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Extension of the Dirac Vector Model to Include Several Configurations

Robert Serber, *Department of Physics, University of Wisconsin*

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The vector model for the electrostatic interactions of a system of n electrons, as originally given by Dirac and as used by J. H. Van Vleck, suffers from the restriction that it allows the energy matrix to be set up completely only for a single spatial configuration. In the present paper this restriction is removed. It is shown how the complete energy matrix may be found by means of the vector model, whatever the number of configurations involved. As an example of the method, the energies of the two ${}^2D$ states arising from the atomic configuration d^3 are calculated. Calculations by this method are simpler than the corresponding calculations using Slater wave functions in that the energy matrix factors according to characteristic values of S.

DIRAC[1] has given a very elegant method for determining the energy levels due to a single configuration of an n electron system, all other configurations being neglected. This method leads in a simple way to the vector model used by J. H. Van Vleck[2] in a previous paper in this journal. However, the restriction to a single configuration is a serious one; for example, if there is degeneracy other than spin degeneracy Dirac's method may give only the mean energy of a number of states. In the present paper this restriction will be removed; it will be shown how, by a simple extension of Dirac's argument, the inter-configurational elements of the energy matrix may be obtained.

Suppose we have a configuration A, specified by n orthogonal orbits, $(\alpha_1|xyz)$, $(\alpha_2|xyz)$, $\cdots(\alpha_n|xyz)$, which are all different. We can obtain $n!$ wave functions of the system by applying in turn all the permutations of the orbits (i.e., α's) among themselves to the wave function

$$\psi^A=(\alpha_1|x_1y_1z_1)(\alpha_2|x_2y_2z_2)\cdots(\alpha_n|x_ny_nz_n).$$

Consider any one of these wave functions, $P\psi^A$. It is clear that the same result is obtained if, instead of applying the permutation P to the orbits, we apply the reciprocal permutation to the coordinates x_i, y_i, z_i, that is

$$P\psi=(P^x)^{-1}\psi. \tag{1}$$

The superscript x indicates a permutation which operates on the coordinates.

The portion of the energy matrix in which the states arising from the given configuration intersect each other is a matrix, H^{AA}, of $n!$ rows and columns, whose elements are given by

$$\begin{aligned}(P_a\alpha|H|P_b\alpha)&=\int(P_a\psi^A)^*HP_b\psi^Ad\tau=\int({P^x}_a{}^{-1}\psi^A)^*H{P^x}_b{}^{-1}\psi^Ad\tau=\int({P^x}_a{}^{-1}\psi^A)^*{P^x}_b{}^{-1}H\psi^Ad\tau\\&=\int({P^x}_b{P^x}_a{}^{-1}\psi^A)^*H\psi^Ad\tau=\int(P_aP_b{}^{-1}\psi^A)^*H\psi^Ad\tau=(P_aP_b{}^{-1}\alpha|H|\alpha),\end{aligned} \tag{2}$$

as can be seen from (1), from the fact that the Hamiltonian function H is invariant under ${P^x}_b{}^{-1}$ and so commutes with it, and from the unitary property of the operator ${P^x}_b$. It is to be understood that the operator preceding ψ^{A*} acts only on ψ^{A*}, and not on the remainder of the integrand. Let $H_P{}^{AA}=(P\alpha|H|\alpha)$. Then it is seen from (2) that the coefficient of $H_P{}^{AA}$ in the energy matrix is itself a matrix, whose elements are zero except when $P=P_aP_b{}^{-1}$, in

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[1] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Chapter XI. The connection between the energy matrix of a single configuration and the representations of the permutation group has also been given by E. Wigner, Zeits. f. Physik **40**, 883 (1927).

[2] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934). This paper will be referred to as *I*.

which case they are unity. But the elements of the matrix representing P are given by $(P_a\alpha|1|PP_b\alpha)$, and so are zero except when $P_a=PP_b$, i.e., when $P=P_aP_b^{-1}$, in which case they also are unity. Thus the coefficient of $H_P{}^{AA}$ is simply the matrix representing P, and H^{AA} can be written

$$H^{AA}=\sum_P H_P{}^{AA}P. \tag{3}$$

Similarly, the portion of the energy matrix arising from a configuration B, specified by the orbits $(\alpha_1'|xyz)$, $\cdots(\alpha_n'|xyz)$, is

$$H^{BB}=\sum_P H_P{}^{BB}P. \tag{4}$$

If the states $P\psi^B$ are ordered in the same way as the states $P\psi^A$, as we shall always suppose done, the matrix P in (3) is identical with P in (4).

