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The Dirac Vector Model in Complex Spectra

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Dirac has shown that the secular problem presented by the permutation degeneracy is formally equivalent to a problem in vector coupling for which the Hamiltonian function is $-\frac{1}{2}\Sigma K_{ij}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)$ where $\mathbf{s}_i$, $\mathbf{s}_j$ are respectively the spin vectors of orbits i, j and K_{ij} is the exchange integral which connects i and j. The vector model can be used in place of Slater's determinantal wave functions to calculate atomic spectral terms, provided one still retains much of Slater's powerful method of diagonal sums. The configuration d^3 is treated as an example. Configurations of the form sa^k ($a=p$, d, $f\cdots$; $0<k<4l_a+2$) are particularly amenable to the vector model, as it enables us immediately to write down the energy of sa^k if that of a^k is known. One thus finds that the two states $S=S_k\pm\frac{1}{2}$ built upon a given configuration S_k, L_k of the core a^k should have a separation proportional to $S_k+\frac{1}{2}$ and independent of L_k. Experimentally, this prediction is confirmed only roughly, like the interval relations found by Slater, because perturbations by other configurations are neglected. Various applications to molecular spectra are given. The Heitler-Rumer theory of valence, which neglects directional effects, has a particularly simple interpretation in terms of the vector model.

In configurations of the form p^n both spin-orbit and electrostatic energy can be calculated by the vector model without use of the invariance of diagonal sums. For this particular configuration the Pauli principle is equivalent to a constraint $2\mathbf{s}_i\cdot\mathbf{s}_j=-(\mathbf{l}_i\cdot\mathbf{l}_j)^2-(\mathbf{l}_i\cdot\mathbf{l}_j)+\frac{1}{2}$ connecting the relative orientations of spin and of angular momentum vectors.

1. Introduction

The method commonly used for calculating energy levels in problems involving permutation degeneracy is that due to Slater.[1] It appears to have been rather generally overlooked that Dirac's[2] vector model is, as we shall show, likewise often very convenient for many computations in complex and molecular spectra. The beauty of the vector method is that it gives a simple kinematical picture for the results and does not require the explicit determination of proper final wave functions.[3] Yet we must grant that many physicists find wave methods easier than matrix ones and to a large extent it is a matter of taste and training whether the Dirac or Slater method is the more tractable. Both of these procedures are simpler than full-fledged group methods and are alike in that they owe their strength essentially to recognition at the outset that the allowable "characters" for the permutation group are very severely limited by the Pauli principle, so that the group technique is more general and complicated than needed.

Before removal of the permutation degeneracy, a typical orbital wave function of the system may be taken to be the product

$$\Psi=\psi_1(x_1,\,y_1,\,z_1)\psi_2(x_2,\,y_2,\,z_2)\cdots\psi_n(x_n,\,y_n,\,z_n) \tag{1}$$

of the wave functions of the n individual electrons, which we shall suppose separately normalized to unity. We shall throughout use the term "orbit" to designate the quantum numbers, etc., of one electron, considered individually, and the term "state" to specify the condition of the entire system of all n electrons. We shall always assume that the only permutation effects which need to be con-

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[1] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[2] P. A. M. Dirac, Proc. Roy. Soc. **A123**, 714 (1929), or *The Principles of Quantum Mechanics*, chapter XI. A brief resumé of Dirac's method is also given in chapter XII of the writer's *Theory of Electric and Magnetic Susceptibilities.*

[3] At first sight it seems as if we would need to find the wave functions if we desire intensities rather than simply energy levels. However, Condon and Ufford find that oftentimes the intensities can be found from the principle of spectroscopic stability without determining the final wave functions; Phys. Rev. **44**, 740 (1933).

sidered are simple exchanges. The higher order permutations will be treated by R. Serber in a paper to appear in the *Physical Review* shortly.[4] They do not enter if the wave functions of the various orbits are orthogonal and are usually neglected even if they are not. Orthogonality of the ψ's will be assumed unless otherwise stated.

We shall, like Slater, use the notation K_{ij} for the exchange integral

$$K_{ij}=\int\cdots\int\psi_i^*(x_1, y_1, z_1)\psi_j^*(x_2, y_2, z_2)H\psi_j(x_1, y_1, z_1)\psi_i(x_2, y_2, z_2)d\tau_1 d\tau_2, \tag{2}$$

and J_{ij} for the Coulomb one

$$J_{ij}=\int\cdots\int\psi_i^*(x_1, y_1, z_1)\psi_j^*(x_2, y_2, z_2)(e^2/r_{12})\psi_i(x_1, y_1, z_1)\psi_j(x_2, y_2, z_2)d\tau_1 d\tau_2. \tag{3}$$

Clearly the Hamiltonian operator H has the structure

$$H=\Sigma_i f(x_i, y_i, z_i, \partial\cdots/\partial x_i, \partial\cdots/\partial y_i, \partial\cdots/\partial z_i)+\Sigma_{j>i}e^2/r_{ij}.$$

We shall throughout omit the Coulomb terms arising from $\Sigma_i f(x_i, \cdots, \partial\cdots/\partial z_i)$, as they enter merely as additive constants in the problems which we shall consider. We shall use Mulliken's Greek notation for the spatial quantum number; thus $2p\pi_+$ means $n=2$, $l=1$, $m_l=+1$ (or $\lambda=+1$ if the axial quantum number is denoted by λ, as in molecular problems). We use the term "configuration" for the totality of states which arise when the orbital quantum numbers of all the orbits are specified, apart from permutations of electrons among the orbits. This agrees with the use of the word configuration in molecular spectroscopy, where three quantum numbers are used to specify an orbit, but atomic spectroscopists do not distinguish between different values of the spatial quantum number. When there is danger of confusion, we shall speak of atomic and spatial configurations. Thus $2p\pi 2p\sigma$, $2p\pi^2$ are two different spatial configurations but represent the same atomic configuration $2p^2$. A single configuration may have several possible values for its resultant spin S and a given value of S for the configuration may yield more than one energy level. The frequency of occurrence ν of any S is obtained by the "branching rule" which is illustrated in Fig. 1 and which is constructed by building up the configuration electron by electron. Electrons in equivalent orbits are not to be counted in constructing the branching patterns, as their resultant spin can only be zero because of the Pauli principle. The analytical formula for ν is

$$\nu=\binom{n}{k}-\binom{n}{k-1}$$

where $k=\frac{1}{2}n-S$, and n is the number of free orbits.[5]

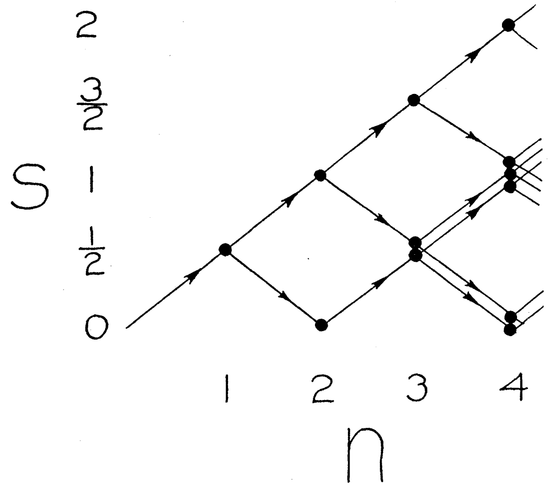

FIG. 1.

For the present we shall consider only the secular problem connected with a single configuration. The problem of treating simultaneously the permutation degeneracy and the interaction of two or more configurations is naturally more complicated (unless this interaction vanishes, as often happens) and will be examined in Serber's article.[4]

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[4] R. Serber, Phys. Rev. to be published, April 1, 1934.

[5] Cf., for instance, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 324, Eq. (14).

Slater's way of solving the permutation problem is to superpose on (1) the Pauli spin functions, permute the arguments, take antisymmetric linear combinations and then construct the secular determinant. Dirac has shown that, instead, we can utilize the theorem that the energy levels are the same as those of a Hamiltonian function

$$\mathcal{H}=\Sigma_{j>i}J_{ij}+\Sigma_{j>i}K_{ij}\mathcal{P}_{ij}=\Sigma_{j>i}J_{ij}-\tfrac{1}{2}\Sigma_{j>i}K_{ij}(1+4\mathbf{s}_i\cdot\mathbf{s}_j) \qquad (4)$$

provided we confine our attention to one configuration. Here $\mathbf{s}_i$ (half Dirac's σ_i) is the spin vector associated with the orbit i, measured in multiples of $h/2\pi$, and $\mathcal{P}_{ij}$ is the permutation matrix associated with interchange of orbits i and j. *All expressions printed in bold-face type are vector matrices.* The proof of (4) we can omit, as it is given by Dirac.[2] The result (4) is, however, fairly obvious from the following considerations. First we remember that the characteristic values of $\mathcal{P}_{ij}$ are ± 1 and that the resultant spin quantum number of i, j has respectively the values 0, 1 when $\mathcal{P}_{ij}=+1,\ -1$. We shall have frequent occasion to use the relation

$$2\Sigma_{j>i}\mathbf{s}_i\cdot\mathbf{s}_j=(\Sigma\mathbf{s}_i)^2-\Sigma\mathbf{s}_i^2=S(S+1)-\tfrac{3}{4}n, \qquad (5)$$

where S is the total-spin quantum number for a system of n non-equivalent orbits. When bold-face type appears on the left and ordinary italic type on the right of an equality, it means that the left side is a matrix and the right side is a typical characteristic value of the matrix. Thus $\mathbf{s}_i^2=s_i(s_i+1)$. This convention obviates the necessity of inserting indices on the left side. The factor $\frac{3}{4}$ is involved in (5) since for a single electron $s_i(s_i+1)=\frac{3}{4}$. When we specialize (5) to $n=2$, the only possible values of S are 0, 1. Hence the characteristic values of the bracketed factor in (4) are ± 1 and this factor is the same as $\mathcal{P}_{ij}$ since these two matrices are simultaneously diagonal with the same characteristic values.

