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ABSTRACT

From Pauli's exclusion principle we derive the rule for the symmetry of the wave functions in the coordinates of the center of gravity of two similar stable clusters of electrons and protons, and justify the assumption that the clusters satisfy the Einstein-Bose or Fermi-Dirac statistics according to whether the number of particles in each cluster is even or odd. The rule is shown to become invalid only when the interaction between the clusters is large enough to disturb their internal motion.

I. INTRODUCTION

THE band spectra of symmetric diatomic molecules show certain striking differences from those of asymmetric molecules. For when the two nuclei of the molecule are identical, the intensity of the individual lines of a band, instead of varying smoothly from line to line, alternates more or less markedly. This alternation may in most cases be understood¹ with the help of a simple rule, but in the case of the N_2 molecule, the theoretical prediction seems to disagree with experiment, in that it leads us to expect those band-lines to be the more intense, which are in fact weaker. In this paper we do not propose to resolve this disagreement; we shall only try to give as direct a derivation as possible of the rule which plays the cardinal part in obtaining the theoretical prediction. For it seems that, in spite of the frequent citations of this rule, no explicit derivation of it from Pauli's exclusion principle has been published. In giving this derivation we shall have to investigate the conditions under which the rule is valid, and the degree of approximation to which it may be expected to hold.

The rule may be stated:

R. "If we have two nuclei, each built up of n electrons and m protons, and if the nuclei are in the "same inner state," then not all the molecular states which would be possible for an asymmetric molecule will be found to occur;

if $n+m$ is $\begin{cases} \text{even,} \\ \text{odd,} \end{cases}$ only those states $\begin{cases} S \\ A \end{cases}$ will occur for which the wave function $\begin{cases} \text{remains unchanged} \\ \text{changes its sign} \end{cases}$ when we interchange the "coordinates" of the nuclei.

¹ See the comprehensive report by R. S. Mullikan, Transactions of the Faraday Society **25**, 611 (1929).

When the nuclei are in different states, the molecule behaves like an asymmetric molecule."

Since we may expect the nuclei to be in their normal state, we should be able by this rule to predict the weight of the states S and the weight of the states A if we knew the degree of degeneracy g of the normal states of the nuclei. Thus there will always be $\frac{1}{2}g(g-1)$ states S and $\frac{1}{2}g(g-1)$ states A possible; if n plus m is even, there will be g states S , if n plus m is odd, g states A , also possible. The relative weights of the states S and A will therefore be

$$\begin{aligned} (g+1)/(g-1) & \text{ if } n+m \text{ is even} \\ (g-1)/(g+1) & \text{ if } n+m \text{ is odd.} \end{aligned} \tag{1}$$

If we ascribe the degeneracy of the normal state of the nuclei to the spatial degeneracy of an angular momentum $sh/2\pi$, then these ratios become

$$\begin{aligned} (s+1)/s & \text{ for } n+m \text{ even} \\ s/(s+1) & \text{ for } n+m \text{ odd.} \end{aligned}$$

From this we see that, since $n+m$ is odd for the nitrogen nucleus, the states A should have a greater weight than the states S . According to the assertions of band spectroscopists, the electronic wave functions of the normal state of the N_2 molecule are symmetric in the coordinates of the nuclei, and there is no resultant electronic angular momentum parallel to the molecular axis. If we accept these assertions, we are led to expect a greater weight for states of odd rotational quantum number than for those of even quantum number; and it is this expectation which is not confirmed by experiment.

Our problem is now so to refine the expressions "internal state" and "interchange the coordinates of the nuclei" in our rule R , that we can derive the rule from the exclusion principle.

II. WAVE PACKETS FOR A SYSTEM OF TWO CLUSTERS

We shall consider first the following preliminary problem: Suppose that we have a system containing $2n$ electrons and $2m$ protons. Suppose further that for any group of n electrons and m protons we could write down a complete set of wave functions u_k for the stationary states k ; how then, using any two of these wave functions u_k and u_l , can we build up a wave packet for the whole system which satisfies the exclusion principle for all the electrons and all the protons in the system? Only when the particles of the system do not interact at all will these wave packets represent the stationary states of the whole system; but with the help of these packets, by linear combination, we shall be able to build up wave functions which do represent stationary states for any interaction energy of the particles. The functions u may for instance represent states of a nucleus, or an atom, or a molecule, or even some aperiodic motion of the n plus m particles; for this preliminary problem we need to make no assumption about them; but we shall see later that only when the functions u represent very stable configurations: i.e. very tight binding of the particles,—can we deduce any significant results; and so we shall call any group of n electrons and m electrons a cluster.

