AB \cdots E/F/PA'B' \cdots E'),$$

in which each parenthesis $(A \cdots E/F/PA' \cdots E')$ represents one integral in the above sum. If F does not involve spin interactions, the integral $(A \cdots E/F/A' \cdots E')$ vanishes unless the spin of A is the same as that of A', B as B', and so on, in which case it reduces to $(ab \cdots e/F/a'b' \cdots e')$, with $a \cdots e'$ the orbital parts of $A \cdots E'$.

For four electrons, for example, with only spin degeneracy (the number of occupied orbits equalling the number of electrons), Slater gave the function $\frac{1}{2}(\Psi_{I} - \Psi_{II} - \Psi_{III} + \Psi_{IV})$ as representing the structure in which orbits a and b are bonded together, and also c and d. Here $\Psi_{I} \cdots \Psi_{IV}$

[1] J. C. Slater, Phys. Rev. **38**, 1109 (1931).
[2] G. Rumer, Nachr. d. Ges. d. Wiss. zu Göttingen, M. P. Klasse, p. 337 (1932).

are functions of the type given above with the following distributions of spins among the orbits:

	a	b	c	d
I	$-$	$+$	$-$	$+$
II	$+$	$-$	$-$	$+$
III	$-$	$+$	$+$	$-$
IV	$+$	$-$	$+$	$-$

The energy matrix element for this function is

$$(abcd/H/abcd)+(abcd/H/bacd)+(abcd/H/abdc)$$
$$-\tfrac{1}{2}(abcd/H/cbad)-\tfrac{1}{2}(abcd/H/dbca)$$
$$-\tfrac{1}{2}(abcd/H/acbd)-\tfrac{1}{2}(abcd/H/adcb)+\text{higher}$$
$$\text{exchange integrals.}$$

With the single exchange integrals negative, as they usually are for orbits on separate atoms, this leads to attraction between a and b and between c and d, and repulsion between other pairs.

Similarly a function can be formulated representing $a-d$ and $b-c$ bonds, and one representing $a-c$ and $b-d$ bonds. These three functions, corresponding to three separate electronic structures of the Lewis type, are, however, not linearly independent; any one can be represented as a combination (sum or difference) of the other two. This linear dependence of structures continues as the number of bonds increases; for n single bonds between $2n$ atoms $(2n)!/2^n n!$ structures can be drawn, of which only $(2n)!/n!(n+1)!$ are independent. In the paper mentioned above, Rumer made the very interesting and important observation that if the orbits are formally arranged in a ring or other concave curve, and straight lines are drawn between orbits bonded together, the structures represented by diagrams in which no lines intersect are independent. This observation forms the starting point for the following treatment.

Let us arrange the orbits in a ring, and then draw arrows between pairs of orbits bonded together, the head of each arrow representing positive spin and the tail negative spin. The wave function for the corresponding structure is then given, except for a normalizing factor $2^{-n/2}$, by the sum of the functions corresponding to this distribution of spins and to those obtained by reversing the arrows, each function having the coefficient $(-1)^R$, in which R is the number of reversals. Thus the $\begin{smallmatrix}a-b\\c-d\end{smallmatrix}$ structure would be represented by the vector-bond diagram $\rightleftarrows$, corresponding to the function

$$\frac{1}{2}\left\{\begin{pmatrix}-+\\+-\end{pmatrix}-\begin{pmatrix}+-\\+-\end{pmatrix}-\begin{pmatrix}-+\\-+\end{pmatrix}+\begin{pmatrix}+-\\-+\end{pmatrix}\right\}.$$

It is verified at once that

$$\bowtie = \updownarrow\uparrow - \rightleftarrows,$$

so that an intersecting pair of arrows can be replaced by the difference of two non-intersecting pairs, the pair connecting head with head and tail with tail having the positive sign. By successive applications of this treatment any structure can be resolved into structures involving no intersecting bonds.