We must now consider the portion of the energy matrix, H^{AB}, in which the states $P\psi^A$ intersect the states $P\psi^B$. The argument which leads to (2) now gives the result

$$(P_a\alpha|H|P_b\alpha')=(P_aP_b^{-1}\alpha|H|\alpha'). \tag{5}$$

Let $H_P{}^{AB}=(P\alpha|H|\alpha')$. Then, comparing (2) and (5) and remembering that the states $P\psi^A$ and $P\psi^B$ are similarly ordered, we see that the coefficient of $H_P{}^{AB}$ in H^{AB} is the same as the coefficient of $H_P{}^{AA}$ in H^{AA}, i.e., is the same as the matrix representing P. In this sense we can write

$$H^{AB}=\sum_P H_P{}^{AB}P. \tag{6}$$

Eq. (6) has been established using a particular representation. We must now show that it holds whatever the representation, provided always that P is represented by the same matrix in (4) as in (3). If we apply a canonical transformation S_A to H^{AA}, which then becomes $S_A^{-1}H^{AA}S_A$, and a transformation S_B to H^{BB}, which becomes $S_B^{-1}H^{BB}S_B$, then H^{AB} becomes $S_A^{-1}H^{AB}S_B$. The proviso stated above requires that $S_A=S_B$; in consequence H^{AB} transforms in the same way as H^{AA} and H^{BB}, and (6) remains valid in the new representation.

RESTRICTIONS IMPOSED BY THE EXCLUSION PRINCIPLE

Not all of the $n!$ states arising from a given configuration are permitted by the exclusion principle. In general, the degree of the secular equation which must be solved to find the energy levels can be greatly reduced if only the states allowed by the exclusion principle are considered. To do this we must obviously take into account the spin variables, as well as the positional variables. For an n electron system there exist 2^n linearly independent functions of the spins. Using these 2^n functions as a basis, we can construct the matrices representing the operators, P^S, which permute the spins among themselves. It has been shown by Wigner[3] that the representations of the P's allowed by the exclusion principle are obtainable from the representations of the P^S's by means of the matrix equation

$$P=\pm P^S, \tag{7}$$

the plus or minus sign being taken according as the permutation in question is even or odd.

Dirac has shown that $P^S{}_{ij}$, which permutes the spins of electrons i and j, can be expressed in terms of the spins by the relation

$$P^S{}_{ij}=\tfrac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j);$$

hence we can write

$$P_{ij}=-\tfrac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j), \tag{8}$$

and any permutation P can be expressed in terms of the spins by writing it as a product of interchanges.

MODIFICATIONS REQUIRED WHEN THE ORBITS ARE NOT DIFFERENT

We must now consider the modifications required in the foregoing arguments when the orbits of a configuration are not all different.

For brevity let us refer to the orbits of any configuration, α_1, α_2, $\cdots\alpha_n$, simply by the numbers 1, 2, $\cdots n$. Suppose the orbits 1 and 2 of configuration B are identical. In this case we will say we have a pair of filled orbits. The permutation P_{12} satisfies the equation $P_{12}{}^2=1$, hence P_{12} has the characteristic values ±1. But if orbits 1 and 2 are identical, any wave function is left unaltered by P_{12}, and so the only nonvanishing states are those for which $P_{12}=1$. In terms of the vector model, this is simply the

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[3] E. Wigner, *Gruppentheorie*, p. 277.

statement that the spins of two electrons in identical orbits must be anti-parallel (see reference 2, § 1).

It has been shown[2] in I that if the perturbations due to other configurations are not considered, the energies of the states arising from the configuration B are the same, except for an additive constant, as if we disregarded the orbits 1 and 2 entirely, and calculated the energy for the remaining $(n-2)$ electron problem. However, if we wish to include other configurations we must adopt a different attack.