As Dirac also briefly mentions, the procedure must be modified when a pair of orbits α, α' belonging to a configuration are identical. Here one must drop from the summation in (4) the term involving $K_{\alpha\alpha'}$, for there is no distinction between exchange and direct Coulomb energy between two identical orbits and the proper mutual energy is already included in $J_{\alpha\alpha'}$. Let q be any third orbit not belonging to the pair. Then since $K_{q\alpha}=K_{q\alpha'}$ and since $\mathbf{s}_\alpha+\mathbf{s}_{\alpha'}=0$ because of the Pauli principle, we have

$$-\tfrac{1}{2}K_{q\alpha}[1+4\mathbf{s}_\alpha\cdot\mathbf{s}_q]-\tfrac{1}{2}K_{q\alpha'}[1+4\mathbf{s}_{\alpha'}\cdot\mathbf{s}_q]=-K_{q\alpha}[1+2(\mathbf{s}_\alpha+\mathbf{s}_{\alpha'})\cdot\mathbf{s}_q]=-K_{q\alpha}. \qquad (6)$$

Let Roman and Greek subscripts be used for orbits which occur once and twice in the configuration. Such orbits we shall call respectively "free" and "filled" (or "paired") orbits. In place of (4) the proper formula is now

$$\mathcal{H}=\Sigma_{j>i}[J_{ij}-\tfrac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)K_{ij}]+\Sigma_{j,\,\mu}[2J_{j\mu}-K_{j\mu}]+\Sigma_{\mu>\eta}[4J_{\mu\eta}-2K_{\mu\eta}]+\Sigma_\mu J_{\mu\mu}. \qquad (7)$$

In this connection it is to be understood that each pair of identical orbits gives rise to only one term in the Greek summations.

Eq. (4) or (7) shows that, except for additive terms, *there is a formal mathematical similarity between the permutation problem associated with a configuration of n free orbits and the problem of n angular momentum vectors, each of quantum number* $\frac{1}{2}$, *whose coupling energies vary as their scalar products.* The configuration can also involve any number of filled orbits, since by (7) such orbits contribute only an additive constant to the energy. Formulas for the coupling energy of 3 and of 4 angular momentum vectors have been given, respectively, by Güttinger and Pauli[6] and by Johnson.[7] Their results can immediately be adapted to our problem but are more general than we need since they did not specialize the quantum numbers of the component vectors to the value $\frac{1}{2}$. This specialization simplifies the formulas materially and enables them to be obtained often by Goudsmit's inspection method.[8]

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[6] W. Güttinger and W. Pauli, Zeits. f. Physik **67**, 762 (1931).

[7] M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931).

[8] S. Goudsmit, Phys. Rev. **35**, 1325 (1930). The inspection method consists in noting that the constants involved in a quadratic secular equation can often be uniquely evaluated if its behavior is known for extreme cases of the coupling parameters. This method will be used to formulate the secular equations for the states of minimum spin in the three and four electron problems, in an article by A. Sherman to appear in *Reviews of Modern Physics.*

The secular equations appropriate to the cases $n=5$, 6, 7, 8 will be considered in a later paper by Serber and Sherman and have, as a matter of fact, already been formulated by Eyring and colleagues[9] for the important states of minimum spin. The latter, however, did not use the vector model but, instead, a Slater procedure based on electron pair bonds. Heisenberg's theory of ferromagnetism involves unfortunately the case $n=N$, where N is the enormous number of atoms composing the microcrystal. Here accurate solution of the secular equation is clearly impossible. The mean energy and mean square energy belonging to a given spin S of the microcrystal can, however, easily be computed by the vector model. This has been done by the writer.[10] The results are the same as obtained by more complicated group theory. Knowing these means one can, of course, determine the constants of Heisenberg's assumed Gaussian spread of energy levels. Quite irrespective of ferromagnetic applications, the formula for the mean energy $\overline{W}$ of those states of a configuration which have a total spin S is often very useful. It is

$$\overline{W}=C-\tfrac{1}{2}[1+(4S^2+4S-3n)/n(n-1)]\Sigma_{j>i}K_{ij}, \tag{8}$$

where C is an additive constant representing the effect of all Coulomb terms and of exchange terms which involve filled orbits (types $j,\ \mu$; $\mu,\ \eta$; and $\mu,\ \mu$ in Eq. (7)). As Dirac has also shown, formula (8) is proved by using (4) or (7) and noting that, on the average, each $\mathbf{s}_i\cdot\mathbf{s}_j$ absorbs $1/(n^2-n)$ of the sum (5) inasmuch as there are $\frac{1}{2}n(n-1)$ pairs of structure $j>i$.

2. Atomic Spectra

In the calculation of atomic spectral terms there is the degeneracy connected with spatial orientation as well as that connected with the permutation problem. Hence the secular problem usually involves more than one configuration. Nevertheless as Slater[1] has ingeniously shown, this complication can very often be circumvented by utilization of the invariance of the spur and the fact that with given L, S the energy is independent of the quantum numbers M_L, M_S. Here M_L, M_S denote, respectively, the projections of the orbital and spin angular momenta $\mathbf{L}$, $\mathbf{S}$ along some arbitrary spatial direction. We shall not consider spin-orbit coupling, so that introduction of the quantum number J is unnecessary and the Hamiltonian function is diagonal in M_L, M_S. Slater always starts with what we shall call an m_l, m_s system of representation, in which the electrons are individually space quantized, so that $M_L=\Sigma m_{l_i}$, $M_S=\Sigma m_{s_i}$. Ordinarily, two or more spatial configurations will lead to the same values of M_L, M_S. Nevertheless, development of an elaborate inter-configurational theory is unnecessary as far as the sum of the roots of the secular equation is concerned. Indeed it is a well-known theorem that this sum equals the invariant spur or diagonal sum of the matrix elements of the Hamiltonian function regardless of what transformations are made and the spur in question clearly is by definition independent of the troublesome off-diagonal elements which represent the interaction of the various spatial configurations. Furthermore, a certain number of individual roots in the sum for a given M_L, M_S are known if we have already solved the secular equations for larger values of M_L, M_S. This is true since a state of given L, S appears once in the secular equation for each pair of values of M_L, M_S consistent with the inequalities

$$M_L=-L,\ -(L-1),\ \cdots,\ L; \qquad M_S=-S,\ -(S-1),\ \cdots,\ S. \tag{9}$$

Let us begin with the state of maximum M_L, M_S consistent with the given atomic configuration and progress to states of lower and lower M_L, M_S. If at each step the degree of the secular determinant never advances by more than one unit and if it is of degree unity for $M_{L\max}$, $M_{S\max}$ as is usually true, all the roots can be calculated without an inter-configurational theory. As Slater shows,[1] these

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[9] A. Sherman and H. Eyring, J. Am. Chem. Soc. **54**, 2661 (1932); H. Eyring and G. E. Kimball, J. Chem. Phys. **1**, 239 (1933).

[10] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 340.

conditions are always met if we confine our attention to a single atomic configuration and if, in addition, this configuration contains no more than one multiplet of any one type. For an example consider the atomic configuration d^3. Here, by well-known principles, the multiplets are

$$^2H,\ ^2G,\ ^2F,\ ^4F,\ ^2D_+,\ ^2D_-,\ ^4P,\ ^2P. \tag{10}$$

One can easily calculate, as we shall show, the energies of all the states (10) except that one obtains in this fashion only the mean energy of the two ^2D multiplets which, following Ufford,[11] we shall denote by $^2D_+$ and $^2D_-$. To isolate the energies of $^2D_+$, $^2D_-$ or to include perturbations by other configurations, it is necessary to have recourse to a more comprehensive theory, such as has been developed by Ufford and Shortley[12] with the Slater method and which will be examined by Serber[4] in the light of the vector model.

Slater[1] develops the following theorem: *the exchange part of the diagonal sum for the energy can be calculated by using an m_l, m_s system of representation and giving an exchange integral K_{ij} the coefficient -1 if the spins of the corresponding orbits are parallel (i.e., if $m_{s_i}=m_{l_i}=\pm\frac{1}{2}$) and the coefficient zero if they are anti-parallel.* This result is readily deducible from our vector model as follows. The diagonal elements such as are involved in the spur have the physical interpretation of being mean values. If the z axis is that of quantization, the angular momentum vectors precess about the z axis so that only the z component is constant and has a mean value different from zero. The precession rates for the various vectors are different, so that the average product equals the product of the averages. Thus

$$-\tfrac{1}{2}[1+4\overline{\mathbf{s}_i\cdot\mathbf{s}_j}]=-\tfrac{1}{2}[1+4\mathbf{s}_{z_i}\mathbf{s}_{z_j}]=-\tfrac{1}{2}[1+4m_{s_i}m_{s_j}]. \tag{11}$$

Eq. (11) embodies the same kinematical principle as in Landé's or Goudsmit's well-known use of the permanence of Γ-sums in strong fields; instead of appealing to our kinematical intuition via the correspondence principle one could, of course, also derive (11) by simple matrix algebra.[13] Clearly, in agreement with Slater, the expression (11) equals -1 if $m_{s_i}=m_{s_j}=\pm\frac{1}{2}$ and vanishes if $|m_{s_i}|=\frac{1}{2}$, $m_{s_i}=-m_{s_j}$.

