

Average Energy of States of Given Multiplicities in Atoms

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By use of the diagonal sum rule, formulas are derived for the weighted mean energy of the multiplets with a given S value in a partly filled shell of equivalent electrons with a given azimuthal quantum number l . As an incidental result, a formula is also derived for the mean energy of multiplet states with a given M_S . The results can be applied to spectroscopic and magnetic problems. They lead to a straightforward proof that the average energy of multiplets increases with the value of S , one of Hund's rules.

IT is well known¹ that one can set up closed formulas for the weighted mean energies of all the multiplets arising from a given configuration in the theory of atomic multiplets. It is less familiar that one can use the same methods to set up formulas for the weighted mean energies of the multiplets of a given multiplicity arising from a partly filled shell of equivalent electrons. Jørgensen² has stated such theorems without giving a proof. On account of the interest of the theorems, it seems worthwhile showing how the results follow from very general and familiar methods of atomic theory. The theorems are useful particularly for shells of equivalent d and f electrons, in which there are many different multiplets of each multiplicity; they can be used to check the correctness of calculations of the energies of the individual multiplets for various numbers of electrons in the shells. The present reason of the author for investigating the theorems is their application in the theory of magnetism; they will be applied to a problem of this type in the following paper.³

The method of proof which we shall use is familiar from the earliest days of the application of the determinantal method to spectral properties; it is substantially the same as that used by Bloch⁴ in his earliest

study of the magnetism of an electron gas, but he was applying it to the free-electron case rather than to atomic shells. We start by finding the number of determinantal functions associated with a shell l^q , where q is the number of electrons in a shell with azimuthal quantum number l , and associated with a particular magnetic quantum number M_S . Then we shall use the sum rule to find the sum of the energies of these determinantal functions, and hence, to find the average energy of the multiplets associated with this M_S . This will include all multiplets whose S equals M_S, M_S+1, \dots . Hence, if we find the functions for a given M_S , and remove from them those with the value M_S+1 , we shall have just those with S equal to the M_S in question.

Let the number of electrons with spin up be $q_\uparrow = \frac{1}{2}q + M_S$, and that with spin-down be $q_\downarrow = \frac{1}{2}q - M_S$. The number of ways of choosing q_\uparrow orbitals from the number $2l+1$ of spin-orbitals with spin up is

$$(2l+1)!/q_\uparrow!(2l+1-q_\uparrow)!,$$

and we have a similar result for the number of ways choosing q_\downarrow orbitals of spin down. Thus the number of determinantal functions associated with a given value of $M_S = \frac{1}{2}(q_\uparrow - q_\downarrow)$ is given by

$$\frac{[(2l+1)!]^2}{(\frac{1}{2}q + M_S)! (\frac{1}{2}q - M_S)! (2l+1 - \frac{1}{2}q - M_S)! (2l+1 - \frac{1}{2}q + M_S)!} \quad (1)$$

Next we must find the sum of the diagonal matrix components of energy for these determinants. We must use the general formula for the diagonal matrix component of energy of a determinantal function, which has two parts. The first is the sum over all spin-orbitals of the one-electron integrals

$$I = \langle i | f | i \rangle = \int u_i^*(1) f_1 u_i(1) dv_1,$$

where f_1 is the one-electron operator (kinetic energy plus potential energy in the field of the nuclei) of the 1st electron, and u_i is the i th spin-orbital. The second part is the sum over all pairs of spin-orbitals of the quantities $\langle ij | g | ij \rangle - \langle ij | g | ji \rangle$, where

$$\langle ij | g | mn \rangle = \int u_i^*(1) u_j^*(2) g_{12} u_m(1) u_n(2) dv_1 dv_2,$$

in which g_{12} is the two-electron operator (repulsion between the 1st and 2nd electrons) for the first and second electrons. The integrations involve summations over spins, and the exchange integral $\langle ij | g | ji \rangle$ is zero for a pair of spin-orbitals with opposite spin. The indices i, j refer to different quantum numbers. In our

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¹ For a general discussion, see J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Inc., New York, 1960), Vol. 1, Chap. 14. The theorems discussed there were given by G. H. Shortley, *Phys. Rev.* **50**, 1072 (1936).

² C. K. Jørgensen, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P. O. Löwdin (Academic Press Inc., New York, 1966), p. 307. See Eqs. (2) and (3).

³ J. C. Slater, following paper, *Phys. Rev.* **165**, 658 (1968).