Let the cartesian coordinates, referred to a fixed axis system, and the component of spin in a fixed direction, of the j th electron be x_j ; similarly let the coordinates and spin of the i th proton be y_i . Let us split up each of the functions u into two functions, a function T_s which depends only on the coordinates of the center of gravity of the cluster, and a function ψ_σ which depends on the relative coordinates of the particles, and on the spin variables:

$$u_k(x_1 \cdots x_n, y_1 \cdots y_m) \rightarrow T_s(x_1 \cdots x_n, y_1 \cdots y_m) \psi_\sigma(x_1 \cdots x_n, y_1 \cdots y_m) \\ = T_s(\alpha) \psi_\sigma(\alpha)$$

$$u_l(x_{n+1} \cdots x_{2n}, y_{m+1} \cdots y_{2m})$$

$$\rightarrow T_t(x_{n+1} \cdots x_{2n}, y_{m+1} \cdots y_{2m}) \psi_\tau(x_{n+1} \cdots x_{2n}, y_{m+1} \cdots y_{2m}) = T_t(\beta) \psi_\tau(\beta)$$

We write α for the arguments $(x_1, x_2 \cdots x_n, y_1, y_2 \cdots y_m)$ and β for the arguments $(x_{n+1}, x_{n+2} \cdots x_{2n}, y_{m+1}, y_{m+2} \cdots y_{2m})$

Since T depends only on the sum of the coordinates of the electrons, and the sum of the coordinates of the protons, and does not involve the spins at all, it must remain unchanged when we make an arbitrary permutation of the arguments x of u among themselves or of the arguments y of u among themselves. On the other hand u must be antisymmetric in its arguments x and in its arguments y , since otherwise it could not represent a stationary state for the cluster allowed by the exclusion principle. Thus ψ must be antisymmetric in the x 's and in the y 's. Let now P be an operator which makes an arbitrary permutation of the x 's and an arbitrary permutation of the y 's in any function of $x_1 \cdots x_{2n}, y_1 \cdots y_{2n}$, and let p be the order of the permutation P . Then the functions

$$F_{st,\sigma\tau} = \frac{1}{(2n)!(2m)!} \sum (-)^p P \{ T_s(\alpha) T_t(\beta) \psi_\sigma(\alpha) \psi_\tau(\beta) \} \quad (2)$$

satisfy the exclusion principle, if the summation be taken over all the $(2n)!(2m)!$ permutations P . There are only $r = (2m)!(2n)!/(m!)^2(n!)^2$ different terms in this sum, since by the antisymmetry of the ψ 's, all of the terms in which the arguments of T_s (and therefore also of T_t) are the same have just the same value. If we define a distribution by the symbol $(x_j \cdots y_i \cdots | x_f \cdots y_g \cdots)$ in which the arguments of T_s are to the left, those of T_t to the right, of the line, and in which the order of the arguments to the left and to the right is indifferent, then we can write

$$F_{st,\sigma\tau} = \frac{1}{r} \sum' (-)^p P \{ T_s(\alpha) T_t(\beta) \psi_\sigma(\alpha) \psi_\tau(\beta) \} \quad (3)$$

where now the summation is taken only over the r different distributions. Now in $F_{st,\sigma\sigma}$ with $\sigma = \tau$, we can combine the term with the distribution

$$(x_j \cdots y_i \cdots | x_f \cdots y_g) \quad (4)$$

with that with the inverted distribution

$$(x_f \cdots y_g \cdots | x_j \cdots y_i).$$

This second term may be derived from (4) by n plus m interchanges, and will therefore appear in the sum with the same sign as (4) if n plus m is even, and with the opposite sign if m plus n is odd. We may therefore write, with $\theta = (-1)^{m+n}$

$$F_{st,\sigma\sigma} = \frac{1}{r} \sum'' (-)^p P \{ \psi_\sigma(\alpha) \psi_\sigma(\beta) [T_s(\alpha) T_t(\beta) + \theta T_s(\beta) T_t(\alpha)] \} \quad (5)$$

