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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XXIX

To: Group 63

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Let us consider the helium atom, containing two electrons and a nucleus. Let a represent a particular set of values of the space quantum numbers n, ℓ, and m_ℓ; let b represent another set of values, etc. Then, for the two electrons we can have varying sets of values, e.g.

$$\Psi_a(1)\ \sigma(1)\ \Psi_a(2)\ \sigma'(2)$$
$$\Psi_a(1)\ \sigma(1)\ \Psi_b(2)\ \sigma'(2)$$
$$\Psi_b(1)\ \sigma(1)\ \Psi_a(2)\ \sigma'(2) \qquad \text{etc.}$$

where σ and σ' are two different spin functions.

In this way one can build up a matrix with various energy values based on a great number of states. This task would be a formidable one, but we must remember that states in different energy levels do not interact very much.

In order to describe the state of the system the spin function and space function of each of the two electrons must be known. However, since the electrons are indistinguishable, the state described by

$$\psi_a(1)\ \sigma(1)\ \psi_b(2)\ \sigma'(2) \qquad \text{(A)}$$

cannot be distinguished from the state described by

$$\psi_b(1)\ \sigma'(1)\ \psi_a(2)\ \sigma(2) \qquad \text{(B)}$$

Pauli stated that since electrons are identical to each other, states A and B cannot be physically distinct. These functions might be replaced by (C) and (D):

$$\psi_a(1)\,\sigma(1)\quad\psi_b(2)\,\sigma'(2) + \psi_b(1)\,\sigma'(1)\,\psi_a(2)\,\sigma(2) \qquad (C)$$

and

$$\psi_a(1)\,\sigma(1)\quad\psi_b(2)\,\sigma'(2) - \psi_b(1)\,\sigma'(1)\,\psi_a(2)\,\sigma(2) \qquad (D)$$

Interchange of electrons 1 and 2 leaves function (C) unchanged and multiplies (D) by (-1). (C) is symmetrical in the coordinates of electrons 1 and 2, while (D) is antisymmetrical in these coordinates. Thus $|\Psi|^2$ is unaltered by interchange of the electrons for both case (C) and case (D), and hence either one might be satisfactory from Pauli's point of view.

Since the perturbation is usually symmetrical in the coordinates of the two electrons, the integral $\int \psi_m^*\, \mathcal{H}'\, \psi_n\, d\tau$ is zero if one of ψ_m and ψ_n is antisymmetric, the other symmetric, for the integrand is then antisymmetric, and the integration over all configurations vanishes when the integrand is antisymmetric. Thus symmetric and antisymmetric systems cannot interact, and since observations on a system imply interaction between observer and system, we can only observe those states which are either:

1) symmetrical in all electrons if we ourselves are in a symmetrical system

2) antisymmetrical in all electrons if we ourselves are in an antisymmetrical system.

In order to conform with experimental evidence Pauli has postulated that our physical universe is antisymmetrical in the coordinates of electrons. Thus the unperturbed states for the two-electron system are all in the form (D):

$$\psi_a(1)\,\psi_b(2)\,\sigma(1)\,\sigma'(2) - \psi_b(1)\,\psi_a(2)\,\sigma'(1)\,\sigma(2) \qquad (D)$$

From expression (D) we see that

I. If $\sigma' = \sigma$ (spin quantum number of both electrons the same)

$$\psi = \sigma(1)\,\sigma(2)\left[\psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2)\right]$$

Therefore, if $\psi_a = \psi_b$ (space quantum numbers of both electrons the same)

$$\psi = 0$$

Conversely,

II. If the space states of both electrons are the same

$$\psi = \psi_a(1)\ \psi_a(2)\ [\sigma(1)\ \sigma'(2) - \sigma(2)\ \sigma'(1)]$$

and, if $\sigma = \sigma'$

$$\psi = 0$$

Thus Pauli's requirement of antisymmetric wave functions leads to the fact that no state can exist in which two electrons are in the same spin and space states. This is the conventional statement of the Pauli exclusion principle, namely that no two electrons can have the same set of four quantum numbers.

The spin function of an electron σ can have only two values. They are + 1/2 and - 1/2 and are sometimes represented simply by + and -. For the two-electron system we have been considering, there are four possible spin combinations. They are:

1.	+ +	$\alpha(1)$	$\alpha(2)$
2.	+ -	$\alpha(1)$	$\beta(2)$
3.	- +	$\beta(1)$	$\alpha(2)$
4.	- -	$\beta(1)$	$\beta(2)$

where we define two spin functions α and β to correspond respectively to the parallel (+) and anti-parallel (-) spin directions. Furthermore, the functions are orthonormal, so

$$\int \alpha\beta\, d\omega = 0 \qquad \text{XXIX-1}$$

$$\int \alpha^2\, d\omega = \beta^2\, d\omega = 1 \qquad \text{XXIX-2}$$

where $\int d\omega$ represents integration over spin coordinates.