Canonical sets of independent structures

Of the various complete sets of independent structures which may be formulated, certain ones may be called "canonical" because of the relative simplicity of the calculation of matrix elements based on them. For a given order of the orbits in a ring, the canonical set of independent structures comprises those with no intersecting bonds; moreover, numbering the orbits in order about the ring, the canonical vector-bond structures for singlet states with spin degeneracy only have arrows drawn from odd to even orbits (the functions for the corresponding distributions of positive and negative spins thus occurring with the positive sign). The eigenfunction for a structure represented by a vector-bond diagram $a\rightarrow b$ $c\rightarrow d$, etc., may be written

$$\frac{1}{2^{n/2}}\sum_R(-1)^R R\left\{\frac{1}{((2n)!)^{\frac{1}{2}}}\sum_P(-1)^P Pa(1)\beta(1)b(2)\alpha(2)c(3)\beta(3)d(4)\alpha(4)\cdots\right\},$$

in which α represents positive spin and β negative spin, P represents the $(2n)!$ permutations of the orbits and their associated spins among the electrons, and R the 2^n operations of interchanging the spin functions α and β for orbits (such as a and b) which are bonded together, that is, of

reversing the arrows in the vector-bond diagram. The factor $(-1)^R$ equals $+1$ for an even number of reversals, -1 for an odd number.

The Coulomb coefficient

To find the coefficient of the Coulomb integral for two structures, superimpose their vector-bond patterns to form the superposition pattern (Fig. 1). The Coulomb coefficient is 2^{-n} times the sum $(-1)^R$ for the different patterns in which each orbit serves either as the head or as the tail
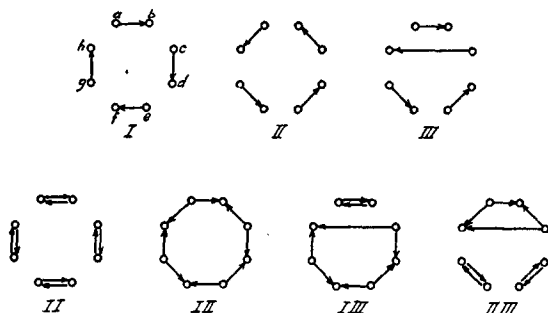

FIG. 1. The vector-bond diagrams for three structures of the canonical set of fourteen for $n=4$, and some of their superposition patterns.

of two arrows which can be made by reversing the arrows, R being the number of reversals. The superposition pattern consists of "islands," or closed polygons formed by an even number of arrows. For each island there are only two satisfactory orientations of the arrows, so that the Coulomb coefficient may be written as $(-1)^r 2^{-(n-i)}$, in which i is the number of islands and r the number of reversals required for an initial satisfactory orientation.

For canonical structures the sign is positive, the Coulomb coefficient being $1/2^{n-i}$. In drawing the superposition pattern for canonical structures the arrows may be replaced by lines.

Coefficients of exchange integrals

Each of the $N!$ permutations may be represented by a permutation diagram, made by drawing an arrow from each orbit in $Pab\cdots e$ to the orbit whose place in $ab\cdots e$ it occupies. Thus if $Pab\cdots e=bd\cdots e$, an arrow is drawn from b to a, from d to b, etc. A closed polygon of arrows is called a cycle of the permutation.[3] A cycle may

be called odd if it involves an even number of arrows, otherwise even. The permutation is odd if it contains an odd number of odd cycles; otherwise it is even. The possible permutations are obtained by drawing polygons of arrows in all possible ways such that each orbit is reached by no arrow or by the head of one and the tail of another. The permutation arrows may intersect.

To find the coefficient of a given exchange integral in a matrix element, $(I/F/PII)$, draw the vector-bond diagram for structure II, change it as indicated by the permutation diagram for P, and form the superposition pattern of I and PII. The coefficient is then given, except for the factor $(-1)^P$, by the above rules for the Coulomb coefficient; that is, it is $(-1)^P(-1)^r 2^{-(n-i)}$.

This procedure may be simplified considerably for single exchange integrals in matrix elements between structures of a canonical set. We first form the superposition pattern of the two structures. If the permutation involves the interchange of orbits in different islands, the number of islands is decreased by one; if the orbits are an odd number of bonds apart in the same island, it is unchanged; if they are an even number apart, it is increased by one. Hence (taking into consideration the factors $(-1)^P$ and $(-1)^r$) it is seen that the coefficient of a single exchange integral for two canonical structures is $2^{-(n-i)}f(p)$, where n is the number of bonds, i is the number of islands in the superposition pattern of the two structures, p the number of bonds in the superposition pattern along the path between the two orbits which are interchanged, and $f(p)$ a factor with the values $-\frac{1}{2}$ for $p=0$, $+1$ for $p=1$, 3, $5\cdots$, and -2 for $p=2$, 4, $6\cdots$. It is not necessary to use arrows in forming the superposition pattern for canonical structures.

Similar rules may be formulated for more complex permutations.