In order to use the formula for the interaction of configurations, (6), we must formally consider the orbits 1 and 2 as different, that is, we must distinguish between them. The states $P\psi^B$ will no longer be orthogonal, for if $P'=P_{12}P$ the states $P'\psi^B$ and $P\psi^B$ are actually identical. The modification in the secular equation required when the states are not orthogonal is a familiar one; we must calculate the matrix elements of $H-W$ rather than the matrix elements of H. Thus (4) must be replaced by

$$(H-W)^{BB}=\sum\nolimits_P (H-W)_P{}^{BB}P. \tag{9}$$

A similar modification is not required in (6), as the states arising from the configuration B will still be orthogonal to those arising from any other configuration, A.

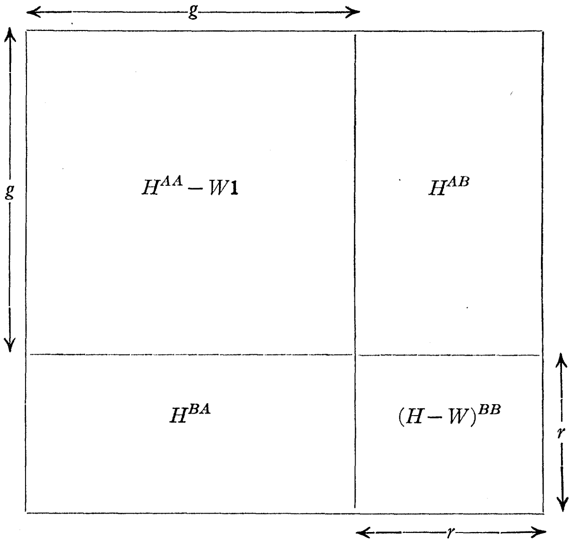

FIG. 1.

Suppose the orbits of A are all different. Let g be the degree (number of rows and columns) of the matrices representing the P's. The complete energy matrix for both configurations, A and B, is of degree $2g$. Its form differs from that shown in Fig. 1 only in that it consists of four squares, each of degree g. Let us use a representation of the P's in which P_{12} is diagonal. In such a representation there will be a number of rows, r in number, for which P_{12} has the characteristic value 1, while for the remaining $(g-r)$ rows P_{12} has the characteristic value -1. But we have seen that when orbits 1 and 2 are identical the only permissible states are those for which $P_{12}=1$. The $(g-r)$ rows and columns arising from B for which $P_{12}=-1$ must accordingly be struck out of the energy matrix, which then takes the form shown in Fig. 1. The symbol P^{BA} will be used to denote the matrix obtained from P by deleting the improper $(g-r)$ rows, and P^{BB} will denote the matrix obtained by deleting the improper $(g-r)$ rows and columns. In place of (6) and (9) we now have

$$\left.\begin{aligned} H^{BA}&=\sum\nolimits_P H_P{}^{BA}P^{BA};\\ (H-W)^{BB}&=\sum\nolimits_P (H-W)_P{}^{BB}P^{BB}.\end{aligned}\right\} \tag{10}$$

If the permutations P' and P are connected by the relation $P'=P_{12}P$, we obviously have

$$(H-W\delta_{BC})_{P'}{}^{BC}=(H-W\delta_{BC})_P{}^{BC}, \quad (C=A,B).$$

Moreover $P'^{BC}=P^{BC}$, since

$$P'(i;j)=\sum\nolimits_k P_{12}(i;k)P(k;j),$$

and in the r rows we have retained $P_{12}(i;k)=\delta_{ik}$. The contribution of P' and P to the energy is accordingly

$$(H-W\delta_{BC})_{P'}{}^{BC}P'^{BC}+(H-W\delta_{BC})_P{}^{BC}P^{BC} =2(H-W\delta_{BC})_P{}^{BC}P^{BC}.$$

The entire group of $n!$ permutations can be divided into one set of $n!/2$ "independent" permutations, and a second set of $n!/2$ permutations which can be obtained by multiplying each permutation of the first set on the left by P_{12}. For example, the six permutations P_{I}, P_{12}, P_{13}, P_{23}, P_{123}, P_{132}, can be divided into an "independent" set P_{I}, P_{13}, P_{23}, and a "dependent" set $P_{12}=P_{12}P_{\text{I}}$, $P_{123}=P_{12}P_{23}$, $P_{132}=P_{12}P_{13}$. Instead of (10) we can write

