

# THE MULTIBODY PROBLEM AND RESONANCE IN QUANTUM MECHANICS-II

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*A translation of:*

**Mehrkörperproblem und Resonanz in der Quantenmechanik -II**

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ABSTRACT. The laws of quantum mechanics are applied to atoms with multiple electrons. In particular we investigate the question regarding the interconnection between quantum resonance phenomena and multiplet structure in the spectrum of complex atoms. Then the same resonance phenomena are studied in the theory of molecules and their band structure where it leads to interpretation of the known intensity anomalies in certain rotation spectra.

The spectra of atoms with two electrons can be, at least qualitatively, described by quantum mechanics [1]. The substantially new viewpoint that emerges in comparison with single electron atoms, involves a certain resonance phenomenon, that leads to subdivisions of the total spectra into non combinable terms, each of which alone is a complete quantum solution. Of these subsystems, one conforms to the PAULI principle [2], which asserts, that “equivalent” electron orbits may not arise. This subsystem was chosen without good justification as the physical solution. Such a choice of physical solution enabled the modifications of the statistics of the sort suggested by BOSE and EINSTEIN [3]. Independently, DIRAC came to similar conclusions [4]. DIRAC especially emphasized, that generally one should chose the solution which is in accord with PAULI’s principle, from which he arrived at the statistics of an ideal gas, which in large measure agrees with FERMI’s theory of degenerate gases [5]. With these considerations the solution for multielectron atoms is in principle at hand. But, to show that the solution so obtained actually corresponds to the observed spectra of such atoms, a number of further considerations are necessary.

## 1. GENERAL PRINCIPLES

The following calculations can be carried out on the one hand on the basis of the usual form of quantum mechanics—in terms of matrices corresponding to the terms of a Fourier series—or on the other hand in terms of SCHRÖDINGER’s waves in phase space. The formal relationships—herein for the multi body problem also—get a more general and systematic mathematical treatment in the formalism recently developed by DIRAC and JORDAN <sup>1</sup>. First, let us review the important basic concepts.

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<sup>1</sup>P. DIRAC [7]. I am indebted to Mr. DIRAC for making this work available to me before its publication. In the mean time I have been informed by Mr. JORDAN’s friendly communications that he has obtained similar results [8], that are equivalent to both DIRAC’s and this author’s [9]. Some of these results were communicated to the author already earlier and independantly by Mr. PAULI. See also the work by LANCZOS [10]. Added in proof: See LONDON [11].

The solution to a problem in quantum mechanics is given by the solution to an eigenvalue problem<sup>2</sup>

$$(1) \quad \mathbf{S}^{-1}\mathbf{H}\mathbf{S} = \mathbf{W}, \text{ or } \mathbf{H}\mathbf{S} - \mathbf{S}\mathbf{H} = 0, \quad \mathbf{S}\tilde{\mathbf{S}}^* = 1,$$

where  $\mathbf{H}$  is the Hamiltonian function of the system as a function of  $\mathbf{p}$  and  $\mathbf{q}$ ,  $\mathbf{W}$  the diagonal matrix in which the elements are the energy eigenvalues, and  $\mathbf{S}$  is the sought transformation matrix. In the original formulation of Eq. (1), both  $\mathbf{p}$  and  $\mathbf{q}$  in  $\mathbf{H}$  are to be expressed as matrices that correspond to Fourier series obtained from an appropriately chosen initial problem. Eq. (1) then becomes, in general, a complicated linear differential equation of infinite order for the  $S_n$ , for which the eigenvalues  $W_n$  are the energy values of the stationary states. According to DIRAC more general matrices can be introduced. Such matrices can be so selected, such that, for example, all  $\mathbf{q}(\mathbf{q}_1, \dots, \mathbf{q}_f)$  of the system are diagonal; but then, by cause of the relations  $\mathbf{p}_k\mathbf{q}_k - \mathbf{q}_k\mathbf{p}_k = h/(2\pi i)$ , the  $\mathbf{p}(\mathbf{p}_1, \dots, \mathbf{p}_f)$  naturally cannot then be diagonal. Likewise, if one introduces any other canonical variables,  $\xi, \eta (\xi_1, \dots, \xi_f; \eta_1, \dots, \eta_f)$  which satisfy the commutation relations, then again the  $\xi$  can be chose to be diagonal. In  $\mathbf{S}$  the energies  $W_n$  then are indexed by  $n$  and expressed in terms of the numbers  $\xi$ ,

$$(2) \quad \mathbf{S} : (S(n, \xi)), \text{ or } (S_n(\xi)).$$

Then Eq. (1) is equivalent<sup>3</sup> to:

$$(3) \quad \left[ H \left( \xi, \frac{h}{2\pi i} \frac{\partial}{\partial \xi} \right) - W_n \right] S_n(\xi) = 0,$$

from which  $S_n(\xi)$  can be determined. In addition to Eq. (3), there are the orthogonality and normalization conditions:

$$(4) \quad \begin{aligned} \mathbf{S}\tilde{\mathbf{S}}^* = 1 \text{ or } \sum_{\xi} S_n(\xi) S_m^*(\xi) &= \delta_{nm}; \\ \int S_n(\xi) S_m^*(\xi) d\xi &= \delta_{nm} = \begin{cases} 1 \text{ for } n = m \\ 0 \text{ for } n \neq m \end{cases}, \end{aligned}$$

depending on whether  $\xi$  is continuous or discrete. Written out completely, these equation are:

