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A THEOREM ON SPACE QUANTIZATION

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In the theory of the multiplet structure of spectral lines frequent use is made of what is known as space quantization of angular momenta. If a_0 and a_1 represent the quantized angular momenta, say, of two electrons, measured in units $h/2\pi$, a_0 and a_1 being either positive integers or half-integers, then their resultant r_1 may not have all the values between the extremes $|a_0 - a_1|$ and $a_0 + a_1$, but only a number of discrete values, differing successively by unity and found from the relation

$$|a_0 - a_1| \leqq r_1 \leqq a_0 + a_1. \tag{1}$$

In a model the vectors a_0 and a_1, on account of their mutual energy depending on the relative orientation, will precess about their resultant r_1. The totality of the discrete values r_1 obeying (1) we shall denote by $\mathbf{r}_1$, and to indicate that they arise from the quantum composition of a_0 and a_1 we shall write

$$\mathbf{r}_1 = \mathbf{a}_0 + \mathbf{a}_1. \tag{2}$$

Let now a third angular momentum a_2 be added to the system. If the mutual energy of orientation between a_0 and a_2 as well as a_1 and a_2 be much smaller than that between a_0 and a_1, the addition of a_2 will hardly influence the original space quantization of a_0 and a_1, and the result will be that a_2 is composed with any of the values r_1 in just the same way as a_0 and a_1 were originally composed, viz., according to

$$|r_1 - a_2| \leqq r_2 \leqq r_1 + a_2. \tag{3}$$

In the model this will mean a precession of r_1 and a_2 about their resultant r_2. Applying (3) to all values r_1 we obtain a manifold of values r_2, for which we may write

$$\mathbf{r}_2 = \mathbf{r}_1 + \mathbf{a}_2 = (\mathbf{a}_0 + \mathbf{a}_1) + \mathbf{a}_2.$$

If more momenta $a_3, \ldots a_m$ be added to the system, such that the mutual energy of orientation of any of these with respect to the preceding ones is much smaller than that among these preceding ones, the above process can be continued, and we finally get a number of values for the last resultant r_m, which we express by

$$\mathbf{r_m} = [(\mathbf{a_0} + \mathbf{a_1}) + \mathbf{a_2}] + \ldots \mathbf{a_m}. \tag{4}$$

From a physical viewpoint it is almost self-evident that if we change adiabatically the parameters which determine the mutual energies of orientation, such that momenta which were at first weakly coupled become now strongly coupled and vice versa, we will not change the manifold of values of the final resultant r_m, representing the total angular momenta of the system. The physical process just considered corresponds to changing the order of addition in (4), and the theorem which is to be proved here states:

If a number of positive integers or half-integers $a_0, a_1, \ldots a_m$ are "added" successively as indicated by (2) and (3), the final result is independent of the order in which they are "added."

This would mean that in (4) all parentheses could be omitted.

Consider then the momenta a_i in the first and second arrangement of the quantities $a_0, a_1, \ldots a_m$. The second can always be obtained from the first by a number of transpositions. Consider one of these transpositions, the arrangement before and after the transposition being, respectively,

$$\begin{array}{l|l|l} a_{n_0}\ a_{n_1} \ldots a_{n_{i-1}} & a_{n_i}\ a_{n_{i+1}} & a_{n_{i+2}} \ldots a_{n_m} \\ a_{n_0}\ a_{n_1} \ldots a_{n_{i-1}} & a_{n_{i+1}}\ a_{n_i} & a_{n_{i+2}} \ldots a_{n_m} \end{array}.$$

The totality of resultants $r_{n_{i-1}}$ is the same in both cases. If we now can show that when we "add" a_i and a_{i+1} to any of these, the result is independent of the order of addition, we will also get the same totality of resultants r_{n_m}. In other words, if we can show that for any three integers or half-integers a, b, c

$$(\mathbf{a} + \mathbf{b}) + \mathbf{c} = \mathbf{a} + (\mathbf{b} + \mathbf{c}), \tag{5}$$

then our theorem is proved.