where now the summation is taken over the $r/2$ different sets of arguments in the ψ_σ 's. When $\tau \neq \sigma$, we have instead,

$$F_{st,\sigma\tau} = \frac{1}{r} \sum'' (-)^p P \{ \psi_\sigma(\alpha) \psi_\tau(\beta) T_s(\alpha) T_t(\beta) + \theta \psi_\sigma(\beta) \psi_\tau(\alpha) T_s(\beta) T_t(\alpha) \}$$

which we may write

$$F_{st,\sigma\tau} = \frac{1}{2r} \sum'' (-)^p P \{ [\psi_\sigma(\alpha) \psi_\tau(\beta) + \psi_\sigma(\beta) \psi_\tau(\alpha)] [T_s(\alpha) T_t(\beta) + \theta T_s(\beta) T_t(\alpha)] \\ + [\psi_\sigma(\alpha) \psi_\tau(\beta) - \psi_\sigma(\beta) \psi_\tau(\alpha)] [T_s(\alpha) T_t(\beta) - \theta T_s(\beta) T_t(\alpha)] \} \quad (6)$$

From (5) we see that $F_{st,\sigma\sigma}$ is $\begin{cases} \text{symmetric} \\ \text{antisymmetric} \end{cases}$ in s and t when $m+n$ is $\begin{cases} \text{even,} \\ \text{odd,} \end{cases}$ and, from (6), that for $\tau \neq \sigma$, $F_{st,\sigma\tau}$ has, for $n+m$ either even or odd, both a symmetric and an antisymmetric part, neither of which vanishes identically. These properties of the wave packets F will make it possible to deduce our rule.

III. SYMMETRY OF WAVE FUNCTIONS FOR A SYSTEM OF TWO CLUSTERS

We should expect that these symmetry properties in s and t would persist in the stationary wave functions built up from the F 's whenever the interaction of the two clusters was too small appreciably to distort the internal configuration of the clusters. In this paragraph we shall have to find the wave functions ϕ for the stationary states of the system of two clusters. We shall see that, when certain matrix components of the interaction energy of the particles may be neglected, the ϕ 's do in fact have the same symmetry in s , t as the corresponding wave packets F ; and we shall see further that the conditions under which we may neglect these matrix components are just those in which the interaction of the clusters does not greatly disturb their internal motion.

Let E be the energy of the system, and H the Hamiltonian; it will in general be given us as an operator on a function of the x 's and the y 's, and it will be 'impartial' to all x 's and 'impartial' to all y 's. The wave equation for $\phi(x_1 \cdots y_{2m})$ will be

$$(H - E) \phi = 0 \quad (7)$$

Since ϕ must satisfy the exclusion principle, and since our original u 's formed a complete set of functions, we may expand ϕ as a linear function of the F 's:

$$\phi = \sum_{\substack{(\sigma, \tau) \\ \sigma \neq \tau}} \sum_s \sum_t a(st, \sigma\tau) F_{st, \sigma\tau} + \sum_{\sigma} \sum_{(s, t)} a(st, \sigma\sigma) F_{st, \sigma\sigma}. \quad (8)$$

Here the summation $\sum_{\substack{(\sigma, \tau) \\ \sigma \neq \tau}}$ is to be taken over all pairs (σ, τ) with $\sigma \neq \tau$, and $\sum_{(s, t)}$ over all pairs (s, t) . We now introduce that part of the irreducible matrix for H which belongs to the term system satisfying the exclusion principle:

$$(st, \sigma\tau | H | s't', \sigma'\tau') = \int dV \tilde{F}_{st, \sigma\tau} H F_{s't', \sigma'\tau'}. \quad (9)$$

The integration $(\int dV \dots)$ is to be taken over the whole domain of all the coordinates, and is to include a summation over the two values of all the spin variables. With the help of this matrix we may write the wave equation for the a 's which is equivalent to (8):

$$\sum_{\substack{(\sigma, \tau) \\ \sigma \neq \tau}} \sum_s \sum_t (s't', \sigma'\tau' | H | st, \sigma\tau) a(st, \sigma\tau) + \sum_{\sigma} \sum_{(s, t)} (s't', \sigma'\tau' | H | st, \sigma\sigma) a(st, \sigma\sigma) = E a(s't', \sigma'\tau'). \quad (10)$$