$$\left.\begin{aligned} H^{BA} &= 2\sum{}'_P H_P{}^{BA} P^{BA}, \\ (H-W)^{BB} &= 2\sum{}'_P (H-W)_P{}^{BB} P^{BB}, \end{aligned}\right\} \quad (11)$$

where the sum is taken only over the $n!/2$ permutations of an "independent" set. As all the exchange and higher order permutation integrals of unity appearing in (11) are clearly zero, the second expression in (11) is simply

$$(H-W)^{BB} = 2\sum{}'_P H_P{}^{BB} P^{BB} - 2W\mathbf{1}.$$

The matrix H^{AB} can be obtained from H^{BA} by use of the Hermitian character of the energy matrix, $H^{AB} = H^{BA\dagger}$. The entire energy matrix has the form shown in Fig. 2, if we put $a = b = 2$.

$\Sigma_P H_P{}^{AA} P - W\mathbf{1}$	$a(\Sigma'_P H_P{}^{BA} P^{BA})^\dagger$
$a\Sigma'_P H_P{}^{BA} P^{BA}$	$b(\Sigma'_P H_P{}^{BB} P^{BB} - W\mathbf{1})$

FIG. 2.

It is often inconvenient to have $-2W$ appear on the diagonal, for example if we wish to use the spur theorem. This difficulty can be avoided by renormalizing the energy matrix, which we can do by dividing each row and each column arising from the configuration B by $\sqrt{2}$. The final form of the energy matrix is given by Fig. 2 with $a = \sqrt{2}$, $b = 1$.

The problem arising when there are two pairs of filled orbits in the configuration B can be handled in the same way. If the orbits 3 and 4 are identical, as well as 1 and 2, we must use a representation in which both P_{12} and P_{34} are diagonal. The only rows and columns arising from B which are retained in the energy matrix are those for which both P_{12} and P_{34} are 1; all others must be struck out. The contribution of any permutation P to the energy matrix will be the same as the contribution of each of the permutations $P_{12}P$, $P_{34}P$, $P_{12}P_{34}P$. In place of (11) we now have

$$\left.\begin{aligned} H^{BA} &= 4\sum{}'_P H_P{}^{BA} P^{BA}; \\ (H-W)^{BB} &= 4\sum{}'_P H_P{}^{BB} P^{BB} - 4W\mathbf{1}, \end{aligned}\right\} \quad (12)$$

where the summation is to be taken over $n!/4$ permutations which do not differ merely by interchanges of identical orbits of B. The matrices P^{BA} in (12) will of course have a smaller number of rows, and the matrices P^{BB} a smaller number of rows and columns, than the corresponding matrices in (11). In order to renormalize the energy matrix each row and column arising from B must be divided by 2. The final form of the energy matrix is given by Fig. 2 with $a = 2$, $b = 1$.

The above arguments are readily generalized. Suppose we have any set of configurations R_1, R_2, $\cdots R_k$. Let r_j be the number of pairs of filled orbits in the configuration R_j. We shall always denote the first pair of filled orbits by 1,2, the second by 3,4, and so forth, and employ a representation in which P_{12}, P_{34}, $\cdots$ $P_{2p-1\,p}$, $\cdots$ are diagonal. This is possible, since these permutations all commute. Then if $r_i \geq r_j$, the matrix $H^{R_iR_j}$, in the normalized form, is given by

$$H^{R_iR_j} = \sqrt{2^{r_i-r_j}}\sum{}'_P H_P{}^{R_iR_j} P^{R_iR_j}, \qquad (13)$$

where the summation is taken only over $n!/2^{r_i}$ permutations which do not differ merely by interchanges of identical orbits of R_i. The matrices $P^{R_iR_j}$ are obtained from the matrices P by striking out the rows which violate the condition that an interchange of identical orbits of R_i has the characteristic value 1, and striking out the columns which violate the condition that an interchange of identical orbits of R_j has the characteristic value 1. The matrix $H^{R_jR_i}$ is obtained from the relation $H^{R_jR_i} = H^{R_iR_j\dagger}$. Eq. (13) is the desired generalization of Dirac's result, (3). Eq. (13) is the same as (3) when $i = j$, $r_i = 0$.