$$\sum_{\xi_1, \xi_2, \dots, \xi_f} S_n(\xi_1, \dots, \xi_f) S_m^*(\xi_1, \dots, \xi_f) = \delta_{nm},$$

or

$$\int S_n(\xi) S_m^*(\xi) d\xi_1, \dots, \xi_f = \delta_{nm}.$$

In the particular case in which  $\xi$  equals the position coordinates  $q$ , and  $\eta$  equals the momenta, Eq. (3) takes the form of SCHRÖDINGER's differential equation. In the case  $\xi = J$  and  $\eta = \omega$  (action-angle variables) for any particular problem, Eq. (3) takes the original form of Eq. (1).  $\mathbf{S}$  is in general the matrix, for which the index  $n$  is discrete and the index  $\xi$  continuous. In the special case  $\xi = q$  and  $\eta = p$ , a column of this matrix,  $S_n(\xi)$ , is an eigenfunction of SCHRÖDINGER's differential equation. The quantities  $S_n(\xi)$  and  $S_n^*(\xi)$  encompass all that can be said about stationary states of atoms. The usual diagonal matrix of a function,  $\mathbf{f}(\xi, \eta)$ , derived from energy eigenvalues is given by

$$(5) \quad \begin{aligned} f_{nm} &= \sum_{\xi} S_n^*(\xi) f \left( \xi, \frac{h}{2\pi i} \frac{\partial}{\partial \xi} \right) S_m(\xi), \text{ or} \\ f_{nm} &= \int S_n^*(\xi) f \left( \xi, \frac{h}{2\pi i} \frac{\partial}{\partial \xi} \right) S_m(\xi) d\xi. \end{aligned}$$

<sup>2</sup>See [6], Chapter 3, Eq. (13).

<sup>3</sup>The equivalence of matrices and operators was noted already by BORN and WIENER [12]. This equivalence played a large role in SCHRÖDINGER's researches [13], and was recognized for its full generality and exploited by DIRAC [4].

The physical interpretation of the product

$$S_n^*(\xi^0)S_n(\xi^0),$$

or alternately in the continuum case

$$S_n^*(\xi^0)S_n(\xi^0)d\xi,$$

is, that it is the probability, that in the stationary state  $n$ , the variable  $\xi = \xi^0$ , or in the continuous case that  $\xi^0 \leq \xi \leq \xi^0 + d\xi$  [1]. The quantities  $S_n(\xi)$  are generally known as the eigenfunctions of the quantum problem. They are functions of as many variables as the problem has degrees of freedom:  $S_n(\xi_1, \dots, \xi_f)$ . If Eqs. (1) or (3) are separable in the degrees of freedom, then  $\mathbf{S}$  can be factored

$$(6) \quad \mathbf{S} = S_n^1(\xi_1), S_n^2(\xi_2), \dots, S_n^f(\xi_f).$$

For the following calculation, the case in which we do not neglect the magnetic moment of the electron, which according to UHLENBECK and GOUDSMIT [14], derives from its rotation. Such an electron has four degrees of freedom [the total angular momentum of spin is not included, as it is fixed at a value  $s = 1/2$ .<sup>4</sup>], e.g., the three coordinates of the center of gravity, the position of the “line of nodes” of the eigenrotation, on which the projection of  $s$  is  $m_s$ . If to first order the interaction between the electromagnets (spin)<sup>5</sup> and orbital motion is ignored, then  $\mathbf{S}$  can be written

$$\mathbf{S}(\xi_1, \xi_2, \xi_3)\mathbf{S}^4(\xi_4).$$

If the line of nodes is chosen for  $\xi_4$ , then SCHRÖDINGER’s theory is needed to treat the orbital electrons to determine  $\mathbf{S}^4$ . This problem still has certain difficulties. But, as the choice of  $\xi_4$  is unconstrained, and the treatment of the orbiting electron in the language of matrices is well known, the determination of  $\mathbf{S}^4(q_4)$  is superfluous; one could, for example, choose  $\xi_4$  as the projection of  $s$  on some fixed external axis,  $m_s$ , so that  $\mathbf{S}^4$  is the unit matrix and  $m_s = \pm 1/2$ .

## 2. MULTIELECTRON ATOMS

§2.1 Research in recent years systematically has revealed the spectra of complex atoms, so that now to each “term” one can attribute a particular motion in the sense of BOHR. Among the important steps in the systematization of spectra, the following deserve note: SOMMERFELD’s  $n, k, j$ -ordering of the terms, LANDE’s theory of the Zeeman effect, CATALÁN’s discovery of multiplets, PAULI’s exclusion principle, the RUSSELL-SAUNDERS model, HUND’s systematization of the spectra of higher order periods of the periodic system, and finally the UHLENBECK-GOUDSMIT hypothesis regarding the angular momentum of an electron. The branch of quantum mechanics covering this matter has been comprehensively surveyed, for details, we recommend ref.: [15].

In the conceptualization of models, that comprise the basis of the ordering of the terms, a certain analogy with classical mechanics, referred to as the “adiabatic” correspondence, is made. Motion of an electron in an atom is considered influenced by the charge on the nucleus and by other electrons, where the latter are described by an average, i.e., the precise interaction of moving electrons is not taken into account. While a continuous exchange of energy between the electrons might be expected to occur—as would be the case in classical electrodynamics—because of the fundamental principle of quantum mechanics,

<sup>4</sup>For the sake of simplicity, these values are given below only in terms of the quantum numbers.