Let the resultants of a and b be called p, and those obtained by "adding" p and c, r. Taking any of these values r, let us ask in how many ways it can be obtained from first "adding" a and b and then c, i.e., how many times r occurs in the manifold $\mathbf{r}$. The first resultant p must obey the relation

$$|a - b| \leqq p \leqq a + b.$$

In order that p when composed with c may give among the new resultants the value r chosen, we must also have

$$|r - c| \leqq p \leqq r + c.$$

These are two conditions for p, and the number of values p obeying both, which is equal to the number of times the chosen value of r occurs in the manifold **r**, depends on the relative magnitude of a, b, c, r. The table shows the 16 cases which have to be distinguished, specified by the inequalities in columns A to D. Column F states the number of times r occurs, while the inequalities in column E in some of the cases express the fact that this number must be positive. Column G gives values a, b, c, d representing these different cases.

	A	B	C	D	E	F	G a, b, c, d
1	$a \geqq b$	$r \geqq c$	$r-c \geqq a-b$	$r+c \geqq a+b$	$r-c \leqq a+b$	$a+b-r+c+1$	3 2 3 5
2				$r+c \leqq a+b$		$2c+1$	3 2 1 3
3			$r-c \leqq a-b$	$r+c \geqq a+b$		$2b+1$	3 1 3 4
4				$r+c \leqq a+b$	$a-b \leqq r+c$	$r+c-a+b+1$	6 2 2 4
5		$r \leqq c$	$c-r \geqq a-b$	$r+c \geqq a+b$	$c-r \leqq a+b$	$a+b-c+r+1$	4 2 6 2
6				$r+c \leqq a+b$		$2r+1$	5 4 3 1
7			$c-r \leqq a-b$	$r+c \geqq a+b$		$2b+1$	3 1 4 3
8				$r+c \leqq a+b$	$a-b \leqq r+c$	$r+c-a+b+1$	6 2 4 2
9	$a \leqq b$	$r \geqq c$	$r-c \geqq b-a$	$r+c \geqq a+b$	$r-c \leqq a+b$	$a+b-r+c+1$	2 3 2 5
10				$r+c \leqq a+b$		$2c+1$	2 3 1 3
11			$r-c \leqq b-a$	$r+c \geqq a+b$		$2a+1$	1 3 2 3
12				$r+c \leqq a+b$	$b-a \leqq r+c$	$r+c-b+a+1$	2 5 2 3
13		$r \leqq c$	$c-r \geqq b-a$	$r+c \geqq a+b$	$c-r \leqq a+b$	$a+b-c+r+1$	2 4 6 2
14				$r+c \leqq a+b$		$2r+1$	4 5 3 1
15			$c-r \leqq b-a$	$r+c \geqq a+b$		$2a+1$	1 3 3 2
16				$r+c \leqq a+b$	$b-a \leqq r+c$	$r+c-b+a+1$	2 5 3 2

We shall show now for one of the cases as an example how equation (5) is proved. Let us take case 4. If we can show that the inequalities of this case

$$a \geqq b \quad (6a) \qquad r \geqq c \quad (6b)$$

$$r - c \leqq a - b \quad (6c) \qquad r + c \leqq a + b \quad (6d)$$

$$a - b \leqq r + c \quad (6e)$$

lead to the inequalities

$$r \leqq a \quad (7a) \qquad a - r \geqq |b - c| \quad (7b)$$

$$r + a \geqq c + b \quad (7c) \qquad a - r \leqq c + b \quad (7d)$$

we shall have proved (5) in this case. For if in the table we interchange a and c everywhere, which corresponds to "adding" first **b** and **c** and then **a**, these are the conditions of case 5 or 13, both of which will give the resultant r $(c + b + r - a + 1)$ times. But that is equal to the number of times r is obtained in case 4 when **a** and **b** are first "added" and **c** afterwards.

(7*a*) follows by adding (6*c*) and (6*d*). (6*c*) gives

$$a - r \geqq b - c,$$

(6*b*) on the other hand

$$r - a \leqq b - c,$$

which together are equivalent to (7*b*). Adding (6*b*) multiplied by 2 and (6*c*) gives (7*c*), while (7*d*) follows directly from (6*e*).