Therefore,

$$\int \alpha(1)^2\ \alpha(2)\ \beta(2)\ d\omega_1\ d\omega_2 = \int \alpha(1)^2\ d\omega_1 \int \alpha(2)\ \beta(2)\ d\omega_2$$

$$= 1 \times 0 = 0$$

The orthogonality of the α and β functions may be illustrated graphically by considering the function plotted along a spin coordinate, as in figure 53. These functions are normalized, so the area under their curves is unity. The overlap integral $\int AB\,d\omega$ is very small because the product AB is small everywhere. The functions α and β are formed by letting the width of A and B decrease, and their height increase in such a manner that their area remains constant. During this process the product AB decreases, and goes to zero as the widths do, at a sufficiently fast rate to make the overlap integral vanish.

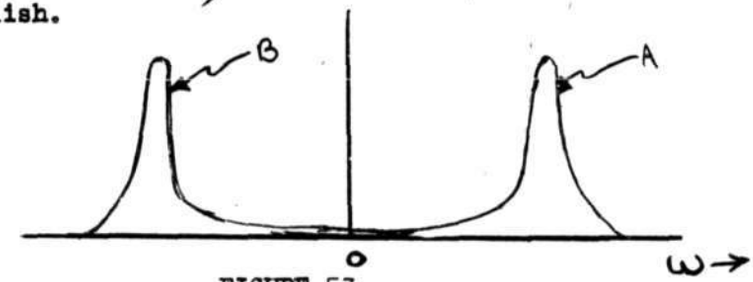


FIGURE 53

Spin combinations (1) and (4) are symmetric. Combinations (2) and (3) are neither symmetric nor anti-symmetric.

According to Pauli's principle we must have an anti-symmetric total wave function. This requires a combination of a symmetric space state and an anti-symmetric spin state or vice versa. If both the spin and space functions are symmetric or antisymmetric, the total wave function is symmetric. In accordance with the exclusion principle, such states do not exist.

However, we have not obtained any spin function which can be defined as anti-symmetric. To do so, a linear combination of the functions $\alpha(1)\ \beta(2)$ and $\beta(1)\ \alpha(2)$ must be used. The four possible spin wave functions are then:

$$\sigma_1 = \alpha(1)\ \alpha(2) \qquad (s)$$

$$\sigma_2 = \frac{1}{\sqrt{2}}\left[\alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)\right] \qquad (s)$$

$$\sigma_3 = \frac{1}{\sqrt{2}}\left[\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)\right] \qquad (a) \qquad \text{XXIX-3}$$

$$\sigma_4 = \beta(1)\ \beta(2) \qquad (s)$$

Equation XXIX-3 defines the four states represented in expression (D) by $\sigma(1)\ \sigma'(2)$ and $\sigma'(1)\ \sigma(2)$. Expression (D) should be rewritten as:

$\psi_a(1)\ \psi_b(2)\ \sigma - \psi_b(1)\ \psi_a(2)\ \sigma'$, where σ and σ' represent any two of the set $\sigma_1, \sigma_2, \sigma_3, \sigma_4$, including the possibility that $\sigma = \sigma'$.

The factor $1/\sqrt{2}$ is introduced to maintain the normality of the spin functions. The functions σ_1 and σ_4 are repeated from the previous set in order that all four spin functions be listed together. It can be seen that three of the spin functions are symmetric and only one is antisymmetric. The set is still orthonormal, as is shown below for one case.

$$\int \sigma_1 \; \sigma_2 \, d\omega_1 \, d\omega_2$$

$$= 1/\sqrt{2} \int \alpha(1) \; \alpha(2) \left[\alpha(1) \; \beta(2) + \beta(1) \; \alpha(2) \right] \; d\omega_1 \, d\omega_2$$

$$= 1/\sqrt{2} \int \left(\alpha(1)^2 \; \alpha(2) \; \beta(2) + \alpha(2)^2 \; \alpha(1) \; \beta(1) \right) d\omega_1 \, d\omega_2$$

$$= 1/\sqrt{2} \left[\int \alpha(1)^2 \, d\omega_1 \int \alpha(2) \; \beta(2) \, d\omega_2 + \int \alpha(2)^2 \, d\omega_2 \int \alpha(1) \; \beta(1) \, d\omega_1 \right]$$

$$= 1/\sqrt{2} \left[1 \times 0 + 1 \times 0 \right] \equiv 0 \qquad q.e.d.$$

In order to consider perturbations we must set up a matrix as in the past. The matrix should represent all possible combinations of the four spin functions with the infinite array of space functions. However, since we have shown that only states with nearly equal energies interact to an appreciable extent, the number of matrix elements can be reduced to include only the low energy states when considering interaction with the unperturbed ground (1s) states.