⁴ F. Bloch, *Z. Physik* **57**, 545 (1929).

case, where all spin-orbitals have the same principal and azimuthal quantum numbers, we may take the index i or j to refer merely to the m_i and m_s of the spin-orbital.

The one-electron integrals are all alike, and are listed in texts on atomic theory.⁵ The two-electron integrals are given by the following formulas:

$$\langle ij | g | ij \rangle = \sum_k c^k(l_i m_{i_i}; l_j m_{i_j}) c^k(l_j m_{i_j}; l_i m_{i_i}) \times F^k(n_i l_i; n_j l_j), \quad (2)$$

where

$$F^k(n_i l_i; n_j l_j) = \int_0^\infty \int_0^\infty R_{n_i l_i}^*(r_1) R_{n_i l_i}(r_2) \frac{r(a)^k}{r(b)^{k+1}} \times R_{n_i l_i}(r_1) R_{n_j l_j}(r_2) r_1^2 r_2^2 dr_1 dr_2, \quad (3)$$

and

$$\langle ij | g | ji \rangle = \sum_k [c^k(l_i m_{i_i}; l_j m_{i_j})]^2 G^k(n_i l_i; n_j l_j), \quad (4)$$

where

$$G^k(n_i l_i; n_j l_j) = \int_0^\infty \int_0^\infty R_{n_i l_i}^*(r_1) R_{n_i l_i}(r_2) \frac{r(a)^k}{r(b)^{k+1}} \times R_{n_i l_i}(r_1) R_{n_j l_j}(r_2) r_1^2 r_2^2 dr_1 dr_2. \quad (5)$$

In these formulas, the c^k 's are defined in texts on atomic structure⁵ in terms of the integrals of a product of three spherical harmonics, and are tabulated in such texts. They are different from zero only for $k=l_1+l_2, l_1+l_2-2, \dots$, so that the summation over k is really only over a small number of values of the index. The quantities $R_{nl}(r)$ are the radial factors in the orbitals of a spherically symmetrical problem, to be multiplied by a spherical harmonic to give the orbital wave function. In the integrals over r , in Eqs. (3) and (5), $r(a)$ and $r(b)$ refer to the smaller and larger, respectively, of r_1 and r_2 . Hartree units of energy are used in Eqs. (3) and (5). We note that for equivalent electrons, for which the principal and azimuthal quantum numbers, n and l , are identical for the i th and j th cases, the G^k 's become identical with F^k 's. On account of the summations over spins, as we have noted before, the exchange integrals $\langle ij | g | ji \rangle$ vanish unless the two spin-orbitals u_i and u_j have the same spin.

We must now carry out the sums of one-electron and two-electron integrals to get the total energy of the determinantal function. As for the one-electron integrals, they are the same for each of the functions, equal to $I(nl)$, where n and l are principal and azimuthal quantum numbers of the partially filled shell of equivalent electrons which we are considering. Hence the contribution of these functions to the total energy is $qI(nl)$. For the two-electron integrals, we handle separately the terms for $k=0$ and $k \neq 0$. All $c^k(l_i m_{i_i}; l_j m_{i_j})$ equal unity for $k=0$, and all $c^k(l_i m_{i_i}; l_j m_{i_j})$ are zero for $k=0$ if $m_{i_i} \neq m_{i_j}$. Hence we see that as far as the terms in $k=0$ are concerned, each of the integrals $\langle ij | g | ij \rangle$ contributes $F^0(nl; nl)$, and each of the

integrals $\langle ij | g | ji \rangle$ contributes $F^0(nl; nl)$ if $i=j$, zero otherwise. Thus we see that the contribution of the two terms $\langle ij | g | ij \rangle - \langle ij | g | ji \rangle$ for $k=0$ is $F^0(nl; nl)$ for each pair of spin-orbitals for which the quantum numbers of the two spin-orbitals are different, zero if the quantum numbers are the same. However, no case occurs in which the quantum numbers are the same, on account of the exclusion principle. Hence the contribution of the terms $k=0$ to the average energy is simply the number of pairs of spin-orbitals, which is $\frac{1}{2}[q(q-1)]$, times $F^0(nl; nl)$. A pair of spin-orbitals makes the same contribution to this term whether the spins are the same or opposite.