In a similar way the proof can be carried through in all the other cases.

Application to Complicated Spectra.—The multiple terms of the complicated spectra are characterized by two momenta $\bar{k}$ and $\bar{r}$ (determining whether the term is an S, P, D... term and what its multiplicity is).* These can be obtained from the vectors k_i and $r_i = \frac{1}{2}$ associated with the individual electrons not in closed groups as follows,[1] provided no two of these electrons have the same total quantum number n and the same values for k. Consider the vectors k_i and r_i in a strong magnetic field that overcomes all the mutual couplings. Then they will precess independently around the direction of the field such that their projections on this direction form a discrete series of values differing successively by unity and obtained from

$$-k_i \leqq m_{k_i} \leqq k_i, \qquad -r_i \leqq m_{r_i} \leqq r_i.$$

Form the sums

$$\bar{m}_k = \Sigma m_{k_i} \qquad \bar{m}_r = \Sigma m_{r_i} \tag{8}$$

for all possible combinations of the m_{k_i} and the m_{r_i}. Then the totality of the values $\bar{m}_k$ is the same as that arising from quantizing a number of momenta $\bar{k}$ in the field such that

$$-\bar{k} \leqq \bar{m}_k \leqq \bar{k}.$$

From our theorem we can show that these values of $\bar{k}$ are the same as those given by

$$\bar{\mathbf{k}} = \mathbf{k}_1 + \mathbf{k}_2 + \ldots \mathbf{k}_m,$$

a result already arrived at in the case of two momenta k by Heisenberg and Goudsmit.[1] For space quantization in an external field can, according to a suggestion of Russell,[2] be regarded as a limiting case of the space quantization of two angular momenta with respect to each other. We only have to let one of the momenta increase beyond limits, and then the quantized positions of the other one with respect to it will be just the same as those in an external field having the same direction as the first momentum; i.e., the projections of the second on the first will form a discrete sequence of values differing successively by unity. Calling the infinite momentum k_0, then the totality of values $\overline{m}_k$ as found in (8) is nothing but the totality of values

$$\lim_{k_0 \to \infty} \{[(\mathbf{k_0} + \mathbf{k_1}) + \mathbf{k_2}] + \ldots \mathbf{k_m}\},$$

each diminished by k_0, and that by our theorem is equal to the totality of values

$$\lim_{k_0 \to \infty} [\mathbf{k_0} + (\mathbf{k_1} + \mathbf{k_2} + \ldots \mathbf{k_m})]$$

each diminished by k_0; i.e., the totality of the quantized projections of all the momenta resulting from the composition of $k_1, k_2, \ldots k_m$. Similar remarks apply to r.

* Using Sommerfeld's quantum numbers which are smaller by $\frac{1}{2}$ than those of Landé.

[1] H. N. Russell and F. A. Saunders, *Astroph. J.*, **61**, 38, 1925; S. Goudsmit, *Zs. Phys.*, **32**, 794, 1925; W. Heisenberg, *Ibid.*, **32**, 841, 1925.

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ON THE HEAT CAPACITY OF NON-POLAR SOLID COMPOUNDS

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In a previous paper,[1] the writer attempted to apply the quantum theory of the heat capacity of solids to aliphatic compounds. By a series of approximations, there was obtained a set of equations giving rough agreement with measured heat capacities over a fair range of temperatures.

By introducing some of the results of infra-red spectroscopy, the general equations of Born will be extended in the present paper to solids of non-polar compounds. These will then be applied to some organic compounds, the rough approximations of the previous work being discarded.

The general theory of the heat capacities of crystalline solids, developed by Born,[2] stated that the first three frequencies are characteristic of the crystal and their contribution to the heat capacity is expressed by Debye functions, and the remaining frequencies are characteristic of the atomic (nuclear) vibrations and their contribution to the heat capacity is expressed by Einstein functions. Nernst[3] arrived at the division of heat capacity into Debye and Einstein functions by considering the Debye functions as characteristic of the molecule; this view was adversely criticized at first because Nernst used it for polar substances, which do not unite to form molecules in the crystal. But X-ray analysis has shown that molecules of many substances, for example, of organic compounds,