Once (11) has been established, the calculation of the levels proceeds in a well-known fashion based on the spur theorem and first described by Slater. Hence details or examples need not be repeated here. Thus, in applying the Dirac model to atomic spectra, one draws very heavily on the powerful Slater technique of diagonal sums and the main difference is that the theorem stated in the preceding paragraph can be proved by the vector model instead of by using determinantal wave functions.

In Slater's original procedure, in order to determine the energies of the states of a given multiplicity, it was necessary first to find the energies of the states of higher multiplicity belonging to the atomic configuration under consideration. This is true since the results for a particular multiplicity are usually obtained by "subtracting out" from the diagonal sums for given M_L, M_S all the roots belonging to states with $S>M_S$. With the aid of the formula (8) based on the vector model (but which could doubtless also be established by other means) it is possible to determine the energy levels for any one multiplicity without the knowledge of those for the higher multiplicities. Another way of saying the same thing is that with (8) one can avoid using the intermediary of individual space quantization for the spin, though such quantization is still needed for the orbit, so that one can begin with the energy values for an m_l, S rather than m_l, m_s system of representation. The former is, of course, nearer the final L, S system. This is only a nominal advantage since the amount of labor saved is not great and since usually one desires the energies of all multiplets belonging to a given configuration. Nevertheless, the m_l, S procedure is an interesting variant from the m_l, m_s one and can also serve as a useful arithmetical check on the latter.

To illustrate and so make more lucid the statements of the preceding paragraph, we shall calculate

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[11] C. W. Ufford, Phys. Rev. **44**, 732 (1934).

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

[13] A. Landé, Zeits. f. Physik **19**, 121 (1923); S. Goudsmit, Phys. Rev. **31**, 946 (1928); W. Heisenberg and P. Jordan, Zeits. f. Physik **37**, 263 (1926) (matrix proof).

the energies of the doublet levels belonging to the configuration d^3 without determining those of the quartets. Out of all the multiplets listed in (10) for d^3, the only one yielded by the spatial configuration $M_L=5$ is ^2H, since all the others demand $M_L<5$. In this configuration there is one free orbit and one closed pair, so that the situation is that covered by (7) when we restrict the i, μ summations to one term each, with no j or η at all, and identify i, μ with $d\pi$, $d\delta^2$, respectively.[14] Hence by (7)

$$W(^2H)=2J(d\delta;\, d\pi)+J(d\delta;\, d\delta)-K(d\delta;\, d\pi). \tag{12}$$

There are two spatial configurations $d\delta d\pi^2$, $d\delta^2 d\sigma$ compatible with $M_L=4$. Both are of the type just discussed, *viz.*, one free orbit and one pair. Hence by (7) and the invariance of the diagonal sum

$$W(^2H)+W(^2G)=2J(d\delta;\, d\pi)+J(d\pi;\, d\pi)-K(d\delta;\, d\pi)+2J(d\delta;\, d\sigma)+J(d\delta;\, d\delta)-K(d\delta;\, d\sigma). \tag{13}$$

When one comes to $M_L=3$, the state of affairs is somewhat different. Here by (10) there are both quartets and doublets, *viz.*, ^2H, ^2G, ^2F, ^4F. From the branching rule given in Fig. 1, one sees that the spatial configuration $d\delta d\pi d\sigma$ admits one quartet and two doublets. The energy spur x for the two doublets is

$$x=2\overline{W}=2[J(d\delta;\, d\pi)+J(d\pi;\, d\sigma)+J(d\delta;\, d\sigma)]. \tag{14}$$

This result is obtained by taking $n=3$, $S=\frac{1}{2}$ in (8) and evaluating the constant C which in the present case consists entirely of Coulombic energy, inasmuch as all three orbits are free. To form the complete spur for $M_L=3$ one must add the part contributed by the other configuration $d\delta^2 d\pi_-$ belonging to $M_L=3$. Hence

$$W(^2H)+W(^2G)+W(^2F)=x+2J(d\delta;\, d\pi_-)+J(d\delta;\, d\delta)-K(d\delta;\, d\pi_-) \tag{15}$$

since $d\delta^2 d\pi_-$ involves one closed pair and so is treated by the same principle as involved in (12).

When $M_L=2$, there is one spatial configuration $d\delta d\pi d\pi_-$ which involves only free orbits and which hence contributes two doublets. Also there are three configurations $d\delta d\sigma^2$, $d\delta^2 d\delta_-$, $d\pi^2 d\sigma$ which involve a pair in each case. Hence applying three times the procedure contained in (12) and once that in (14), we find

$$\begin{aligned} W(^2H)+W(^2G)+W(^2F)+W(^2D_+)+W(^2D_-)=&[2J(d\delta;\, d\sigma)+J(d\sigma;\, d\sigma)-K(d\delta;\, d\sigma)]\\ &+[2J(d\delta;\, d\delta_-)+J(d\delta;\, d\delta)-K(d\delta;\, d\delta_-)]+[2J(d\pi;\, d\sigma)+J(d\pi;\, d\pi)-K(d\pi;\, d\sigma)]\\ &+2[J(d\delta;\, d\pi)+J(d\delta;\, d\pi_-)+J(d\pi;\, d\pi_-)]. \end{aligned} \tag{16}$$

It is, of course, only a trivial matter to solve (12), (13), (15), (16) for $W(^2H)$, $W(^2G)$, $W(^2F)$, $W(^2D_+)+W(^2D_-)$. If one also desires $W(^2P)$ one must also compute the diagonal sums for $M_L=1$ but we shall not do this explicitly as no new principles are involved. By means of Slater's tables[15] or Brinkman's[16] evaluation of the product of three spherical harmonics by the symbolic method, the J's and K's may be expressed in terms of the Slater-Condon F's and G's. One thus finally finds the same formulas for the energy levels of d^3 as those given by Condon and Shortley.[17] The isolation of $^2D_+$, $^2D_-$ with the extended Dirac method will be given by Serber.[4]

Almost closed shells. Shortley's[18] results on shells which are more than half completed can be nicely and succinctly formulated in terms of the vector model. Suppose that one has an atomic configuration of the form $a^x b^{\tau-y}$, where a, b symbolize s, p, d, f etc., and where $\tau=4l_b+2$, $y\leqq\frac{1}{2}\tau$. Clearly τ has the significance of being the maximum number of electrons allowed in the b shell by the Pauli principle. One has the following rule: *Apart from an additive constant common to all the multiplets, the energy levels belonging to $a^x b^{\tau-y}$ are given by the same formulas as those of $a^x b^y$ if in the latter one replaces J_{ij} by $-J_{ij}$*

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[14] We henceforth write $d\pi$, $d\delta$ for $d\pi_+$, $d\delta_+$. It is thus to be understood that $m_l>0$ unless a negative sign is appended, as in, e.g., $d\pi_-$.

[15] J. C. Slater, Phys. Rev. **34**, 1312 (1929).

[16] H. C. Brinkman, Zeits. f. Physik **79**, 762 (1932).

[17] E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

[18] G. H. Shortley, Phys. Rev. **40**, 185 (1932).

and if one takes the exchange potential to be $+\frac{1}{2}[1-4\mathbf{s}_i\cdot\mathbf{s}_j]K_{ij}\dagger$, *rather than* $-\frac{1}{2}[1+4\mathbf{s}_i\cdot\mathbf{s}_j]K_{ij}$ *as in* (4), *whenever i refers to an electron in the group a^x and j to one in b^y, or vice versa.* Here the expression $K\dagger$ is defined by $K\dagger(n_il_im_{l_i};\, n_jl_jm_{l_j}) = K(n_il_im_{l_i};\, n_jl_j-m_{l_j})$. No sign reversals (or substitutions of $K\dagger$ for K) in either the Coulomb or exchange terms are, however, to be made when they connect orbits which both belong to a^x or both to b^y.

A corollary of the above rule, obtained by taking $x=0$, is that the levels of the configuration b^{r-y} are, apart from a constant, the same as those of b^y. If $\mu=4l_a+2$ and if one applies the rule twice in succession, first reducing $a^{\mu-x}b^{r-y}$ to a^xb^{r-y} and then a^xb^{r-y} to a^xb^y, there are two successive sign changes which cancel and so one sees that the energy levels of $a^{\mu-x}b^{r-y}$ are the same as those of a^xb^y, except for a constant.

The proof of the rule we shall omit, as it has already been given by Shortley[18] except for formulation in terms of the vector model. The demonstration is substantially the same with either the Slater or Dirac method, centering about Eq. (11) appropriate to the m_s, m_l system of representation, and applies only to problems amenable to the method of diagonal sums.