<sup>5</sup>*Translator:* HEISENBERG used the terms ‘magnet’ or ‘electromagnet’ which have been replaced by ‘spin.’ For the sake of readability for the modern eye, in this translation the latter term is used throughout.

it does not occur [16] (compare with FRANCK-HERTZ scattering experiments), so that finally the “adiabatic” correspondence might be expected to yield the actual regularities of the spectra, which in fact it does. Quantitative analysis of this correspondence is possible naturally only with quantum mechanics.

This coarse correspondence could not, however, provide a complete interpretation of the actual quantum theoretical processes, in so far as even in quantum mechanics account should be taken of the finer electronic interactions. This aspect of quantum mechanics cannot be rendered in terms of mechanical images. This is so, because these detailed electron interactions, as well as interactions by means of external radiation, are characterized by the direct appearance of the effects of discontinuities [1]. Quantum mechanics arose in the first instance from an effort to understand the interaction of external radiation with atomic electrons in terms of these very principles. Quantum mechanics provides just this treatment for the finer interactions via the resonance phenomena that we consider herein.

The lack of an analogue for the detailed interaction of electrons with the imagery from coarse correspondences must lead to conflicts between models and observations. Such conflicts are to be found in the existence of ‘multiplets.’ These multiplets arise, as is well known, by cause of the fact that the electrons’ magnetic moments (spins), in the sense of UHLENBECK-GOUDSMIT, align themselves parallel or antiparallel and then are added ( $l$ ) to orbital angular momentum ( $j$ ). In a mechanical model, the electrons would not be parallel, as the interaction is vanishingly small. Even were the interaction large, the effect would not depend on the relative orientation of the electron, rather on the relative orbital position; the electrons would not be parallel. We expect, therefore, than for an interpretation of the multiplet structure, quantum resonance plays a crucial role.

§2.2 Because the forces that link spin with the orbital motion generally are very weak, these forces can be neglected in a first approximation. From empirical evidence for this problem, one can conclude, that the whole term system for an atom can be divided into subsystems, between which there are no interrelationships (e.g., ortho- and para-helium).

To begin, we carry out this separation into noninteracting subsystems for  $n$  point symmetric electrons. We do so starting with a noninteracting system and then consider the interaction as a perturbation. In the unperturbed state the electrons exist in various stationary states, for which the eigenfunctions  $l, m, \dots, p$  are ascribed. The number of electrons, from which the coordinates of the eigenfunctions depend, are attached to the eigenfunctions as indices (e.g.,  $l_1, m_2, \dots, p_n$ ). The eigenfunction for the unperturbed total system can be expressed as the product of the eigenfunctions of the individual electrons. The unperturbed problem exhibits a  $n!$  degeneracy, as the exchange of the individual eigenfunctions gives the same total system eigenfunction. Thus, arbitrary aggregations of such products can be taken as the system eigenfunction.

If the separation of the term systems of the unperturbed problem into incompatible subsystems is made, then this separation (in so far as all electrons are identical and subject to identical inter electron forces) cannot be perturbed by any type of interaction. That is, the type of separation into incompatible subsystems is totally independent of the specific type of interaction, while at the same time being the crucial step in the solution of the problem with interaction. The separation can be effected in two ways:

1. A series of non compatible term systems is defined by the fact, that an eigenfunction of any of the subsystems, multiplied by a symmetric function of the electrons, can be expressed only in terms of eigenfunctions of the very same subsystem. Or:

2. Let  $u$  and  $v$  be eigenfunctions of two distinct subsystems such that the integral  $\int u^* v f d\xi$  [See: Eq. (5).] vanishes whenever  $f$  is a symmetric function of the electrons.



and it follows that

$$(14) \quad (1 - \omega^{\lambda-\mu}) \int \gamma_{\omega^\lambda}^* \gamma_{\omega^\mu} f d\xi = 0.$$

Thus, the integral on the left side, which determines the combinations, is null for  $\lambda \neq \mu$ , that is, the systems  $\Gamma_{\omega^\lambda}, \Gamma_{\omega^\mu}$  do not combine with each other, just combinations within a system  $\Gamma$  are possible.

The separation into incompatible subsystems can often be continued, so that a few or all systems  $\Gamma$  can be further divided into subordinate subsystems. Consider a particular eigenfunction  $\Gamma_{\omega^\lambda}$ :

$$(15) \quad U_{\omega^\lambda} = 1/\sqrt{v} \left( u + \omega^\lambda S u + \omega^{2\lambda} S^2 u, \dots, \omega^{(v-1)\lambda} S^{v-1} u \right).$$

Suppose there is a new substitution  $T$  of grade  $\mu$ , such that

$$(16) \quad \begin{aligned} & T(1 + \omega^\lambda S + \omega^{2\lambda} S^2 + \dots + \omega^{(v-1)\lambda} S^{v-1}) \\ &= (1 + \omega^\lambda S + \omega^{2\lambda} S^2 + \dots + \omega^{(v-1)\lambda} S^{v-1})T, \end{aligned}$$

then we can construct the function ( $\varepsilon^\mu = 1$ ):

$$(17) \quad Z_{\omega^\lambda, \varepsilon^k} = 1/\sqrt{v} \left( U_{\omega^\lambda} + \varepsilon^k T U_{\omega^\lambda} + \varepsilon^{2k} T^2 U_{\omega^\lambda} + \dots + \varepsilon^{(\mu-1)k} T^{\mu-1} U_{\omega^\lambda} \right),$$

and thus divides the the term system  $\Gamma_{\omega^\lambda}$  into  $\mu$  new incompatible subsystems; as per Eq. (13) only terms with the same  $\varepsilon$  exponent can be combined. The condition, Eq. (16), must be satisfied, however, in order that the eigenfunction  $TU_{\omega^\lambda}$  still belongs to the system  $\Gamma_{\omega^\lambda}$ .