ORTHOGONAL AND NON-ORTHOGONAL ORBITS

If the different orbits are orthogonal, as we have so far supposed to be the case, the number of terms which it is necessary to consider in setting up the matrix $H^{R_iR_i}$ can be considerably reduced by taking into account the fact that the Hamiltonian function representing the electrostatic interactions between electrons contains no terms involving the coordinates of more than two electrons. It is evident from the form of the Hamiltonian function that if in the integral $H_P{}^{R_iR_i}$ more than two electrons are in different orbits, the integral will be zero. But this will surely be the case if P is any permutation involving more than two orbits, i.e., any permutation other than the identity, P_{I}, or a simple interchange, P_{kl}. It should be noted in this connection that permutations involving an interchange of identical orbits do not appear in (13). When $i=j$, (13) may accordingly be written

$$H^{R_iR_i}=[H_{P_{\text{I}}}{}^{R_iR_i}1+\sum_{k<l} H_{P_{kl}}{}^{R_iR_i}P_{kl}{}^{R_iR_i}]. \tag{14}$$

Interchanges of identical orbits are to be omitted from the summation. Here $H_{P_{\text{I}}}{}^{R_iR_i}$ is the ordinary "Coulomb" energy, while the coefficients $H_{P_{kl}}{}^{R_iR_i}$ are the usual exchange integrals.

When the orbits are not orthogonal, as in molecular problems, (13) is still valid if we write $H-W$ in place of H. The method for solving the resulting secular equation has been discussed in *I*.

CALCULATION OF THE MATRICES REPRESENTING THE P'S

We have seen that any permutation P can be expressed in terms of the spin variables by means of (8). From the form of (8) it is evident that P is invariant under a rotation of spin axes. The P's, and the energy, which is a function of the P's, can accordingly have no matrix elements between states of different S or M_S, and for each characteristic value of S we obtain a representation of the P's which is independent of M_S.

The first task in finding these representations is to express the spin wave functions belonging to a given S and M_S, for an n electron system, in terms of one-electron spin functions. The representative of any P^S, i.e., any permutation of spin orbits, can then be calculated, and P obtained by use of (7).

The wave functions are found by repeated application of the familiar formula for the compounding of two vectors S_1, S_2 to a resultant S,

$$\psi^{S_1S_2}{}_{SM_S}=\sum{}_\mu s^{S_1S_2}{}_{S\mu M_S-\mu}\psi_{S_1\mu}\psi_{S_2M_S-\mu}.$$

General formulas for the coefficients $s^{S_1S_2}{}_{S\mu M_S-\mu}$ have been given by Wigner.[4] The matrices P_{12}, P_{34}, $\cdots$ will be diagonal if we begin by compounding s_1 and s_2 to a resultant S_{12}, s_3 and s_4 to a resultant S_{34}, etc., and then proceed to compound S_{12} and S_{34} to S' and so forth until the total spin, S, is diagonal. Only one value of M_S need be considered; it is simplest to take $M_S=S$. For the single state with $S=n/2$ all the electron spins are parallel, and it follows directly from the vector model, (8), that any odd permutation is represented by -1, any even permutation by $+1$.

The case $n=4$ will serve as an example of the method, and also of some devices which considerably shorten the labor in more complicated cases. From four electrons we obtain one quintet state, three triplet states, and two singlet states, as can be seen from Fig. 1 of reference 2. The wave functions, $\psi^{S_{12}S_{34}}{}_{11}$, of the three triplet states can be expressed in terms of two-electron spin wave functions as

$$\begin{gathered}\psi^{11}{}_{11}=(1/\surd 2)[\psi_{11}(s_1s_2)\psi_{10}(s_3s_4)-\psi_{10}(s_1s_2)\psi_{11}(s_3s_4)],\\ \psi^{10}{}_{11}=\psi_{11}(s_1s_2)\psi_{00}(s_3s_4),\qquad \psi^{01}{}_{11}=\psi_{00}(s_1s_2)\psi_{11}(s_3s_4).\end{gathered} \tag{15}$$

The two electron wave functions are given by

$$\psi_{11}(s_is_j)=\xi_i\xi_j;\qquad \psi_{10}(s_is_j)=(1/\surd 2)(\xi_i\eta_j+\eta_i\xi_j);\qquad \psi_{00}(s_is_j)=(1/\surd 2)(\xi_i\eta_j-\eta_i\xi_j), \tag{16}$$

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[4] E. Wigner, reference 3, p. 206.

where ξ_i is the spin wave function of the ith electron for $m_s=\frac{1}{2}$, and η_i is the spin wave function for $m_s=-\frac{1}{2}$.