3. MOLECULAR SPECTRA

In molecules, there is no longer the degeneracy with respect to M_L and so this degeneracy cannot be used to depress the degree of the secular equations. The energy is still independent of M_S (neglecting, as always, spin-orbit coupling). As in the preceding section, use of individual space quantization for the spin in evaluating the diagonal sums can be avoided by using Eq. (8). Because the M_L degeneracy is lost, the information derivable from the diagonal sum of the energy is naturally much less than in the atomic case.

In the molecular case the orbital wave functions are in general no longer orthogonal. Nevertheless the corrections for non-orthogonality are easily made if we consider only the terms arising from simple permutations. This is not rigorous, since triple permutations, for instance, do not yield wave functions always orthogonal to the original wave function but this "higher order non-orthogonality" is not usually of paramount importance and is often neglected in the literature. (It will, however, be considered by Serber.[4]) Let

$$W=f(J_{12},\ J_{13},\ \cdots J_{1N},\ J_{23},\ \cdots J_{N-1N},\ K_{12},\ \cdots,\ K_{N-1N}) \tag{17}$$

be the solution obtained by disregarding all corrections for non-orthogonality, of whatsoever kind. Here N denotes the total number of orbits, both free and filled. Let Δ_{ij} be the value of the integral (2) when H is stricken out. To include accurately the effect of non-orthogonality as involved in simple permutations, one may use the following rule: substitute $K_{ij}-\Delta_{ij}W$ for each K_{ij} in (17),[19] solve this modified form of (17) for W and take only the root which agrees with (17) when every Δ_{ij} vanishes. That this is the proper answer is readily demonstrated from the fact that the secular determinant involves the matrix elements of $H-W$, with W appearing off the principal diagonal when the wave functions are not orthogonal.

4. CASE THAT CERTAIN COMPONENT SPINS ARE GOOD QUANTUM NUMBERS

The total spin vector $\mathbf{S}$ commutes with the Hamiltonian function and its magnitude is a constant of the motion which can immediately be quantized. This means that in Mulliken's terminology, the total spin S is a "good quantum number." Sometimes the resultant spins of certain groups of orbits which constitute only a portion of the complete system[20] may also be good quantum numbers. If

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[19] Here the subscripts i, j relate to both free and filled orbits rather than free orbits only as in (7).

[20] We do not mean the trivial case that the "certain groups" consist entirely of filled orbits. Filled groups have rigorously zero resultant spin by the Pauli principle. On the other hand, it is not necessary that the orbits involved in Eq. (18), etc., be all free. For instance, in the application to sa^k, some of the k electrons belonging to a^k may have identical spatial quantum numbers and so occur in filled pairs. Since, by (7), filled orbits introduce only an additive constant in the Hamiltonian function, they never introduce any complication.

$$K_{ij} \text{ is independent of } i \text{ for } i \leqq k \text{ and } j > k, \tag{18}$$

then the magnitude of the resultant spin $\mathbf{S}_k = \mathbf{s}_1 + \cdots + \mathbf{s}_k$ of the first k orbits may be quantized simultaneously with that of the total spin $\mathbf{S}$, so that

$$\mathbf{S}_k^2 = S_k(S_k+1), \qquad \mathbf{S}^2 = S(S+1).$$

To prove this, we note that when (18) is satisfied, Eq. (7) becomes

$$\mathcal{H} = C - \tfrac{1}{2}\Sigma_{i,j=1\cdots k\,(j>i)}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)K_{ij} - \tfrac{1}{2}\Sigma_{i,j=k+1\cdots n\,(j>i)}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)K_{ij} + D, \tag{19}$$

with C as in (8) and also with the abbreviation

$$D = -\tfrac{1}{2}\Sigma_{j=k+1\cdots n}[k+4\mathbf{S}_k\cdot\mathbf{s}_j]K_{ij}. \tag{20}$$

The important thing is that D is a function of $\mathbf{S}_k$ rather than of $\mathbf{s}_1\cdots\mathbf{s}_k$ separately. Now it is easily verified that $\mathbf{S}_k^2$ commutes with $\mathbf{s}_i\cdot\mathbf{s}_j$ if i, j are both in the group $1\cdots k$ or both in the group $k+1\cdots n$. Also $\mathbf{S}_k^2$ obviously commutes with $\mathbf{S}_k$ and with $\mathbf{s}_j$ for $j>k$. Hence $\mathbf{S}_k^2$ commutes with the complete Hamiltonian function (19) and with $\mathbf{S}$, and so can be quantized. (In the general case where (18) is not satisfied, $\mathbf{S}_k^2$ cannot be quantized since it does not commute with $\mathbf{s}_i\cdot\mathbf{s}_j$ if i, j relate to different groups.)

In case K_{ij} is independent of j as well as of i in (18), the magnitude of spin $\mathbf{S}_{>k} = \mathbf{s}_{k+1} + \cdots + \mathbf{s}_i$ can also be quantized so that $\mathbf{S}_{>k}^2 = S_{>k}(S_{>k}+1)$. Then Eq. (20) reduces to

$$D = -\tfrac{1}{2}K_{1n}[k(n-k)+4\mathbf{S}_k\cdot\mathbf{S}_{>k}] = -\tfrac{1}{2}K_{1n}\{k(n-k)+2[S(S+1)-S_k(S_k+1)-S_{>k}(S_{>k}+1)]\}, \tag{21}$$

and, except for an additive term (21) which can be evaluated immediately,[21] our n-electron problem factors into the k and $n-k$ electron problems. Formula (21) can always be used to simplify (20) when $k=n-1$, as then there is only one possible value for j in (18).

Some important cases in which the preceding theorem can be used to good advantage are the following:

I. Atomic configurations of the form sa^k ($a=p$, d, etc; $0<k<4l_a+2$). One of the nicest applications is to an s electron outside an incomplete shell of equivalent electrons.[22] Because of the spherical symmetry of the s wave function, the Coulomb and exchange integrals, $J(s;a)$, $K(s;a)$ connecting the s electron with any given electron of the a group are independent of the spatial quantum number of the latter and so do not involve any of the Greek indices. (These statements do not apply to interatomic integrals involving s electrons in molecular problems, since the wave functions of s and a are not concentric if they relate to different atoms.) Hence we can apply (19) and (21), taking $S_{>k}=\frac{1}{2}$ and $n=k+1$. So we find

$$W = W(a^k) - \tfrac{1}{2}K_{as}\{k+2[S(S+1)-S_k(S_k+1)-\tfrac{3}{4}]\} + kJ_{as} \tag{22}$$

where S_k and $W(a^k)$ are, respectively, the spin and the energy of the configuration a^k without addition of the s electron. It is particularly to be noted that *in configurations of the form* sa^k, *the spin of the "core" is rigorously a good quantum number* (when we neglect, as we do throughout, spin-orbit distortion and perturbations by other atomic configurations). This point does not appear to have been generally realized by spectroscopists.

One can use (22), for example, to calculate the levels of the configuration sp^3 in terms of the Slater-Condon F's and G's if the corresponding formulas for p^3 are already known. This application was used in a previous discussion of the carbon spectrum by the writer.[23] The formulas thus obtained for sp^3 agree with those calculated by Johnson[24] with Slater's method.

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[21] When, on the other hand, K_{ij} is not independent of j in (18), one cannot use (21) and D ceases to be an additive constant or even a diagonal matrix.

[22] The writer is indebted to Dr. R. Schlapp for mentioning to him that configurations of the form sa^k are more easily treated by the vector model than by other methods.

[23] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

[24] M. H. Johnson, Jr., Phys. Rev. **39**, 209 (1932).

According to (22), the interval $h\Delta\nu$ between the two states $S=S_k\pm\frac{1}{2}$ of the atom which can be built upon a given spin configuration S_k of the core should have a value

$$h\Delta\nu=2\,|K_{as}|\,(S+\tfrac{1}{2}) \tag{23}$$

independent of the azimuthal quantum number L_k of the core. To test this prediction the following data are available[25, 26]

Ti I: $3d^34s$: ${}^1P-{}^3P=1970$, ${}^1D-{}^3D=2740$, ${}^1G-{}^3G=3120$, ${}^1H-{}^3H=2670$, $\frac{1}{2}[{}^3P-{}^5P]=2410$, $\frac{1}{2}[{}^3F-{}^5F]=2480$ cm^{-1}

Co I: $3d^84s$: ${}^2P-{}^4P=4500$, ${}^2F-{}^4F=3710$	Fe I: $3d^74s$: ${}^3P-{}^5P=5210$, ${}^3F-{}^5F=4940$ cm^{-1}
Ni II: $3d^84s$: ${}^2P-{}^4P=4300$, ${}^2F-{}^4F=4820$	Ti II: $3d^24s$: ${}^2P-{}^4P=6620$, ${}^2F-{}^4F=4560$ cm^{-1}

If (23) were strictly valid, the various intervals quoted for a given ion should be equal. The very appreciable deviations from equality are doubtless due mainly to perturbations by other configurations and, to a lesser extent, to the influence of spin-orbit forces. It is well known that such perturbations often cause the intervals between the different levels of a configuration to have ratios which differ widely from those calculated by means of the Slater-Condon F's and G's, and (22) or (23) represents the same order of approximation as involved in F, G relations.