By (5), (6) we have

$$F_{st, \sigma\tau} = \theta F_{ts, \tau\sigma}$$

and

$$a(st, \sigma\tau) = \theta a(ts, \tau\sigma). \quad (11)$$

Suppose now that we may set

$$(st, \sigma\tau | H | s't', \sigma'\tau') = 0 \text{ for } (\sigma, \tau) \neq (\sigma', \tau'). \quad (12)$$

We shall have later to see under what circumstances, and to what approximation, (12) is legitimate; but if we accept it, then we see that (10) reduces to a series of independent equations, one for each pair of values of (σ, τ)

$$\begin{aligned} \sigma = \tau: \sum_{(s, t)} (\sigma\sigma, s't' | H | \sigma\sigma, st) a(\sigma\sigma, st) &= E a(\sigma\sigma, s't') \\ \sigma \neq \tau: \sum_s \sum_t (\sigma\tau, s't' | H | \sigma\tau, st) a(\sigma\tau, st) &= E a(\sigma\tau, s't') \end{aligned}$$

For each such pair of values (σ, τ) we thus get a set of solutions $a(st)$; for $\sigma = \tau$ these will be $\begin{cases} \text{symmetric} \\ \text{antisymmetric} \end{cases}$ in s and t when $m+n$ is $\begin{cases} \text{even;} \\ \text{odd;} \end{cases}$ for $\sigma \neq \tau$ both symmetric and antisymmetric functions are possible. If we define the "state" of the cluster by the σ 's, then this result is fully equivalent to the rule (R) given at the beginning of this paper. We may see this directly in the following way: for the quantum numbers s, t , we may take directly the value of the components of the total momenta of the two clusters; if we introduce the center of gravity coordinates of the two clusters, X, Y by the conditions

$$\begin{aligned} sX - Xs &= h/2\pi i; & sY - Ys &= 0; \\ tY - Yt &= h/2\pi i; & tX - Xt &= 0; \end{aligned} \quad (13)$$

then we get the transformation functions:

$$(st/XY) = e^{-2\pi i/h(sX+tY)}. \quad (14)$$

The wave functions for the stationary states of the whole system are then given as functions of X , Y by

$$\sum_{s,t} a(st, \sigma\tau)(st/XY). \quad (15)$$

For $\sigma = \tau$, these must be $\begin{cases} \text{symmetric} \\ \text{antisymmetric} \end{cases}$ in X and Y when $n+m$ is $\begin{cases} \text{even;} \\ \text{odd;} \end{cases}$ for

$\sigma \neq \tau$ they may have either symmetry.

We have now only to consider the conditions for the validity of (12). If the states σ , τ of the isolated clusters are degenerate, then the matrix elements of H corresponding to transitions between such degenerate states—states in which the isolated clusters have the same internal energy,—may be made to vanish by choosing suitably the u 's which give the stationary states of the clusters. The terms

$$(st, \sigma\tau | H | s't', \sigma'\tau')$$

in which the states (σ, τ) and (σ', τ') correspond to different energy levels of the clusters, will, since the original u 's were chosen to make the internal energy of the isolated clusters a diagonal matrix, represent the matrix components of the interaction and interchange energy of the particles in one cluster with those in the other; and if the particles in the cluster are very tightly bound together, these energies will be very small compared to the energy differences of two stationary states σ , σ' of the isolated cluster. The terms which were neglected in (12) therefore, will give in this case only very small correction terms to the a 's of the order of the ratio of the interaction energy of the two clusters to their proper energy; in general these correction terms will be neither symmetric nor antisymmetric in s and t , so that only for very stable clusters may we expect a rule like (R) to hold: for the two identical *atoms* of a symmetric molecule no such rule as (R) holds, since here the interaction energy of the atoms is of the same order of magnitude as their proper energy. Even in this case, of course, the exclusion principle for the electrons and protons reduces the number of possible stationary states; but here we cannot say just what states are excluded by investigating only the symmetry of the corresponding wave functions in the coordinates of the center of gravity of the clusters, but must study in detail the symmetry of the functions in the coordinates of all the elementary particles. The importance of the rule (R) arises from the circumstance, that in the dynamical treatment of most atomic and molecular problems we do not need to know anything about the structure of the nuclei, except that they are stable: we may treat them as point charges, with, in some cases, a spin s which gives a proper intrinsic degeneracy. And whenever this is so, we may use a rule like (R) to determine what states of the system survive the exclusion principle.