For the first and second of the states (15), the spins of electrons 1 and 2 are parallel, so $P_{12}=-1$; for the third they are anti-parallel, so $P_{12}=1$. Similarly, the characteristic values of P_{34} are $-1, 1, -1$. This is a rather trivial illustration of a fact which is very useful when n is greater than 4; if we have found the P's for the cases $n=r$ and $n=p$ we can immediately write down, for the case $n=r+p$, all the P's which involve only the first r or the last p orbits. The labor involved in calculating the matrix elements of the remaining P's can be greatly reduced by taking advantage of relations between the P's, obvious symmetry properties of the wave functions, and the fact that the matrices representing simple interchanges are both Hermitian and unitary. For example, from (15) and (16) we find

$$P^S{}_{13}\psi^{01}{}_{11}=-(1/\sqrt{2})\psi^{11}{}_{11}+\tfrac{1}{2}\psi^{10}{}_{11}+\tfrac{1}{2}\psi^{01}{}_{11}. \tag{17}$$

This equation determines the last column of the matrix representing $P^S{}_{13}$. If both sides of (17) are multiplied by P^S, the left side becomes $P^SP^S{}_{13}\psi^{01}{}_{11}=P^S{}_kP^S\psi^{01}{}_{11}$, with $P^S{}_k=P^SP^S{}_{13}P^{S-1}$. Choose $P^S=P^S{}_{(13)(24)}$. Then $P^S{}_k=P^S{}_{13}$, and inspection of (15) immediately shows that $P^S{}_{(13)(24)}\psi^{01}{}_{11}=\psi^{10}{}_{11}$, $P^S{}_{(13)(24)}\psi^{10}{}_{11}=\psi^{01}{}_{11}$, $P^S{}_{(13)(24)}\psi^{11}{}_{11}=-\psi^{11}{}_{11}$. Hence

$$P^S{}_{13}\psi^{10}{}_{11}=(1/\sqrt{2})\psi^{11}{}_{11}+\tfrac{1}{2}\psi^{10}{}_{11}+\tfrac{1}{2}\psi^{01}{}_{11},$$

and the second column of the matrix representing $P^S{}_{13}$ is determined. The third column can now be found by using the fact that $P^S{}_{13}$ is unitary and Hermitean. The matrix representing $P^S{}_{23}$ is found by means of the relation $P^S{}_{23}=P^S{}_{12}P^S{}_{13}P^S{}_{12}$, which, in view of the diagonal form of $P^S{}_{12}$, shows how $P^S{}_{23}$ may be obtained by simply changing certain signs in $P^S{}_{13}$. Similarly, $P^S{}_{14}$ is determined by $P^S{}_{14}=P^S{}_{34}P^S{}_{13}P^S{}_{34}$, and $P^S{}_{24}$ by $P^S{}_{24}=P^S{}_{34}P^S{}_{23}P^S{}_{34}$.

Using (7), we find for $n=4$, $S=1$,

$$P_{12}=\begin{vmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{vmatrix},\quad P_{34}=\begin{vmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{vmatrix},\quad P_{13}=\begin{vmatrix}0 & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}}\\ -\sqrt{\frac{1}{2}} & -\frac{1}{2} & -\frac{1}{2}\\ \sqrt{\frac{1}{2}} & -\frac{1}{2} & -\frac{1}{2}\end{vmatrix},$$

$$P_{14}=\begin{vmatrix}0 & \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}}\\ \sqrt{\frac{1}{2}} & -\frac{1}{2} & \frac{1}{2}\\ \sqrt{\frac{1}{2}} & \frac{1}{2} & -\frac{1}{2}\end{vmatrix},\quad P_{23}=\begin{vmatrix}0 & -\sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}}\\ -\sqrt{\frac{1}{2}} & -\frac{1}{2} & \frac{1}{2}\\ -\sqrt{\frac{1}{2}} & \frac{1}{2} & -\frac{1}{2}\end{vmatrix},\quad P_{24}=\begin{vmatrix}0 & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}}\\ \sqrt{\frac{1}{2}} & -\frac{1}{2} & -\frac{1}{2}\\ -\sqrt{\frac{1}{2}} & -\frac{1}{2} & -\frac{1}{2}\end{vmatrix}.$$