Eq. (16) is satisfied by all systems  $\Gamma_{\omega^\lambda}$  whenever  $S$  and  $T$  commute, i.e., when

$$(18) \quad ST = TS.$$

Elementary group theory provides methods to find a substitution  $T$  satisfying this condition if  $S$  is specified. If  $\omega^\lambda$  is a primitive  $v$ -th root of 1, then  $T$  must satisfy Eq. (18) in order to be able to also satisfy Eq. (16).

Even when  $\omega^\lambda$  is not a primitive  $v$ -th root of 1, there still exist substitutions  $T$ , that do not commute with  $S$  but still satisfies Eq. (16). In general term systems  $\Gamma_{\omega^\lambda}$  that do not correspond to a primitive root of  $\omega^\lambda$ , are susceptible to being subdivided further than those that do correspond to primitive roots.

It should be mentioned, that the identity substitution 1 and an arbitrary power of  $S^r$  of  $S$  satisfy Eq. (18) for  $T$ , but still do not lead to a new division of  $\Gamma_{\omega^\lambda}$ .

The question: 'Into how many incompatible subsystems the term system for an  $n$ - electron atom can be divided?', cannot be answered in full generality with the considerations outlined here. But, with the procedure described herein, one can always find the subsystems. As it is an important practical matter to find the appropriate subdivision in as few steps as possible, it is the substitutions of high grade that are the most challenging. The grade of a division is easy to estimate by a cyclical enumeration. A cyclical substitution can be written in the form  $a_1 a_2 \dots a_z$  which means in manner described above, Eq. (8)

$$(19) \quad \left( \begin{array}{c} a_1 a_2 \dots a_z \\ a_2 a_3 \dots a_1 \end{array} \right).$$

The grade of this substitution equals the number of elements,  $z$ . Every substitution can be decomposed into a product of multiple cyclic substitutions based on various elements. If  $z_1, z_2, \dots$  the grade of the various cycles into which  $S$  can be subdivided, then

$$z_1 + z_2 + \dots = n$$

and the smallest common multiples of  $z_1, z_2 \dots$  give the grade of  $S$ . In the case of 12 electrons in various quantum orbits, for example, substitutions of the form

$$S = (12345)(6789\ 10\ 11\ 12).$$

would be available. The grade of  $S$  here is  $5 \cdot 7 = 35$  and the procedure described above yield 35 incompatible subsystems. Moreover,

$$S = (123)(4567)(89\ 10\ 11\ 12),$$

has grade  $3 \cdot 4 \cdot 5 = 60$  incompatible subsystems. Obviously this is the maximum of incompatible subsystems that the above procedure can yield in one step for  $n = 12$ .

If any of the eigenfunctions  $l, m, \dots, p$  are identical, i.e., there are equivalent electrons, then the total of the number of terms of different energies is no longer  $n!$ , rather it is  $n!/(n_\alpha!n_\beta!\dots)$ , where  $n_\alpha, n_\beta, \dots$  gives the number of electrons in states  $\alpha, \beta$ . In order to use the above procedure in this case, one must chose the substitution  $S$  for which the grade is  $n!/(n_\alpha!n_\beta!\dots)$  and then with it carry out the distribution into non combinable terms.

As a concrete example, consider Lithium,  $n = 3^6$ . The eigenfunction of the initial system is:

$$u = l_1 m_2 p_3.$$

We assume that  $l, m$  and  $p$  are distinct. The cyclic substitution is the one of higher grade, (123). Let  $\varepsilon$  be a primitive root of 1, so that from Eq. (12) we get:

$$(20) \quad \begin{aligned} U_1 &= 1/\sqrt{3}\{l_1 m_2 p_3 + l_2 m_3 p_1 + l_3 m_1 p_2\}, \\ U_\varepsilon &= 1/\sqrt{3}\{l_1 m_2 p_3 + \varepsilon l_2 m_3 p_1 + \varepsilon^2 l_3 m_1 p_2\}, \\ U_{\varepsilon^2} &= 1/\sqrt{3}\{l_1 m_2 p_3 + \varepsilon^2 l_2 m_3 p_1 + \varepsilon l_3 m_1 p_2\}. \end{aligned}$$

Among the eigenfunctions, Eqs. (20), the combinations  $m_1 l_2 p_3$  did not occur. Thus, there exists a second series,  $W_1, W_\varepsilon, W_{\varepsilon^2}$ . The three incompatible term systems can be denoted most simply as:

$$(21) \quad \Gamma_\eta = \left\{ \begin{array}{l} \gamma'_\eta = 1/\sqrt{3}\{l_1 m_2 p_3 + \eta l_2 m_3 p_1 + \eta^2 l_3 m_1 p_2\} \\ \gamma''_\eta = 1/\sqrt{3}\{m_1 l_2 p_3 + \eta m_2 l_3 p_1 + \eta^2 m_3 l_1 p_3\} \end{array} \right\},$$

where  $\eta$  for the three systems takes the values  $1, \varepsilon, \varepsilon^2$ . The term systems  $\Gamma_\varepsilon$  and  $\Gamma_{\varepsilon^2}$  cannot be further subdivided, as with the substitution (123) only the powers of this substitution are exchangeable.  $\Gamma_1$ , contrariwise, belongs to a non primitive root of 1. If one chooses as substitution  $T$  an arbitrary transposition, then Eq. (16) is valid for it. The grade is 2, the two incompatible subsystems belong to the roots  $+1$  and  $-1$ . The eigenfunctions are:

$$(22) \quad \Gamma_{1,1} : \frac{1}{\sqrt{2}}(\gamma'_1 + \gamma''_1); \quad \Gamma_{1,-1} : \frac{1}{\sqrt{2}}(\gamma'_1 - \gamma''_1).$$

$\Gamma_{1,1}$  and  $\Gamma_{1,-1}$  are the well known symmetric and antisymmetric term systems respectively.