Next we consider the terms in the integrals corresponding to $k \neq 0$. We wish to sum the quantities $\langle ij | g | ij \rangle - \langle ij | g | ji \rangle$ over all pairs of indices i and j which appear in one of the determinantal functions enumerated in Eq. (1), and over all of these determinantal functions. Since $\langle ij | g | ij \rangle - \langle ij | g | ji \rangle$ is automatically zero for $i=j$, we may replace the sum over pairs i, j for which $i \neq j$ by half the double sum over all values of i and j . In the process of summing over all determinantal functions we sum separately over m_{i_i} and m_{i_j} . Then we can use two theorems concerning these summations, derived originally by Shortley.⁶ These are

$$\sum_j \langle ij | g | ij \rangle = (2l_j + 1) F^0(n_i l_i; n_j l_j), \quad (6)$$

and

$$\sum_j \langle ij | g | ji \rangle = \left(\frac{2l_j + 1}{2l_i + 1} \right)^{1/2} \sum_k c^k(l_i 0; l_j 0) G^k(n_i l_i; n_j l_j). \quad (7)$$

In these theorems the summation over j is over the $2l_j + 1$ possible values of m_{i_j} . These theorems are used in proving the formula for the average energy of a configuration, quoted in Ref. 1.

From Eq. (6) we see that the terms $\langle ij | g | ij \rangle$ will contribute only to the terms for $k=0$, which we have already considered. Hence for the terms $k \neq 0$ we need sum only the terms $\langle ij | g | ji \rangle$. From Eq. (7) we see that in the present case, where $l_i = l_j$, this reduces to

$$\sum_j \langle ij | g | ji \rangle = \sum_k c^k(l_0; l_0) F^k(nl; nl). \quad (8)$$

If we now sum over the index i as well as j , and divide by 2 since we will otherwise count each pair twice, we have that the sum of $-\langle ij | g | ji \rangle$ over the pairs of indices m_{i_i}, m_{i_j} is given by

$$(\text{terms for } k=0) - \frac{1}{2}(2l+1) \sum_{k \neq 0} c^k(l_0; l_0) F^k(nl; nl). \quad (9)$$

Since there are $\frac{1}{2}(2l+1)2l$ pairs of indices i and j , where now $i \neq j$, we can then use an average value of exchange, for $k \neq 0$, equal to the value in Eq. (9), divided by $\frac{1}{2}[(2l+1)2l]$. That is, we have (average value of)

$$\langle ij | g | ij \rangle - \langle ij | g | ji \rangle = F^0(nl; nl) - f, \quad (10)$$

where

$$f = (1/2l) \sum_{k \neq 0} c^k(l_0; l_0) F^k(nl; nl). \quad (11)$$

⁵ See for example, J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Inc., New York, 1960), Vol. 1, Sec. 13-3. For the tabulation, see, Vol. 2, Appendix 20.

⁶ See Shortley, Ref. 1.

This average holds when the two spin-orbitals have the same spin. For spin-orbitals with opposite spin, the term in f in Eq. (10) is absent.

For a given determinantal function, we shall then have q_{\uparrow} spin-orbitals with spin up, and q_{\downarrow} with spin down. There will be $\frac{1}{2}q_{\uparrow}(q_{\uparrow}-1)$ pairs with spin up, and $\frac{1}{2}[q_{\downarrow}(q_{\downarrow}-1)]$ with spin down. Each of these pairs, on the average, will contribute an amount given by Eq. (10) to the sum of two-electron integrals. We shall then find for the average energy of all the determinantal functions associated with a given M_S the value

$$qI(nl) + \frac{1}{2}[q(q-1)]F^0(nl; nl) - \left\{ \frac{1}{2}[q_{\uparrow}(q_{\uparrow}-1)] + \frac{1}{2}[q_{\downarrow}(q_{\downarrow}-1)] \right\} f. \quad (12)$$

By using the relations between q_{\uparrow} , q_{\downarrow} , and M_S , the average energy of terms with given M_S can be rewritten as

$$qI(nl) + \frac{1}{2}[q(q-1)]F^0(nl; nl) - \left[\frac{1}{2}q\left(\frac{1}{2}q-1\right) + M_S^2 \right] f. \quad (13)$$