In a similar way we obtain for $n=4$, $S=0$,

$$P_{12}=P_{34}=\begin{vmatrix}-1 & 0\\ 0 & 1\end{vmatrix},\quad P_{13}=P_{24}=\begin{vmatrix}\frac{1}{2} & \sqrt{\frac{3}{4}}\\ \sqrt{\frac{3}{4}} & -\frac{1}{2}\end{vmatrix},\quad P_{14}=P_{23}=\begin{vmatrix}\frac{1}{2} & -\sqrt{\frac{3}{4}}\\ -\sqrt{\frac{3}{4}} & -\frac{1}{2}\end{vmatrix}. \tag{18}$$

The representation of higher order permutations can be found by multiplication of these representations of the interchanges.

The representations of P_{12}, P_{13}, and P_{23} which we have just found for $n=4$, $S=0$ are also the representations of these permutations for $n=3$, $S=\frac{1}{2}$, for, on removing the fourth electron, a state $S=0$ of the four electron problem evidently goes over into a state $S=\frac{1}{2}$ of the three electron problem.

Application to the Atomic Configuration d^3

As an example of the use of (13) we shall calculate the energies of the two ${}^2D$ levels arising from the atomic configuration d^3. It has been shown[2] in I how the vector model can be used, as an alternative to Slater's method, to find the energies of the other levels arising from this configuration, but of course either method gives only the mean energy of the ${}^2D$ states. To separate them we must set up the complete secular determinant for $M_L=2$.

The orbits having $m_l=2, 1, 0, -1, -2$ will be denoted by $d\delta$, $d\pi$, $d\sigma$, $d-\pi$, $d-\delta$, respectively. The four configurations which have $M_L=2$ are

$$A: (d\pi, d-\pi, d\delta), \quad B: (d\sigma, d\sigma, d\delta), \quad C: (d\pi, d\pi, d\sigma), \quad D: (d\delta, d\delta, d-\delta).$$

All the orbits of A are different, so the matrices P_{ij}^{AA} are simply those given in (18). The orbits 1 and 2 are the same in B, C, D, so P_{ij}^{XA}, $(X=B, C, D)$, is the second row of P_{ij}, and P_{ij}^{XY}, $(X, Y=B, C, D)$, is the element in the second row, second column of P_{ij}. The energy matrix for the doublet states is shown below.

$H_{\rm I}^{AA}-H_{12}^{AA}+\frac{1}{2}H_{13}^{AA}+\frac{1}{2}H_{23}^{AA}$	$\sqrt{\frac{3}{4}}[H_{13}^{AA}-H_{23}^{AA}]$	$\sqrt{\frac{3}{2}}[H_{13}^{BA}-H_{23}^{BA}]$	$\sqrt{\frac{3}{2}}[H_{13}^{CA}-H_{23}^{CA}]$	$\sqrt{\frac{3}{2}}[H_{13}^{DA}-H_{23}^{DA}]$
$\sqrt{\frac{3}{4}}[H_{13}^{AA}-H_{23}^{AA}]$	$H_{\rm I}^{AA}+H_{12}^{AA}-\frac{1}{2}H_{13}^{AA}-\frac{1}{2}H_{23}^{AA}$	$\sqrt{2}[H_{\rm I}^{BA}-\frac{1}{2}H_{13}^{BA}-\frac{1}{2}H_{23}^{BA}]$	$\sqrt{2}[H_{\rm I}^{CA}-\frac{1}{2}H_{13}^{CA}-\frac{1}{2}H_{23}^{CA}]$	$\sqrt{2}[H_{\rm I}^{DA}-\frac{1}{2}H_{13}^{DA}-\frac{1}{2}H_{23}^{DA}]$
$\sqrt{\frac{3}{2}}[H_{13}^{BA}-H_{23}^{BA}]$	$\sqrt{2}[H_{\rm I}^{BA}-\frac{1}{2}H_{13}^{BA}-\frac{1}{2}H_{23}^{BA}]$	$H_{\rm I}^{BB}-\frac{1}{2}H_{13}^{BB}-\frac{1}{2}H_{23}^{BB}$	$H_{\rm I}^{CB}-\frac{1}{2}H_{13}^{CB}-\frac{1}{2}H_{23}^{CB}$	$H_{\rm I}^{DB}-\frac{1}{2}H_{13}^{DB}-\frac{1}{2}H_{23}^{DB}$
$\sqrt{\frac{3}{2}}[H_{13}^{CA}-H_{23}^{CA}]$	$\sqrt{2}[H_{\rm I}^{CA}-\frac{1}{2}H_{13}^{CA}-\frac{1}{2}H_{23}^{CA}]$	$H_{\rm I}^{CB}-\frac{1}{2}H_{13}^{CB}-\frac{1}{2}H_{23}^{CB}$	$H_{\rm I}^{CC}-\frac{1}{2}H_{13}^{CC}-\frac{1}{2}H_{23}^{CC}$	$H_{\rm I}^{DC}-\frac{1}{2}H_{13}^{DC}-\frac{1}{2}H_{23}^{DC}$
$\sqrt{\frac{3}{2}}[H_{13}^{DA}-H_{23}^{DA}]$	$\sqrt{2}[H_{\rm I}^{DA}-\frac{1}{2}H_{13}^{DA}-\frac{1}{2}H_{23}^{DA}]$	$H_{\rm I}^{DB}-\frac{1}{2}H_{13}^{DB}-\frac{1}{2}H_{23}^{DB}$	$H_{\rm I}^{DC}-\frac{1}{2}H_{13}^{DC}-\frac{1}{2}H_{23}^{DC}$	$H_{\rm I}^{DD}-\frac{1}{2}H_{13}^{DD}-\frac{1}{2}H_{23}^{DD}$