The integral

$$\int \psi_a(1)^* \; \psi_b(1)^* \; \sigma \quad \mathcal{H} \; \psi_p(2) \qquad \psi_q(2) \; \sigma' \, d\tau \, d\omega$$

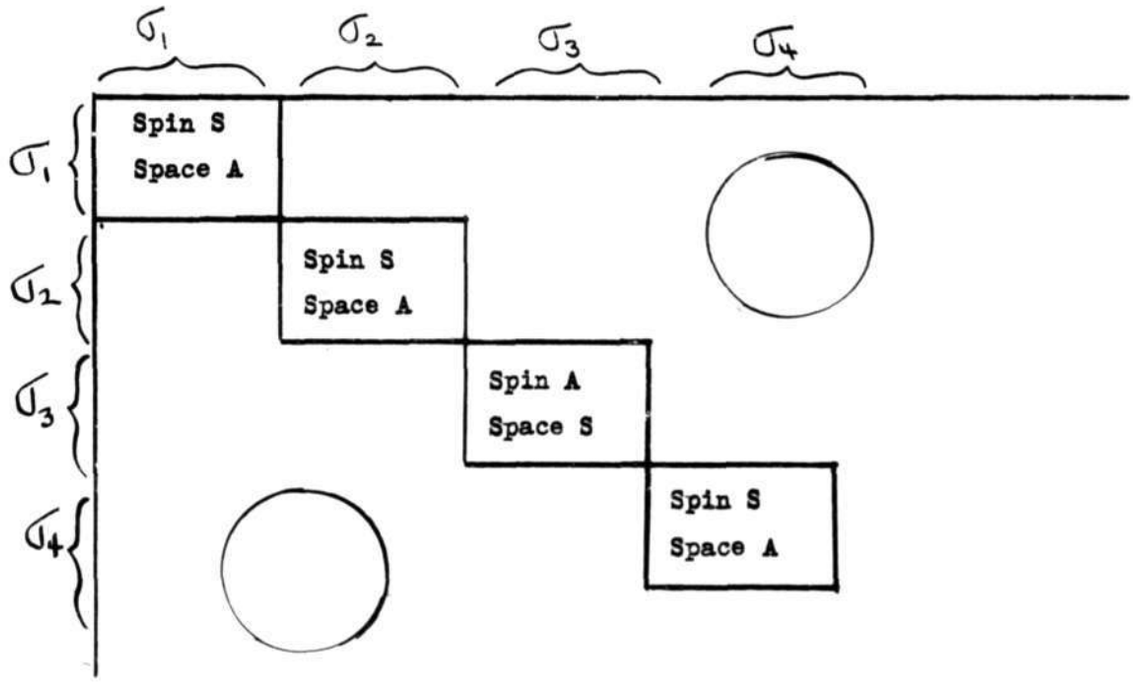
represents one element of a matrix which includes the spin and space functions. $d\tau \, d\omega$ is an element of configuration space including space and spin coordinates.

Since $\mathcal{H}$ does not depend on the spin coordinates, the above integral may be rewritten as

$$\int \psi_a(1)^* \; \psi_b(1)^* \quad \mathcal{H} \; \psi_p(2) \; \psi_q(2) \, d\tau \int \sigma \, \sigma' \, d\omega$$

The entire integral therefore is equal to zero if the spin portion is zero. Since the four spin functions are orthogonal, only terms corresponding to the same spin functions give a non-zero resultant.

Thus by grouping together all unperturbed states with the same spin functions we can subdivide our matrix into four sub-matrices, each corresponding to one of the four spin matrices. Each sub-matrix will contain all the space functions (an infinite number.) All elements outside the sub-matrices correspond to the interaction of states with different spin functions, and are therefore identically zero. This is indicated below:



Since the total wave function is antisymmetric, the three symmetric spin functions combine with an antisymmetric space function. The list of antisymmetric space functions is the same in each case, thus giving a set of triple roots, and hence triply degenerate energy levels (triplets). The symmetric space function gives rise to singlets.

The triply degenerate level is split into triplet levels when a magnetic field is applied. In the absence of an external field the energy is independent of spin orientation, but when the field is imposed the three orientations of the parallel spins correspond to three different energy levels.

This can be indicated graphically by representing the spin direction by arrows, each of magnitude 1/2 (in units of $\hbar$).

Then:

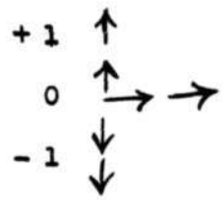
$$\sigma_1 = \alpha(1)\ \alpha(2) \qquad \uparrow\uparrow$$

$$\sigma_2 = 1/\sqrt{2}\ [\alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)] \qquad \rightarrow\rightarrow$$

$$\sigma_3 = 1/\sqrt{2}\ [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)] \qquad \uparrow\downarrow$$

$$\sigma_3 = \beta(1)\ \beta(2) \qquad \downarrow\downarrow$$

The possible resultant spin vectors are therefore:



where the lowest energy state is represented by the spin vector in the direction of the external field, and the highest state occurs with the spin vector directed opposite to the external field.

Signed _____
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