The sum of the energies of all determinantal functions with the given M_S is the average value of Eq. (12) or (13), multiplied by the number of such functions, as given in Eq. (1). We may now investigate the average energy of all multiplets with a given S value. By the sum rule, as we have mentioned before, we know that the sum of the energies of all multiplet functions corresponding to $S, S+1, S+2, \dots$ equals the sum of the energies of all determinantal functions with $M_S=S$. If we find a sum in the same way for M_S+1 , this will give the sum of energies of all multiplet functions corresponding to $S+1, S+2, \dots$. Thus we subtract this from the sum of all energies corresponding to $M_S=S$. The number of determinantal functions corresponding to M_S and S is the number given by Eq. (1), minus the same function with M_S+1 substituted in place of M_S . If we carry these steps through, finding the sum of all energies of multiplets corresponding to S , and then dividing by the number of such multiplet states, we find the result that the average energy of multiplets of given S value, in configuration l^q , is given by

$$qI(nl) + \frac{1}{2}[q(q-1)]\{F^0(nl; nl) - f\} + \left(\frac{1}{2}q - S\right)\left(\frac{1}{2}q + S + 1\right)\left[\frac{2l+1}{2l+2}\right]f, \quad (14)$$

where f is given by Eq. (11).

For the states of maximum multiplicity, we have $S = \frac{1}{2}q$, provided the shell is no more than half-filled, or q is no greater than $2l+1$. Thus in this case the average energy of the states of maximum multiplicity is $qI + \frac{1}{2}[q(q-1)](F^0 - f)$, the last term of Eq. (14) representing the energy difference from this state of maximum multiplicity. If we find the average energy of multiplets with $S-1$, minus that with S , we find average energy of multiplets $S-1$,

$$\begin{aligned} & \text{minus average energy of multiplets } S \\ & = 2S\left[\frac{2l+1}{2l+2}\right]f. \quad (15) \end{aligned}$$

Since f is necessarily positive, we have in Eq. (15) a straightforward proof of Hund's rule, as applied to the average energy: the average energy increases as S decreases, or the multiplets with the largest S have the lowest average energy.

If the shell is more than half-filled, a different form of the equation is more convenient, since in this case the S for the state of maximum multiplicity equals half the number of holes in the shell, rather than half the number of electrons. Since the shell can hold $2(2l+1)$ electrons, the number of holes is $2(2l+1) - q$. The convenient form for Eq. (14) in this case states that the average energy of multiplets of given S value, in configuration l^q , is

$$\begin{aligned} & qI(nl) + \frac{1}{2}[q(q-1)]\{F^0(nl; nl) - f\} \\ & - (2l+1)(2l+1-q)f + (2l+1 - \frac{1}{2}q - S) \\ & \times (2l+1 - \frac{1}{2}q + S + 1)\left[\frac{2l+1}{2l+2}\right]f, \quad (16) \end{aligned}$$

which can be derived from Eq. (14) by straightforward algebraic manipulation. Here, as in Eq. (14), the last term vanishes when we are dealing with the state of maximum multiplicity, so that the earlier terms give the energy of this state of maximum multiplicity. The separations of the energies of the various multiplets for the case of q holes with a shell more than half-filled are of course identical with those for the case of q electrons, with a shell less than half-filled.

We can set up an equivalent formula, more symmetrical than Eqs. (14) or (16), in which the terms independent of S represent the average energy of all multiplets in the configuration, rather than the energy of the multiplets of the maximum multiplicity. From Ref. 1 it is known that the average energy of all multiplets in the configuration l^q is given by

$$qI(nl) + \frac{1}{2}[q(q-1)]\{F^0(nl; nl) - [2l/(4l+1)]f\}. \quad (17)$$

If we make a transformation of Eq. (14) or (16) so that the expression of Eq. (17) forms the constant term, we find that the average energy of multiplets of given S value, in configuration l^q , is given by

$$\begin{aligned} & qI(nl) + \frac{1}{2}[q(q-1)]\{F^0(nl; nl) - [2l/(4l+1)]f\} \\ & + \left\{ \frac{3}{4}(4l+1) \right\} q\left[\frac{2(2l+1)-q}{2l+2}\right] - S(S+1) \left\{ \right. \\ & \left. \times \left[\frac{2l+1}{2l+2}\right]f. \quad (18) \right\} \end{aligned}$$

The last term of this formula, unlike Eqs. (14) and (16), depends symmetrically on q and $2(2l+1) - q$, or on the number of electrons and of holes in the shell, so that it can be used conveniently whether the shell is more or less than half-filled.