For brevity we have written H_{12}^{AA} in place of $H_{P_{12}}^{AA}$, and so forth. The coefficients $H_P^{R_iR_j}$ can readily be expressed in terms of the integrals

$$(\alpha\beta;\, \gamma\epsilon)=\int (d\alpha\,|\,x_1y_1z_1)^*(d\beta\,|\,x_2y_2z_2)^*r_{12}^{-1}(d\gamma\,|\,x_1y_1z_1)(d\epsilon\,|\,x_2y_2z_2)d\tau_1d\tau_2,$$

and these in turn in terms of the Slater-Condon parameters F_0, F_2, F_4. To quote a few examples,

$H_{\rm I}^{AA}=(\pi-\pi;\ \pi-\pi)+(\pi\delta;\ \pi\delta)+(-\pi\delta;\ -\pi\delta)$; $H_{12}^{AA}=(\pi-\pi;\ -\pi\pi)$; $H_{\rm I}^{BB}=(\sigma\sigma;\ \sigma\sigma)+2(\sigma\delta;\ \sigma\delta)$; $H_{13}^{BB}=H_{23}^{BB}=(\sigma\delta;\ \delta\sigma)$; $H_{\rm I}^{BA}=(\sigma\sigma;\ \pi-\pi)$; $H_{13}^{BA}=H_{23}^{BA}=0$; $H_{\rm I}^{CB}=0$; $H_{13}^{CB}=H_{23}^{CB}=(\pi\pi;\ \sigma\delta)$.

Three of the five characteristic values of the energy matrix are already known; namely ${}^2H$, ${}^2G$, ${}^2F$. The mean of the two ${}^2D$ levels can be found by subtracting the known characteristic values from the spur of the energy matrix. In a similar way, the mean square of the ${}^2D$ levels can be found by subtracting the squares of the known characteristic values from the spur of H^2. This spur is $\mathrm{Sp}\,H^2=\sum_{ij}|H_{ij}|^2$, i.e., it is simply the sum of the squares of the elements of the energy matrix. The energies of the two ${}^2D$ states are then given by

$${}^2D_{\pm}=\tfrac{1}{2}\alpha\pm\tfrac{1}{2}(2\beta-\alpha^2)^{\frac{1}{2}} \quad \text{with} \quad \alpha={}^2D_{+}+{}^2D_{-}, \quad \beta=({}^2D_{+})^2+({}^2D_{-})^2.$$

On carrying out the arithmetic we check the result previously obtained by Shortly and Ufford[5] by means of Slater wave functions. One advantage of the present method is that the secular determinant factors according to characteristic values of S; the Slater wave functions do not lead to such a factorization.

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[5] C. W. Ufford and G. H. Shortley, Phys. Rev. **42**, 167 (1932).