In the systems  $\Gamma_{1,1}$  and  $\Gamma_{1,-1}$  the problem of the unperturbed atom is not degenerate, as for both, only one term each of particular energy arises. Within  $\Gamma_\varepsilon$  and  $\Gamma_{\varepsilon^2}$  there is nevertheless a certain degeneracy insofar as in each a term with the same energy as in the unperturbed systems occurs. This degeneracy is lifted by the interaction in a way depending on the particulars of the interaction.

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<sup>6</sup>Added in proof: In a recent article WIGNER, [18], has independently obtained results for the three electron atom that are equivalent to those given herein.

The matrix, of the given unperturbed interaction energies, has four significantly different terms, and average:  $W_{l,m,p;l,m,p} = A$ , and three resonance terms, that correspond to the exchange of two electrons:

$$W_{l,m,p;m,l,p} = B; \quad W_{l,m,p;p,m,l} = C; \quad W_{l,m,p;l,p,m} = D.$$

The interaction induces a perturbation, that by well known principles is given by the following determinant:

$$\begin{vmatrix} W - A & -(B + \eta C + \eta^2 D) \\ -(B + \eta^2 C + \eta D) & W - A \end{vmatrix}.$$

This yields the six solutions (Note:  $B + \eta C + \eta^2 D$  is replaced by  $Re^{2i\phi}$ ):

$\Gamma_1$	$\Gamma_\epsilon$	$\Gamma_{\epsilon^2}$
$W = A + B + C + D$ or $\frac{1}{\sqrt{2}}(\gamma_1^I - \gamma_1^{II})$	$W = A + R$ or $\frac{1}{\sqrt{2}}(e^{i\phi}\gamma_\epsilon^I + e^{-i\phi}\gamma_\epsilon^{II})$	$W = A + R$ or $\frac{1}{\sqrt{2}}(e^{-i\phi}\gamma_{\epsilon^2}^I + e^{i\phi}\gamma_{\epsilon^2}^{II})$
$W = A - B - C - D$ or $\frac{1}{\sqrt{2}}(\gamma_1^I + \gamma_1^{II})$	$W = A - R$ or $\frac{1}{\sqrt{2}}(e^{i\phi}\gamma_\epsilon^I - e^{-i\phi}\gamma_\epsilon^{II})$	$W = A - R$ or $\frac{1}{\sqrt{2}}(e^{-i\phi}\gamma_{\epsilon^2}^I - e^{i\phi}\gamma_{\epsilon^2}^{II})$

Table 1

In Table (1) there is a characteristic degeneracy still, insofar as each term of the system  $\Gamma_\epsilon$  has the same energy as one term of  $\Gamma_{\epsilon^2}$ . Formally this is due to the fact, that the matrix elements of the interaction terms  $B, C$  and  $D$  are real. This holds true for any type of interaction and thus the degeneracy is a substantial feature of the resonance phenomenon. Eventually in connection with the discussion of the multiplet structure, we shall return to this point. Here we note, that this degeneracy leads to some indeterminacy in the division into incompatible subsystems.

If two electrons are equivalent, say  $l = m$ , then the  $\Gamma$  classification yields a full term scheme with each eigenfunction  $\gamma_\eta^I = \gamma_\eta^{II}$ . In this case there are no degeneracies within a subsystem  $\Gamma_\eta$ , further, if  $A = D$  and  $B = C$ ; one gets solutions:

$\Gamma_{1,1}$	$\Gamma_\epsilon$	$\Gamma_{\epsilon^2}$
$W = A + 2B$ Eigenfunction $\gamma_1$	$W = A - B$ Eigenfunction $\gamma_\epsilon$	$W = A - B$ Eigenfunction $\gamma_{\epsilon^2}$

Table 2

§2.3 If for the term spectrum of an atom described above, spherically symmetric electronic configurations are assumed, then changes that appear when spin orbital interaction cannot be neglected, can be taken into account. To begin we seek to derive the facts of the multiplet structure, that is the fact that spin is always parallel or antiparallel.

The eigenfunction for the whole system, which consists of orbital electronic eigenfunctions, so long as the spin interaction is small, consist of products of orbital and spin eigenfunctions. When multiple eigenfunctions belong to the same energy—as the calculations presented above show happens often by inclusion of the interaction—, then linear aggregates of products of orbital and spin eigenfunctions come into consideration.