Ia. Configurations of the type $a^kmsns(m\neq n)$ can be treated by means of (19), (20), but one can no longer use (21). Such configurations will be considered more fully by R. W. Merrill.

II. Body-centered arrangements. Consider a molecular or crystalline structure in which k identical atoms are equidistant from the remaining atom $k+1$ and suppose that in each atom the only electron not in a closed shell is in an s-state. Then one may use (22) with S_k symbolizing the collective spin of the k atoms and $W(a^k)$ their energy in the absence of atom $k+1$. This type of application of the vector model has been discussed by Eyring and colleagues[27] and need not be elaborated here. It shows that the secular problem for the body-centered cube is no more difficult than for the pure cube, if directional valence be disregarded.

III. For checking purposes it is sometimes useful to see if (19) is satisfied when the simplification (18) is artificially imposed in problems in which actually (18) is not satisfied. It is well to make K_{ij} also independent of j in (18), as then one can use (21). Thus errors in arithmetic might be detected in complicated formulas by seeing that they reduce properly when artificial simplifications are imposed. This principle has been used by Seitz and Sherman[28] in molecular problems.

IV. Heitler-Rumer theory. In the chemistry of the light elements the valence electrons (other than those of H atoms) are all in incomplete 2-quantum orbits and are in four kinds of states: *viz.*, $2s$, $2p\sigma_x$, $2p\sigma_y$, $2p\sigma_z$. Here $2p\sigma_x$ means a $2p\sigma$ orbit when the spatial quantization is relative to the x axis, etc. To simplify calculations, it has often been assumed in the literature, notably in the work of Heitler and Rumer,[29] that the inter-atomic Coulomb and exchange integrals connecting the two quantum orbits of one atom and an orbit q of a second atom are the same for all four kinds, so that

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[25] I wish to thank Mr. R. Serber for perusal of Bacher and Goudsmit's book to obtain the separations listed in this table. The numerical figures are often only reliable to 50 cm^{-1} or so since the various terms have a multiplet structure whereas we are interested only in electrostatic energy. In each case an attempt has been made to subtract out the spin-orbit energy but this correction can only be made approximately when the Landé interval rule is not obeyed.

[26] When singlet-triplet separations are quoted in the table, it is to be understood that the two terms whose difference is taken are both built on doublet states of the core a^k. Similarly triplet and quartet core states are implied in connection with the doublet-quartet and triplet-quintet separations, respectively. Note that in Ti I, the ${}^3P$ terms involved in ${}^1P-{}^3P$ and ${}^3P-{}^5P$ are unlike, *viz.*, $3d^3({}^2P)4s\,{}^3P$ and $3d^3({}^4P)4s\,{}^3P$, respectively. In comparing the singlet-triplet and triplet-quintet separations in Ti I, the latter have been multiplied by $\frac{1}{2}$ in the table since (23) has twice as large a value for $S=\frac{3}{2}$ as for $S=\frac{1}{2}$.

[27] A. E. Stearn, C. Lindsley and H. Eyring, to appear in J. Chem. Phys.

[28] F. Seitz and A. Sherman, J. Chem. Phys. **2**, 11 (1934).

[29] W. Heitler and G. Rumer, Zeits. f. Physik **68**, 12 (1931).

$$A(2p\sigma_x;\, q) = A(2p\sigma_y;\, q) = A(2p\sigma_z;\, q) = A(2s;\, q). \qquad (A = J \text{ or } K). \tag{24}$$

Actually this is not true (except that $A(2p\sigma_x;\, q) = A(2p\sigma_y;\, q)$ if q is a $p\sigma_z$ or s orbit and z is the inter-atomic axis). The assumption (24) is in a certain sense equivalent to saying that all valence electrons are effectively in s states. In reality two electrons at most could be in a common s state and even then their resultant spin would be zero, precluding free valence. We have shown elsewhere[23] that it is usually a poor approximation thus to ignore directional valence but our point is now that if this is done, one has a mathematical problem which has a particularly simple interpretation in terms of the vector model. When all the 2-quantum exchange integrals can thus be considered identical, the spin of each atom becomes a "good quantum number" since the exchange integrals can be taken outside the summation over the electrons of an atom. With the Heitler-Rumer theory one can easily convince oneself that the valence attraction is maximized by making the spin of each atom assume its maximum possible value. To illustrate these ideas consider the molecule CNOH. Because of the Pauli principle, the number of free valence electrons for the C, N, and O atoms are respectively 4, 3, 2, so that we may take $S_{\mathrm{C}} = 2$, $S_{\mathrm{N}} = 3/2$, $S_{\mathrm{O}} = 1$. Apart from intra-atomic terms, Coulomb terms and exchange terms involving closed shells, the Hamiltonian function (7) is thus

$$\mathcal{H} = -\tfrac{1}{2}K_{\mathrm{CN}}[4\times3 + 4\mathbf{S}_{\mathrm{C}}\cdot\mathbf{S}_{\mathrm{N}}] - \tfrac{1}{2}K_{\mathrm{CO}}[4\times2 + 4\mathbf{S}_{\mathrm{C}}\cdot\mathbf{S}_{\mathrm{O}}] - \tfrac{1}{2}K_{\mathrm{NO}}[3\times2 + 4\mathbf{S}_{\mathrm{N}}\cdot\mathbf{S}_{\mathrm{O}}]. \tag{25}$$

Except for an additive constant, this is a four-vector problem of precisely the general type considered by Johnson[7] and his results are immediately available. Usually one is interested only in the secular equation for the two states of zero spin. Since this equation is a quadratic, it may be evaluated by Goudsmit's[8] inspection method without even resorting to Johnson's work. In other molecules treated by Heitler and Rumer there is often only one state of minimum spin and then the results may be obtained particularly simply. In CNH, for example, the exchange energy is thus $3K_{\mathrm{CN}} + K_{\mathrm{CH}} - 3K_{\mathrm{HN}}$ since the spins of N and H must be parallel to each other and anti-parallel to that of C in order to neutralize the spin of the latter.[30] If the molecule is composed of only two atoms, we have the elementary two-vector problem and the inter-atomic exchange energy is given by (21), with S_k, $S_{>k}$ denoting the spins of the two atoms and K_{1n} the inter-atomic exchange integral. This result has been mentioned by Dirac himself,[31] who notes that this diatomic formula is the same as that previously obtained by Heitler[32] with rather abstruse group theory. Born[33] re-derives the same formula with Slater's method, without noting that the vector model is still simpler when one has only s electrons.

The model of the benzene molecule without directional valence which has recently been considered by M. Markov[34] is clearly simply the six-vector problem with the value 3/2 for each constituent spin, since Markov assumes three equivalent valence electrons for each CH group. The geometrical symmetry of the benzene ring makes the problem much more tractable than if the groups were unevenly spaced.

V. Distant atoms. Even if the inter-atomic exchange integrals are not regarded as the same for all types of two quantum orbits, it may still be a valid approximation to regard the spin of the atom as a good quantum number. This will be true if the atom is so remote from other atoms that the intra-atomic exchange integrals are large compared to inter-atomic ones. In (4) or (7) we can then, in accordance with the well-known theory of vector coupling,[35] replace $\mathbf{s}_i\cdot\mathbf{s}_j$ by

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[30] The coefficient of K_{CN} is 3 because $-\tfrac{1}{2}[3\times4 + 4\mathbf{S}_{\mathrm{N}}\cdot\mathbf{S}_{\mathrm{C}}] = 3$ when $S_{\mathrm{N}} = \tfrac{3}{2}, S_{\mathrm{C}} = 2, S_{\mathrm{N+C}} = \tfrac{1}{2}$. Similarly $-2[1 + \mathbf{S}_{\mathrm{H}}\cdot\mathbf{S}_{\mathrm{C}}] = 1$ when $S_{\mathrm{H}} = \tfrac{1}{2}$, $S_{\mathrm{C+H}} = \tfrac{3}{2}$; and $-\tfrac{1}{2}[3 + 4\mathbf{S}_{\mathrm{H}}\cdot\mathbf{S}_{\mathrm{N}}] = -3$ when $S_{\mathrm{H+N}} = 2$. Note that in the three vector problem presented by $\mathbf{S}_{\mathrm{C}}$, $\mathbf{S}_{\mathrm{N}}$, $\mathbf{S}_{\mathrm{H}}$ it is usually impossible to diagonalize simultaneously $\mathbf{S}^2{}_{\mathrm{N+C}}$, $\mathbf{S}^2{}_{\mathrm{C+H}}$, $\mathbf{S}^2{}_{\mathrm{H+N}}$ and in consequence $S_{\mathrm{N+C}}$, $S_{\mathrm{C+H}}$, $S_{\mathrm{H+N}}$ do not usually represent good quantum numbers. However, the particular case $S = 0$ in which we are interested is an exception and is achieved only when $\mathbf{S}^2{}_{\mathrm{N+C}}$, $\mathbf{S}^2{}_{\mathrm{C+H}}$, $\mathbf{S}^2{}_{\mathrm{H+N}}$ are simultaneously diagonal and correspond, respectively, to quantum numbers $S_{\mathrm{N+C}} = \tfrac{1}{2}$, $S_{\mathrm{C+H}} = \tfrac{3}{2}$, $S_{\mathrm{H+N}} = 2$.