This last form [Eq. (18)] is that stated by Jørgensen,² though he does not give it in just the form we have used. He does not present the coefficients of the various terms in analytic forms in terms of f , as we have done, but rather gives separate formulas for each l value. It is convenient to have this information, so as not to have to consult tables of the c^k 's. Consequently we give

in Eq. (19) the values of f for p , d , and f electrons:

$$\begin{aligned} p: f &= \frac{1}{5}F^2(n1; n1), \\ d: f &= (1/14)[F^2(n2; n2) + F^4(n2; n2)], \\ f: f &= (2/45)F^2(n3; n3) + (1/33)F^4(n3; n3) \\ &\quad + (50/1287)F^6(n3; n3). \end{aligned} \quad (19)$$

By substituting these expressions in Eq. (18), we get the results of Jørgensen (except that it is to be noted that he has made an error in the coefficients of F^4 for f electrons). We can equally well use Eq. (19) in the expressions of Eqs. (14) and (16).

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Exchange in Spin-Polarized Energy Bands

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In an atom, or a crystal, with net magnetic moment, the Hartree-Fock equations for electrons with spins up (that is, parallel to the net magnetization) and spins down (opposite) are different. By using different wave functions for the different spins, one attains spin-polarized calculations, which are more accurate than the ordinary restricted Hartree-Fock type. One-electron energies for electrons of spin up and down will differ. The method has been used in recent calculations of energy bands in ferromagnetic and antiferromagnetic crystals. The present paper studies the essential feature of the calculations, the nature of the exchange integrals responsible for the energy difference between spin-up and spin-down energies. This is done both in terms of the rigorous Hartree-Fock method, and in terms of the free-electron exchange method which is used in the energy-band calculations. It is shown that the two methods are consistent with each other, the free-electron exchange method giving a good approximation to the spin-polarization effect. Correlation can be taken into account by decreasing the difference in exchange energy between spin up and spin down, in a way similar to what must be done in the theory of atomic multiplets, in using empirical F^k integrals which are smaller than those found by the Hartree-Fock method. Such a decrease in exchange effect has been found necessary to get agreement with experiment in the spin-polarized energy-band calculations.

1. INTRODUCTION

A NUMBER of recent papers, by Wakoh and Yamashita,¹ Switendick,² Connolly,³ Cho⁴, and DeCicco⁵ have shown that it is possible to calculate spin-polarized energy bands, that is, separate energy bands for electrons with spins pointing up and spins pointing down, in a magnetic crystal. The potentials in which electrons of the two spin orientations move

differ on account of exchange effects. One fills these energy bands up to a common Fermi level, and since the bands for spin pointing up have lower energies, one will find more electrons of spin up than of spin down. The exchange effect for electrons of either spin increases (as a negative contribution to the energy) with the density of electrons of that spin. Consequently, the preponderance of electrons with spins up, or along the direction of magnetization in a magnetized ferromagnetic material, leads to the lower bands for these electrons, and we have the ingredients for a self-consistent treatment of ferromagnetism. The writers quoted above have shown that such self-consistency can in fact be achieved, for a number of ferromagnetic crystals, and they have shown that similar arguments can be applied to antiferromagnetism. It is the purpose of the present paper to look somewhat more critically into their methods and results.

The calculations which have been made in the papers cited above have been based on the simplified treatment of exchange, derived from the theory of a free-electron gas, suggested some years ago by the author.⁶ Since

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¹ S. Wakoh and J. Yamashita, *J. Phys. Soc. Japan* **19**, 1342 (1964); J. Yamashita, M. Fukuchi, and S. Wakoh, *ibid.* **18**, 999 (1963); J. Yamashita, *ibid.* **18**, 1010 (1963); S. Wakoh, *ibid.* **20**, 1894 (1965); J. Yamashita, S. Wakoh, and S. Asano, from *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P.-O. Löwdin (Academic Press Inc., New York, 1966), p. 497.

² A. C. Switendick, M.I.T. Ph.D. thesis, 1963 (unpublished); *J. Appl. Phys.* **37**, 1022 (1966).

³ J. W. D. Connolly, Ph.D. thesis, University of Florida, 1966 (unpublished); J. W. D. Connolly, S. J. Cho, J. B. Conklin, Jr., and J. C. Slater, Quarterly Progress Report No. 62 Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, 1966, p. 3 (unpublished). J. W. D. Connolly, *Phys. Rev.* **159**, 415 (1967).

⁴ S. J. Cho, *Phys. Rev.* **157**, 632 (1967).

⁵ P. DeCicco and A. Kitz, Quarterly Progress Report No. 63, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, 1967, p. 2 (unpublished); *Phys. Rev.* (to be published).

⁶ J. C. Slater, *Phys. Rev.* **81**, 385 (1951); **82**, 538 (1951); *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Inc., New York, 1960), Vol. 2, Sec. 17-3 and Appendix 22.