*Eigenfunctions of the total system should be antisymmetric with respect to the electrons.* Let us start from an unperturbed system in which the spin-orbital interaction is taken to

vanish, and in this system count the positions of the spins relative to an arbitrarily selected direction. Now, the spin orbital interaction energy will be considered a perturbation that determines the secular oscillation of the spins relative to the time average of the orbital motion. This perturbation energy is a symmetric function of the electrons. The interaction of a particular electron and all other electrons and their spins depends on the orientation of these spins relative to the orientation of all other electrons' orbital positions and the orientations of their spins. Because of the antisymmetry of the total wave functions, all electrons execute the same "motion" (in various phases); thus the average perturbation energy can depend only on: the orientation of the spin relative to an average orbital axis—in atoms this can be only the directions of the total electronic momentum, in two-atom molecules one could consider the line joining the nuclei—, and secondly from the relative orientations of the spins. To first impressions, it might seem that the final orientation of the spins depends on the pairwise average perturbation energy. This is not so, however. Rather the angular momentum of the spins,  $s_i$ , depends on a quantized momentum  $s$  in the usual structure rules, that is, with only "parallel" or "antiparallel" orientations. To get insight here, let us consider a simple mechanical example: Instead of an interaction dependant on the direction of the total electronic momentum,  $l$ , let us introduce another force comprised of two parts, one corresponding to an external force, and the other among the spins, but dependant only on their relative orientation. Although the Hamiltonian of this system consists of two terms, one for each of the interactions, the Hamiltonian of the perturbed system is not so composed. The electron interaction with the average orbital motion corresponds to what we have attributed to the external force; but, the average spin interaction still depends on the relative orientations of the electrons' spins to the axis  $l$ . One can easily see, that in the case in which the above two interactions are additive, if the assertion above about the aggregation of  $s_i$  is correct, then it is correct in general.

Let us now consider the quantum mechanical treatment of this case.

In the "unperturbed" system in which electronic spin interaction is neglected, each electron has two possible orientations relative to others, as an axially symmetric force  $m_s = \pm 1/2$ ; for which there corresponds two eigenfunctions  $S^4(\xi_4)$ , that for the sake of simplicity we shall denote  $\alpha$  and  $\beta$ . The number of the electrons to which these functions belong, that is, from which these variables are dependant, is given by an index:  $\alpha_1, \alpha_2, \dots, \alpha_n; \beta_1, \beta_2, \dots, \beta_n$ . In the unperturbed system there are degeneracies insofar as all states have the same energy that belongs to a given value of  $\sum m_s$ , i.e., to a particular total momentum about the axis of the exterior field; now for a given number of electrons  $n$ , the state with the eigenfunctions  $\alpha$  and  $\beta$  is given by  $m = \sum m_s$  and

$$(23) \quad n_\alpha + n_\beta = n, \quad \frac{1}{2}(n_\alpha - n_\beta) = m.$$

For values  $s > 1/2$  these considerations cannot be carried out. *The multiplet structure of complex spectra is linked to the special value  $s = 1/2$ .* The exterior force imposed no other requirement on the unperturbed problem than that  $\sum_n m_s = m$  shall be quantized, and that this requirement not come into conflict by giving excessive spin interaction energy. Contrariwise: the actual distribution of systems of equal energy— $n!/(n_\alpha!n_\beta!)$  in number—into systems of different energy on the basis of vanishingly small mutual interaction follows quite independent of exterior forces, i.e., it corresponds to the parallel- and antiparallel orientations of the spins.

The just mentioned degeneracy for vanishing interaction is completely analogous to the degeneracy in §2.2 and therefore can be denoted as a resonance. The oscillation frequency corresponding to this resonance is the simple precession frequency of the spin vector  $s_i$

about the axis  $s$  of the total angular momentum of the electrons. One should not associate a complicated exchange motion of the electrons with this notion of resonance.

For the actual calculation of the eigenfunctions to which the multiplets belong certain formulas pertain: The interaction energy between any two of the electrons, 1 and 2 say, will be a matrix, containing diagonal elements and two each elements that correspond to the exchange of electrons. In other words: for two electrons there are four states, characterized by:

	I	II	III	IV
$m_1...$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$m_2...$	$+\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$

Table 3

The matrix of the interaction energies comprises only transitions for  $m = \text{const.}$ , as they depend only on the relative direction from 1 to 2; that is, only transitions from  $II$  to  $III$ . Further,  $H_{I,I} = H_{IV,IV} = a$ ;  $H_{II,II} = H_{III,III} = b$ ;  $H_{III,II} = H_{II,III} = c$ . These three constants satisfy the relation:

$$(24) \quad a = b + c.$$

This is easily seen to be so from the treatment of the problem with two electrons. The total energy of the system,  $W$ , (given that external forces are neglected) is in the state  $m = 1$  (that is:  $m_1 = m_2 = 1/2$ ) obviously  $H_{I,I} = a$  (eigenfunction  $\alpha_1\alpha_2$ ), likewise in the state  $m = -1$  ( $m_1 = m_2 = -1/2$ )  $H_{IV,IV} = a$  (eigenfunction  $\beta_1\beta_2$ ). In the state  $m = 0$  there is a degeneracy, that leads to the equation discussed in ref. [1], namely:

$$\mathbf{W} = \mathbf{S}^{-1}\mathbf{HS},$$

and to the determinate

$$(25) \quad \begin{vmatrix} W - H_{II,II} & -H_{II,III} \\ -H_{III,II} & W - H_{III,III} \end{vmatrix} = 0.$$

Which gives:

$$(W - b)^2 = c^2, \quad W = b + c, \quad \text{and} \quad W = b - c.$$

The state characterized by  $W = b + c$  has the eigenfunction  $1/\sqrt{2}(\alpha_1\beta_2 + \alpha_2\beta_1)$ ; it is symmetric in electrons 1 and 2 and belongs therefore to the triplet system.  $W = b - c$  belongs to the eigenfunction  $1/\sqrt{2}(\alpha_1\beta_2 - \alpha_2\beta_1)$  and constitutes the singlet system. So long as there are no external forces acting on the spins, the three states in the triplet system have the same energy, that is  $a = b + c$ . In the following calculations we shall always express  $b$  in terms of  $a$  and  $c$ .