[31] P. A. M. Dirac, Proc. Roy. Soc. **A123**, 733 (1929).

[32] W. Heitler, Zeits. f. Physik **47**, 855 (1928); Phys. Zeits. **31**, 197 (1930).

[33] M. Born, Zeits. f. Physik **64**, 729 (1930), Eq. (55).

[34] M. Markov, J. Chem. Phys. **1**, 784 (1933).

[35] Cf., for instance, Hund, *Linienspektren*, p. 123. It must be cautioned that (26) cannot be applied to a system composed of two *identical* atoms or radicals a, b when $S_a \neq S_b$. The reason is that there is then a degeneracy difficulty arising from the fact that the energy is the same for $S_a = x$, $S_b = y$ as for $S_a = y$, $S_b = x$, making it necessary to consider off-diagonal elements in S_a, S_b.

$$\overline{\mathbf{s}_i\cdot\mathbf{s}_j}=\frac{\overline{(\mathbf{s}_i\cdot\mathbf{S}_a)}(\mathbf{S}_a\cdot\mathbf{S}_b)\overline{(\mathbf{S}_b\cdot\mathbf{s}_j)}}{\mathbf{S}_a{}^2\mathbf{S}_b{}^2}=\overline{(\mathbf{s}_i\cdot\mathbf{S}_a)}\,\overline{(\mathbf{S}_b\cdot\mathbf{s}_j)}\left[\frac{S(S+1)-S_a(S_a+1)-S_b(S_b+1)}{2S_a(S_a+1)S_b(S_b+1)}\right] \tag{26}$$

in cases where i and j relate to electrons of different atoms a, b, respectively. The kinematical principle involved in (26) is that only the components of $\mathbf{s}_i$, $\mathbf{s}_j$ parallel to $\mathbf{S}_a$, $\mathbf{S}_b$, respectively, are effective when we discard off-diagonal matrix elements and so take average values. Eq. (26) may be further simplified by using the relation

$$2\mathbf{s}_i\cdot\mathbf{S}_a=S_a(S_a+1)-S_{a-i}(S_{a-i}+1)+s_i(s_i+1) \tag{27}$$

if the spin S_{a-i} of atom a exclusive of electron i is a good quantum number: this will be the case if (a) atom a has only two valence electrons, in which case $S_{a-i}=\frac{1}{2}$, $S_a=0, 1$; (b) if a has only equivalent valence electrons except for i and if in addition a is an s electron; or (c) if a has its maximum multiplicity $S_a=\frac{1}{2}n$ where n is the number of free electrons. The expression $\mathbf{S}_b\cdot\mathbf{s}_j$ may be similarly simplified if conditions analogous to (a), (b), (c) are met in atom b.

In case the exchange integrals within radicals are large in absolute magnitude compared to those connecting electrons of different radicals, the remarks of the preceding paragraph (except item (b)) all apply with the word "radical" everywhere substituted for "atom."

As an illustration, consider the interaction of an H atom with a C atom so distant as not to destroy the Russell-Saunders coupling of the carbon atom, though close enough so that the inter-atomic forces overpower the spin-orbit coupling, which can hence be disregarded. These conditions are equivalent to saying that the atomic L, S, but not J, remain good quantum numbers. Apart from the contributions of the closed $1s$ and $2s$ shells, the inter-atomic energy for the states built on the ${}^3P$ state of C is given by the following formulas:

$$W({}^3P1s\,{}^{3\pm1}\Pi)=a+b-\tfrac{1}{2}(c+d)[1+(1\pm\tfrac{1}{2})(2\pm\tfrac{1}{2})-\tfrac{3}{4}-2], \tag{28}$$

$$W({}^3P1s\,{}^4\Sigma)=2b-2d,\qquad W({}^3P1s\,{}^2\Sigma)=2b+d \tag{29}$$

inasmuch as here $S_a=1$, $S_b=\frac{1}{2}$, $S=1\pm\frac{1}{2}$, $S_{a-i}=\frac{1}{2}$ in (26), (27). We have used the abbreviations

$$a=J(2p\sigma;\,1s),\qquad b=J(2p\pi;\,1s),\qquad c=K(2p\sigma;\,1s),\qquad d=K(2p\pi;\,1s).$$

The index $1s$, of course, relates to the H atom. The formulas for the states built upon ${}^1D$ or ${}^1S$ are

$$W({}^1D1s\,{}^2\Delta)=2b-d,\qquad W({}^1D1s\,{}^2\Pi)=a+b-\tfrac{1}{2}(c+d), \tag{30}$$

$$W({}^1D1s\,{}^2\Sigma)=2(\tfrac{2}{3}a+\tfrac{1}{3}b)-\tfrac{2}{3}c-\tfrac{1}{3}d,\qquad W({}^1S1s\,{}^2\Sigma)=2(\tfrac{1}{3}a+\tfrac{2}{3}b)-\tfrac{1}{3}c-\tfrac{2}{3}d. \tag{31}$$

In obtaining these results we have utilized the fact that the orbital wave functions for Σ states of the C atom are of the form

$$\Psi=\alpha\psi_{2p\sigma}(1)\psi_{2p\sigma}(2)+\beta\psi_{2p\pi+}(1)\psi_{2p\pi-}(2)+\gamma\psi_{2p\pi-}(1)\psi_{2p\pi+}(2)$$

with α, β, $\gamma=(\frac{2}{3})^{\frac{1}{2}}$, $(\frac{1}{6})^{\frac{1}{2}}$, $(\frac{1}{6})^{\frac{1}{2}}$ for ${}^1D$; $(\frac{1}{3})^{\frac{1}{2}}$, $-(\frac{1}{3})^{\frac{1}{2}}$, $-(\frac{1}{3})^{\frac{1}{2}}$ for ${}^1S$; 0, $(\frac{1}{2})^{\frac{1}{2}}$, $-(\frac{1}{2})^{\frac{1}{2}}$ for ${}^3P$. This is proved by the Wigner[36] formulas or otherwise.

VI. Atoms with strongly coupled cores. The same principles as involved in V can also be utilized in atomic problems where the electrons outside the core are not all of the s type, so that the spin of the core is not rigorously a good quantum number, but where the core is so firmly bound that its spin can nevertheless be quantized with good approximation.

VII. Electron pairs. Very often, because of directional valence, the exchange forces between two electrons i and j of different atoms are large compared to all other exchange forces acting on i and j which depend on the alignment of $\mathbf{s}_i$ and $\mathbf{s}_j$. Then the resultant spin $\mathbf{s}_i+\mathbf{s}_j$ will represent a good

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[36] E. Wigner, *Gruppentheorie*, p. 206; J. H. Bartlett, Jr., Phys. Rev. **38**, 1623 (1931).

quantum number, which will have the value 0 for the state of deepest energy in the usual molecular case $K_{ij}<0$. Then if q is any electron other than i, j

$$\overline{\mathbf{s}_i\cdot\mathbf{s}_q}=\overline{\mathbf{s}_j\cdot\mathbf{s}_q}=\tfrac{1}{2}(\mathbf{s}_i+\mathbf{s}_j)\cdot\mathbf{s}_q=0 \quad \text{so that} \quad -\tfrac{1}{2}\overline{[1+4\mathbf{s}_i\cdot\mathbf{s}_q]}=-\tfrac{1}{2} \quad \text{whereas} \quad -\tfrac{1}{2}[1+4\mathbf{s}_i\cdot\mathbf{s}_j]=+1.$$

Under such circumstances we say that i, j form an electron pair (not to be confused with the pairs involved in filled orbits) and we have the theorem that the exchange coefficient is $+1$ between two members of a pair and is $-\frac{1}{2}$ between a member of a pair and any electron outside the pair. This principle is constantly used in any molecular calculation for which electron pairing is a good approximation.[37] It has already been employed in (30), (31) since the two electrons of C form a pair in the singlet cases.

As an illustration, consider a CH molecule at a C–H distance so small that the inter-atomic forces disrupt the L, S structure of the C atom. This is the case at the actual inter-nuclear distance. Then we can no longer neglect the matrix elements connecting ${}^1D1s\,{}^2\Pi$ and ${}^3P1s\,{}^2\Pi$ or ${}^1D1s\,{}^2\Sigma$ and ${}^1S\,{}^2\Sigma$, which was done to obtain (28)–(31). Quite approximately the H electron is paired with a $2p\sigma$ electron in the deepest state $2p\pi 2p\sigma 1s\,{}^2\Pi$, replacing the intra-atomic pairing involved in Eq. (30) and so the formula for this state is $a+b+c-\frac{1}{2}d$ rather than (28) or (30). Formulas for the other states of CH at close distances will be given by J. R. Stehn in a paper in the *Journal of Chemical Physics.*

VIII. Combination of (*IV*) *and* (*V*). One can obtain, for example, Heitler and Rumer's results on NH_2-NH_2 (hydrazine), by applying simultaneously the principles involved in *IV* and *V*. The spin of each NH_2 radical can be treated as a good quantum number because the binding forces internal to the NH_2 radicals are larger than those between two such radicals. Inside NH_2, the spin of the N atom and the collective spin of the two H atoms are good quantum numbers in virtue of the hypothesis (24) and the equidistance of the two H atoms from N. We can use (26), (27) if we substitute S_i, S_j for s_i, s_j. (This modification is necessary because the spin of the N atom is not a one-electron unit.) The state of deepest energy is obtained by taking $S_i=S_j=S_{\rm N}=\frac{3}{2}$, $S_a=S_b=S_{\rm NH_2}=\frac{1}{2}$, $S_{a-i}=S_{b-j}=S_{\rm H_2}=1$. If we neglect the forces between H atoms of different radicals, the exchange energy connecting the two radicals is thus[38] $-\frac{1}{2}(3\times 3+4\overline{S_i\cdot S_j})K_{\rm NN}=-\frac{1}{3}K_{\rm NN}$.