An example: Six electrons with only spin degeneracy. Placing the six orbits in a ring in the order $abcdef$, the five structures forming a canonical set are those given in Fig. 2. It is seen that

$$\int I F I dv = Q+ab+cd+ef-\tfrac{1}{2}ac-\tfrac{1}{2}ad-\tfrac{1}{2}ae-\tfrac{1}{2}af$$
$$-\tfrac{1}{2}bc-\tfrac{1}{2}bd-\tfrac{1}{2}be-\tfrac{1}{2}bf-\tfrac{1}{2}ce-\tfrac{1}{2}cf-\tfrac{1}{2}de-\tfrac{1}{2}df$$
$$+\cdots,$$

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[3] The theory of permutation groups is discussed in standard treatises such as W. Burnside, *The Theory of Groups*, Second Edition, Cambridge University Press, 1911.
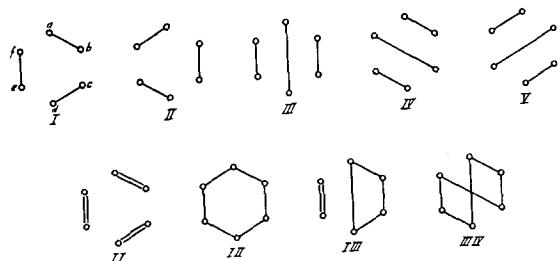
FIG. 2. The five canonical structures for $n=3$, and some of their superposition patterns.

in which Q is the Coulomb integral $(ab\cdots f/F/ab\cdots f)$, ab the single exchange integral $(ab\cdots f/F/ba\cdots f)$, etc. As in this case, it is true in general that in diagonal matrix elements the coefficient of bonding single exchange integrals is $+1$, of nonbonding $-\frac{1}{2}$. From the superposition pattern of I and II we obtain

$$\int \mathrm{I} F \mathrm{II} dv = \tfrac{1}{4}(Q + ab + bc + cd + de + ef + fa + ad$$
$$+ be + cf - 2ac - 2bd - 2ce - 2df - 2ea - 2fb$$
$$+ \cdots),$$

and similar expressions for the other matrix elements can be quickly written.[4] The determination of the coefficients of each of the 720 integrals would be, of course, quite a task, even by this simple method, but any one of them is easily found. Thus from Fig. 3 it is seen that in $\int \mathrm{I} F \mathrm{II} dv$
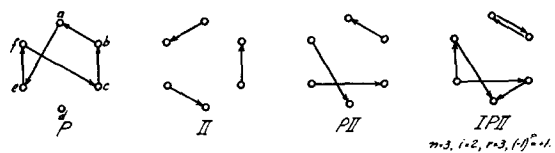

FIG. 3. The permutation diagram for P $abcdef = bcfdae$, and the superposition pattern for I PII.

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[4] A. Sherman and H. Eyring (J. Am. Chem. Soc. **54**, 2661 (1932)) have published matrix elements for this six-electron system, giving the Coulomb and single exchange integrals. Their coefficients do not show the regularities which our treatment leads to, since their five functions do not form a canonical set.

the coefficient of $(abcdef/F/bcfdae)$ is $-\frac{1}{2}$. The complete matrix for the forty-two independent structures given by ten electrons with only spin degeneracy, retaining only Coulomb and single exchange integrals, can be set up in a few hours.

EXTENSION TO MORE GENERAL SYSTEMS

The foregoing treatment can be extended to states of arbitrary multiplicity by the artifice of including in the system additional electrons and phantom orbits. To represent N electrons and N orbits in states with resultant spin S (multiplicity $2S+1$), form a ring of the real and phantom orbits; a canonical set of electronic structures is then obtained by drawing in all possible ways such that no bonds intersect a phantom bond between each of $2S$ phantom orbits and a real orbit and a real bond between each pair of remaining real orbits. Rules regarding reversal of bond arrows (different numbers of arrow heads on phantom orbits correspond to different M_S values) and the calculation of exchange integral coefficients are easily formulated.

A canonical set of structures for a system with more orbits than electrons is obtained by arranging all the orbits (including phantom orbits for $S>0$) in a ring and then drawing non-intersecting bonds to a number determined by the number of electrons and the multiplicity. If two electrons occupy the same orbit, forming an unshared pair, a loop is drawn with its ends at the orbit.

The bond diagrams provide an obvious simple method of determining the allowed spectral terms for equivalent electrons with Russell-Saunders coupling, which may be convenient for the reason that it separates states of different multiplicity at the start.

The methods developed in this paper have been applied in a discussion of the structure of aromatic substances, free radicals, etc., to be published soon.