Three interacting electronic spins in an external force field provide a good example of the application of these principles. There is one state without a degeneracy, i.e.,  $m = 3/2$ . Let  $K_\alpha$  denote the effect on the energy from the external force when  $m_s = +1/2$ , and  $K_\beta$  when  $m_s = -1/2$ . Thus, when  $m = 3/2$ , this energy differential is given by  $3K_\alpha + 3a$ , for which the eigenfunction is  $\alpha_1\alpha_2\alpha_3$ . For the state with  $m = 1/2$  then, there is a triple degeneracy with three eigenfunctions:  $\alpha_1\alpha_2\beta_3$ ,  $\alpha_3\alpha_2\beta_1$ ,  $\alpha_2\alpha_3\beta_1$ , all pertaining to the same energy. This energy, which arises from the external force, equals  $2K_\alpha + K_\beta$ . If one lets  $W - 2K_\alpha - K_\beta - a - 2b = W - 2K_\alpha - K_\beta - 3a + 2c$  be denoted by  $X$ , then one arrives at the

determinate

$$\begin{array}{l} (123) \\ (231) \\ (312) \end{array} \left| \begin{array}{ccc} X & -c & -c \\ -c & X & -c \\ -c & -c & X \end{array} \right|.$$

The solutions are:

$$(26) \quad \begin{array}{ll} X_1 = 2c, & \text{eigenfunction } \delta_1 = 1/\sqrt{3}(\alpha_1\alpha_2\beta_3 + \alpha_2\alpha_3\beta_1 + \alpha_3\alpha_1\beta_2), \\ X_2 = X_3 = -c & \text{eigenfunctions } \delta_\varepsilon = 1/\sqrt{3}(\alpha_1\alpha_2\beta_3 + \varepsilon\alpha_2\alpha_3\beta_1 + \varepsilon^2\alpha_3\alpha_1\beta_2), \end{array}$$

where  $\varepsilon$  is one or the two primitive roots of the equation:  $\varepsilon^2 = 1$ . Now,  $X_1$  has an eigenfunction symmetric for all electrons and therefore has the same term-system as for the solution  $m = 3/2$  and  $\alpha_1\alpha_2\alpha_3$ . In this case the energy  $W$  equals:

$$W = 2K_\alpha + K_\beta + 3a.$$

For vanishing external force, this is the energy of the state  $m = 3/2$ . The calculations for  $m = -1/2$  and  $m = -3/2$  are analogous to those for  $m = 1/2$  and  $m = 3/2$ , and for which we get the following table

Table (4)	Quartet system	Two Doublet systems
$m = 3/2$ $m = 1/2$ $m = -1/2$ $m = -3/2$	$W = 3a + \begin{cases} 3K_\alpha \\ 2K_\alpha + K_\beta \\ K_\alpha + 2K_\beta \\ 3K_\beta \end{cases}$	$W = 3a - 3c + \begin{cases} 2K_\alpha + K_\beta \\ K_\alpha + 2K_\beta \end{cases}$

Table 4

Between the two doublet systems there is a degeneracy, in so far as they belong to the same energy value. The separation into  $\delta_\varepsilon$ -systems, i.e., into quartets and doublets, is completely analogous to division into  $\Gamma$  systems in Table 1. Quartets and doublets do not combine with each other.

The calculation of the spin eigenfunctions and their multiplet structure for more than three electrons is best achieved using the methods of §2.2—The number of the various multiplets for  $n$  electrons can be determined easily by the usual structure rules. The number of terms for a given value of  $m$ , per Eq. (23), equals:

$$(27) \quad \frac{n!}{n_\alpha!n_\beta!} = \frac{n!}{\left(\frac{n}{2} + m\right)! \left(\frac{n}{2} - m\right)!}.$$

That is, it is always true:

$$(28) \quad \frac{n!}{\left(\frac{n}{2} + m\right)! \left(\frac{n}{2} - m\right)!} \frac{n!}{\left(\frac{n}{2} + m + 1\right)! \left(\frac{n}{2} - m - 1\right)!} = \frac{n!(2m + 1)}{\left(\frac{n}{2} + m + 1\right)! \left(\frac{n}{2} - m\right)!}.$$

Multiplets have multiplicity  $2m$ , where  $m$  is a multiple of  $1/2$ , and depends on whether  $n/2$  is the same multiple of  $1/2$ . Various multiplets of the same multiplicity have the same energy so long as the center of gravity for the electrons is fixed.

In an atom, the electromagnets (spins) do not orient themselves in relation to external forces, rather in relation to the total angular momentum,  $l$ , of all the electrons. Should an atom be subjected to a strong external magnetic field—we are considering here, for example, the PASCHEN-BACK effect—, then the magnets (spins) do orient themselves in relation to this external field. In this extreme case, the eigenfunctions of the whole atom can be expressed as products, or sums of products, of electron orbital eigenfunctions and their spin eigenfunctions.

We would like to specify here the complete term chart including the spins for the three electron problem. That is, the solutions from §2.2, Table 1 (p. 8) should be combined with the solutions from this Section, Eqs. (26), so that the total solution is antisymmetric.