Other examples of the vector model in molecular structure will be given by A. Sherman in an article on valence to appear in *Reviews of Modern Physics.*

5. THE INTERACTION OF A GROUP OF EQUIVALENT *p* ELECTRONS

The vector model has a very striking application to a group of equivalent p electrons. Here, once the energy levels have been determined for p^2, it is possible to derive expressions for the energies of the configurations $p^3\cdots p^6$ without appealing to the method of diagonal sums at all. We might characterize our treatment of d^3 in Section 2 as based on the intermediary of an S, m_l system of quantization, whereas we shall show that for $p^3\cdots p^6$ not even this intermediary is necessary and one can write down formulas for the energy directly in the S, L system. The trick is to note that when we are restricting ourselves to one particular configuration, the matrices are of finite, low degree, so that certain matrix identities are readily established.

First consider the interaction of two equivalent p electrons. Here the terms allowed by the Pauli principle are ${}^1D$, ${}^3P$, ${}^1S$. Now since

$$2\mathbf{s}_i\cdot\mathbf{s}_j+\tfrac{3}{2}=S(S+1), \qquad 2\mathbf{l}_i\cdot\mathbf{l}_j+4=L(L+1) \tag{32}$$

we see that $\mathbf{s}_i\cdot\mathbf{s}_j$, $\mathbf{l}_i\cdot\mathbf{l}_j$ are both diagonal for these terms. Furthermore the characteristic values of

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[37] For other examples and references see J. H. Van Vleck, J. Chem. Phys. **1**, 177, 219 (1933).

[38] This result agrees with that obtained p. 39 of the H–R paper[29] by the Slater method. Since presumably $K_{\rm NN}<0$, the interaction energy of the two NH_2 radicals is positive and hence repulsive with the present type of calculation, whereas actually hydrazine is a stable compound.

$\mathbf{s}_i\cdot\mathbf{s}_j+\frac{1}{2}(\mathbf{l}_i\cdot\mathbf{l}_j+\frac{1}{2})^2-\frac{3}{8}$ are all zero by (32) inasmuch as the allowed pairs of values for L, S are 2, 0; 1, 1; 0, 0. Hence we have the matrix identity

$$2\mathbf{s}_i\cdot\mathbf{s}_j=-(\mathbf{l}_i\cdot\mathbf{l}_j)^2-(\mathbf{l}_i\cdot\mathbf{l}_j)+\tfrac{1}{2}, \tag{33}$$

which, of course is valid in any system of representation, since a null matrix remains a null matrix under any canonical transformation. Eq. (33) has an interesting kinematical interpretation. It shows that *the Pauli principle uniquely determines the angle between the two* **s** *vectors once the angle between the two* **l** *vectors is given.* Now consider the energy of interaction between our two equivalent *p* electrons. In terms of the Slater-Condon F's and G's, it is known that[39]

$$W(^3P)=F_0-5F_2, \qquad W(^1D)=W_0+F_2, \qquad W(^1S)=F_0+10F_2. \tag{34}$$

Hence we have the identity

$$W=F_0+[-5-3\mathbf{l}_i\cdot\mathbf{l}_j-12\mathbf{s}_i\cdot\mathbf{s}_j]F_2, \qquad \text{or} \qquad W=F_0+[-8+3\mathbf{l}_i\cdot\mathbf{l}_j+6(\mathbf{l}_i\cdot\mathbf{l}_j)^2]. \tag{35}$$

We have written the identity in two forms which are equivalent in view of (33). To prove (35), we have only to note that (35) reduces to (34) when one uses (32) and substitutes the proper values of L and S. It may be remarked that the most general function of the relative orientation of two equivalent p electrons is a polynomial of degree 2 in $\mathbf{l}_i\cdot\mathbf{l}_j$, for any polynomial of higher degree can immediately be depressed to a quadratic by means of the identity

$$(\mathbf{l}_i\cdot\mathbf{l}_j)^3=-2(\mathbf{l}_i\cdot\mathbf{l}_j)^2+(\mathbf{l}_i\cdot\mathbf{l}_j)+2. \tag{36}$$

(36) is a consequence of the fact that the characteristic values of $q=\mathbf{l}_i\cdot\mathbf{l}_j$ are 1, -1, -2 by (32), so that $(q^2-1)(q+2)=0$.

Configurations $p^3\cdots p^6$. We are now in a position to calculate immediately the energies of $p^n(n=3,\cdots 6)$. We have only to note that here by (35) the matrix of the interaction is

$$W=\tfrac{1}{2}n(n-1)(F_0-5F_2)+\Sigma_{j>i}(-3\mathbf{l}_i\cdot\mathbf{l}_j-12\mathbf{s}_i\cdot\mathbf{s}_j)F_2. \tag{37}$$

This is brought to diagonal form by diagonalizing $\Sigma\mathbf{s}_i\cdot\mathbf{s}_j$ and $\Sigma\mathbf{l}_i\cdot\mathbf{l}_j$, for then (37) reduces to

$$W=\tfrac{1}{2}n(n-1)F_0+\tfrac{1}{2}[-5n^2+20n-3L(L+1)-12S(S+1)]F_2, \tag{38}$$

in virtue of (5) and the analogous relation

$$2\Sigma_{j>i}\mathbf{l}_i\cdot\mathbf{l}_j+2n=L(L+1) \tag{39}$$

obeyed by the **l** vectors.[40]

If we substitute the proper values of n, L, and S, one finds that (38) gives exactly the same energy levels as those deduced by Slater and by Condon and Shortley.[39] For instance, for the configuration p^3, the only terms allowed by the Pauli principle are ^2P, ^2D, ^4S so that in (38) we must use $n=3$ and the following pairs of values of L, S: 1, $\frac{1}{2}$; 2, $\frac{1}{2}$; or 0, $\frac{3}{2}$. Eq. (38) shows immediately that the energy levels of p^{6-n} are the same as those of p^n except for an additive constant, since both configurations involve the same L, S pairs. This, of course, agrees with the general theorem on almost closed shells given near the end of section 2.

Spin-orbit Energy. It is well known that in the expression $A\mathbf{L}\cdot\mathbf{S}$ for the spin-orbit energy of a group of equivalent electrons in Russell-Saunders coupling, the constant of proportionality A is not the

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[39] J. C. Slater, Phys. Rev. **34**, 1316 (1929); E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931). To avoid fractions we use the Condon-Shortley rather than Slater convention in the definition of the F's.

[40] It is clearly to be understood that in the coupling problems which we consider, individual terms in the summation in (5) or (39) are not diagonal except when $n=2$. Instead only the complete sums are diagonal. The identities (33), (36) are nevertheless valid for any value of n.

same as the value a appropriate to a one-electron system. The standard method of determining A in terms of a and the number of electrons n is that due to Goudsmit.[41] It is based on the invariance of the diagonal sum or spur in the passage from m_l, m_s to S, L quantization, as applied to the matrix $a\Sigma\mathbf{l}_i\cdot\mathbf{s}_i$. In the m_l, m_s this sum is simply $a\Sigma m_{l_i}m_{s_i}$. With our vector model, one can write down the spin-orbit energy in the L, S system without using the spur theorem or the intermediary of m_l, m_s quantization, by the following procedure which furnishes a rather interesting alternative to Goudsmit's method.

In Russell-Saunders coupling, spin-orbit energy has the value

$$a\Sigma\mathbf{l}_i\cdot\mathbf{s}_i=[a\Sigma_i\overline{(\mathbf{l}_i\cdot\mathbf{L})(\mathbf{s}_i\cdot\mathbf{S})}/L(L+1)S(S+1)]\mathbf{L}\cdot\mathbf{S}=A\mathbf{L}\cdot\mathbf{S}, \tag{40}$$

since there is no correlation between the rate of precession of $\mathbf{l}_i$ about $\mathbf{L}$ and that of $\mathbf{s}_i$ about $\mathbf{S}$,[42] so that we may project $\mathbf{l}_i$ along $\mathbf{L}$ and $\mathbf{s}_i$ along $\mathbf{S}$ in taking mean values. The final form of (40) is simply the definition of A. We have been very careful in (40) to write the average energy as proportional to the average of the product $(\mathbf{l}_i\cdot\mathbf{L})(\mathbf{s}_i\cdot\mathbf{S})$ rather than to the product of the averages of $(\mathbf{l}_i\cdot\mathbf{L})$ and $(\mathbf{s}_i\cdot\mathbf{S})$. It is tempting at first to try the latter, for then the calculation is particularly simple inasmuch as all equivalent electrons are on a par, making $n\overline{(\mathbf{l}_i\cdot\mathbf{L})}=\mathbf{L}^2$, $n\overline{(\mathbf{l}_i\cdot\mathbf{L})}=\mathbf{S}^2$. Then we would have $A=a/n$, which is an incorrect formula for the A constant since by trying a few simple examples one finds that it does not agree with the results of Goudsmit's method of diagonal sums. It does not, for instance, give a zero A for $p^3\,{}^2D$. Our vector model immediately removes this paradox by making it clear that it is not at all correct to replace the average of the product by the product of separate averages.[43] Eq. (33) shows that there is a constraint between $\mathbf{l}_i\cdot\mathbf{l}_j$ and $\mathbf{s}_i\cdot\mathbf{s}_j$, so that the motions of $\mathbf{l}_i$ and $\mathbf{s}_i$ are not independent and consequently

$$\overline{(\mathbf{l}_i\cdot\mathbf{L})(\mathbf{s}_i\cdot\mathbf{S})}\neq\overline{(\mathbf{l}_i\cdot\mathbf{L})}\,\overline{(\mathbf{s}_i\cdot\mathbf{S})}\cdot \tag{41}$$

For instance, it might be that the times when $\mathbf{l}_i$ is parallel to $\mathbf{L}$ are those when $\mathbf{s}_i\cdot\mathbf{S}$ is near its maximum, and then the left side of (41) is greater than the right side. Thus we cannot in general divide the bar in Eq. (41). (In the particular case of only two electrons this is allowable, as then each factor in (41) is constant, and $A=a/2$.)

Since $\mathbf{L}=\Sigma\mathbf{l}_i$, $\mathbf{S}=\Sigma\mathbf{s}_i$ we see from (40) that the correct formula for A may be written

$$A=a\Sigma_i\{\Sigma_j(\mathbf{l}_i\cdot\mathbf{l}_j)\Sigma_k(\mathbf{s}_i\cdot\mathbf{s}_k)\}/[L(L+1)S(S+1)]. \tag{42}$$

First let us consider the configuration p^3. Here, $\mathbf{s}_i^2=\frac{3}{4}$, $\mathbf{l}_i^2=2$,

$$\Sigma_i\{\Sigma_j(\mathbf{l}_i\cdot\mathbf{l}_j)\Sigma_k(\mathbf{s}_i\cdot\mathbf{s}_k)\}=3\times2\times\tfrac{3}{4}+2\Sigma_{j>i}[2\mathbf{s}_i\cdot\mathbf{s}_j+\tfrac{3}{4}\mathbf{l}_i\cdot\mathbf{l}_j+(\mathbf{l}_i\cdot\mathbf{l}_j)(\mathbf{s}_i\cdot\mathbf{s}_j)]+\Sigma_i{}'_{,j,k}(\mathbf{l}_i\cdot\mathbf{l}_j)(\mathbf{s}_i\cdot\mathbf{s}_k). \tag{43}$$

The prime attached to the summation means that no terms are to be included in which any two of the indices i, j, k are equal. The relation

$$(2\Sigma_{j>i}\mathbf{l}_i\cdot\mathbf{l}_j)(2\Sigma_{j>i}\mathbf{s}_i\cdot\mathbf{s}_j)=[L(L+1)-2n][S(S+1)-\tfrac{3}{4}n]$$

when applied to a three electron system gives us

$$4\Sigma'_{i,j,k}(\mathbf{l}_i\cdot\mathbf{l}_j)(\mathbf{s}_i\cdot\mathbf{s}_k)+4\Sigma_{j>i}(\mathbf{l}_i\cdot\mathbf{l}_j)(\mathbf{s}_i\cdot\mathbf{s}_j)=[L(L+1)-6][S(S+1)-\tfrac{9}{4}], \tag{44}$$

inasmuch as no terms of the form i, j, k, l (i, j, k, l all unequal) are encountered until there are four electrons or more. The triple sum on the right of (43) can now be eliminated by means of (44). Furthermore certain terms in (43) and (44) can be simplified by the relation

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[41] S. Goudsmit, Phys. Rev. 31, 946 (1928).

[42] Use of (40) is equivalent to rejection of off-diagonal elements in L, S and so amounts to assuming that Russell-Saunders coupling is a good approximation, as is always true in light atoms.

[43] We could, however, divide the bar in (26), as in electrostatic problems there is nothing analogous to the constraint (33). The bar is incorrectly divided in Goudsmit's[41] spin-orbit Eq. (3), but fortunately he does not use his Eq. (3) in cases where this matters.

$$(\mathbf{l}_i\cdot\mathbf{l}_j)(\mathbf{s}_i\cdot\mathbf{s}_j)=\tfrac{1}{2}(\mathbf{l}_i\cdot\mathbf{l}_j)^2-\tfrac{1}{4}(\mathbf{l}_i\cdot\mathbf{l}_j)-1=-\mathbf{s}_i\cdot\mathbf{s}_j-\tfrac{3}{4}(\mathbf{l}_i\cdot\mathbf{l}_j)-\tfrac{3}{4}, \tag{45}$$

which is a consequence of (33) and (36). By (44), (45), (5) and (39), the right side of (43) may be written

$$\tfrac{9}{4}+\tfrac{3}{8}[L(L+1)-6]+\tfrac{3}{2}[S(S+1)-\tfrac{9}{4}]+\tfrac{1}{4}[L(L+1)-6][S(S+1)-\tfrac{9}{4}] \tag{46}$$

when $n=3$. The only pairs of values of L, S which occur for p^3 are $1, \tfrac{1}{2}$; $2, \tfrac{1}{2}$; $0, \tfrac{3}{2}$ and so the expression (46) vanishes. This is, of course, in accord with the fact that the configuration p^3 represents half completion of the shell p^6 and so is devoid of multiplet structure (in our degree of approximation) by one of Goudsmit's theorems. Because (46) and hence (43) vanish for $n=3$, we have the matrix relation

$$(\mathbf{l}_i^2+\mathbf{l}_i\cdot\mathbf{l}_j+\mathbf{l}_i\cdot\mathbf{l}_k)(\mathbf{s}_i^2+\mathbf{s}_i\cdot\mathbf{s}_j+\mathbf{s}_i\cdot\mathbf{s}_k)=0. \tag{47}$$

Since (47) is a matrix identity, it is valid for any group of three electrons i, j, k even though occurring in p^4, p^5, etc.

To calculate the values of A appropriate to p^4, p^5, we note that when there are more than three electrons

$$\begin{aligned}\Sigma_i\{\Sigma_j(\mathbf{l}_i\cdot\mathbf{l}_j)\Sigma_k(\mathbf{s}_i\cdot\mathbf{s}_k)\}=\Sigma'(\mathbf{l}_i^2+\mathbf{l}_i\cdot\mathbf{l}_j+\mathbf{l}_i\cdot\mathbf{l}_k)(\mathbf{s}_i^2+\mathbf{s}_i\cdot\mathbf{s}_j+\mathbf{s}_i\cdot\mathbf{s}_k)-\tfrac{1}{2}n[(n-1)(n-2)-2]\tfrac{3}{4}\times 2\\ -2(n-3)\Sigma_{j>i}\{\tfrac{3}{4}\mathbf{l}_i\cdot\mathbf{l}_j+2\mathbf{s}_i\cdot\mathbf{s}_j+(\mathbf{l}_i\cdot\mathbf{l}_j)(\mathbf{s}_i\cdot\mathbf{s}_j)\},\end{aligned}$$

or using (42), (45), (47), (5), (39), we finally have

$$A=-(n-3)a/L(L+1). \tag{48}$$

This gives the proper result, *viz.*, that the A's for p^4, p^5 are the negative of those for p^2, p. For instance $A=-\tfrac{1}{2}a$ for $p^4\ {}^3P$. It is interesting to note that (48) is a correct formula for the A constants for the entire range of the p group, checking with Goudsmit's results in every case.[44]

The preceding methods cannot be extended, at least in a simple way, to other configurations, such as, for example, equivalent d electrons or non-equivalent p electrons. The reason in the equivalent case is that the algebraic equations which are identically fulfilled are of too high a degree to reduce the problem sufficiently. For instance, with d^n the scalar product $\mathbf{s}_i\cdot\mathbf{s}_j$ is uniquely determined by $\mathbf{l}_i\cdot\mathbf{l}_j$ but is now a polynomial of degree 4 in $\mathbf{l}_i\cdot\mathbf{l}_j$, whereas it was of degree 2 in the case of p^n. If i and j are non-equivalent electrons, the value of $\mathbf{s}_i\cdot\mathbf{s}_j$ ceases to be uniquely determined by $\mathbf{l}_i\cdot\mathbf{l}_j$. Thus except for p^n, one must fall back on spur methods, at least as applied to the **L** part of the problem. Our calculations for p^n by the full vector method applied to both **L** and **S** rather than by our usual Dirac vector scheme applicable only to **S** must be regarded as a special procedure which is available only for the configuration p^n and which is of interest primarily because of the kinematical insight furnished into the Pauli principle.

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[44] For singlet or for S states, the values of A given by (48) have no meaning, as such states are devoid of multiplet structure. For this reason we need not worry over the fact that (40) reduces to the indeterminate form 0/0 when L or S vanishes, or that (48) becomes infinite when $L=0$.