Table (5)	Energy	Eigenfunction
No equivalent electrons, i.e., $m, p, l$ all different	Quartet system $W = A - B - C - D$ 1. Doublet system $W = A - R$ 2. Doublet system $W = A + R$	$\delta_l / \sqrt{2} (\gamma_1^I - \gamma_1^{II})$ $1/2 \{ \delta_\epsilon (e^{-i\phi} \gamma_{\epsilon^2}^I - e^{i\phi} \gamma_{\epsilon^2}^{II})$ $+ \delta_{\epsilon^2} (e^{i\phi} \gamma_\epsilon^I - e^{-i\phi} \gamma_\epsilon^{II}) \}$ $1/2 \{ \delta_\epsilon (e^{-i\phi} \gamma_{\epsilon^2}^I + e^{i\phi} \gamma_{\epsilon^2}^{II})$ $+ \delta_{\epsilon^2} (e^{i\phi} \gamma_\epsilon^I + e^{-i\phi} \gamma_\epsilon^{II}) \}$
Two equivalent electrons i.e., $l = m$	Doublet system $W = A - B$	$\frac{1}{\sqrt{2}} \{ \delta_\epsilon \gamma_{\epsilon^2} - \delta_{\epsilon^2} \gamma_\epsilon \}$

Table 5

The interaction of the spins was neglected in these energy values. The same considerations can be applied to all atoms for which all electrons, up to three, are found in closed groups. The eigenfunctions of the total system are not products, rather sums of products of eigenfunctions from §2.2 and Eq. (26). This occurs always whenever eigenfunctions of different systems,  $\Gamma$ , yield the same energy values.

To foster a comparison of Table 5 with empirical observations, we note to begin, that the various multiplets in the term diagrams differ on the scale of the resonance interactions. The term with the highest multiplicity has the lowest value, as the quantities  $B, C, D$ , are, as in the theory of the helium spectrum (see: ([1]), p. 508), are in general positive. Empirically it is seen that generally the term with the highest multiplicity, given equal quantum numbers, has the lowest value, a fact that here too is evident. This is so as the term with the highest multiplicity corresponds to symmetric eigenfunctions of all spins, if the eigenfunctions  $l, m, \dots, p$  are different. (For the maximal value  $m = n/2$ , the only associated eigenfunction is  $\alpha_1, \alpha_2, \dots, \alpha_n$ .) Therefore they must be the spherically symmetric electron eigenfunctions which are to be multiplied by the spin eigenfunctions to give the needed antisymmetric total eigenfunctions. Their corresponding energy values always contain the resonance contribution with a minus sign (See: [1], Eq. (19), and is therefore smaller than all other energy values. If some electrons are bound into isolated groups, the above considerations still pertain, so long as resonance with the completed shells can be neglected.

With respect to Table 5, note, that—analogue to the Helium problem—within an atom, in the end combinations between doublet and quartic systems arise with a relative strength, which corresponds to the relative separation of the various multiplets. On the other hand, the various doublet systems combine with each other with normal intensities.

§2.4. In the previous Sections we have treated the motion of the center of gravity of the electrons separate from that of the spins, and got the total solution as a combination of both. In order to study this problem from all sides, we shall reverse this procedure and begin with an atom with spinning electrons.

We take it that there is a strong external field, and that the interactions between electrons can be neglected. In this case each electron separately can be considered to be in a

stationary state. As the spin interaction with the orbital motion is negligible, the eigenfunctions can be expressed according to Eq. (6) as products. Again we consider the indices  $l, m, \dots, p$  as pertaining to the orbital motions and  $\alpha, \beta$  to the spin. The total wave function, then, can be designated, e.g.,  $l_1 \alpha_1$ . If the interaction of the spin with the orbital motion is large, then such a product is not possible and we use for this case the designation:  $l_1^\alpha$ .

In this case the unperturbed system is not degenerate; the antisymmetric eigenfunction serving as the solution is given by its determinate:

$$(29) \quad \begin{vmatrix} l_1^\alpha & m_1^\alpha & \dots & p_1^\beta \\ l_2^\alpha & m_2^\alpha & \dots & p_2^\beta \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ l_n^\alpha & m_n^\alpha & \dots & p_n^\beta \end{vmatrix}.$$

As shorthand for this determinant, let us use the symbol

$$\begin{array}{c} l^\alpha \quad m^\alpha \quad \dots \quad p^\beta \\ 1 \\ 2 \\ \vdots \\ n \end{array} \left| \begin{array}{c} \dots \\ \dots \\ \dots \\ \dots \end{array} \right|.$$

If, however, spin interaction can be neglected in comparison with electron orbital energy (that is, the separation within a multiplet is small with respect to the separation between the multiplets), then the unperturbed system is degenerate even in the presence of an arbitrarily large external force. That is, one can arbitrarily distribute the “ $\alpha$ ” and “ $\beta$ ” states of the spin among the orbital eigenfunctions  $l, m, \dots, p$ . In other words, there arises the degeneracy described in §2.3, which results in the separation of the multiplets. If the eigenfunctions  $l, m, \dots, p$  are all different, then the number of determinants belonging to the same energy of the unperturbed problem is given by Eq. (23) and the number of multiplets by Eq. (28). If two of them are identical, say the first two, the determinants:

$$\begin{array}{c} l^\alpha \quad l^\alpha \quad \dots \quad p^\beta \\ 1 \\ 2 \\ \vdots \\ n \end{array} \left| \begin{array}{c} \dots \\ \dots \\ \dots \\ \dots \end{array} \right| \quad \text{and} \quad \begin{array}{c} l^\beta \quad l^\beta \quad \dots \quad p^\beta \\ 1 \\ 2 \\ \vdots \\ n \end{array} \left| \begin{array}{c} \dots \\ \dots \\ \dots \\ \dots \end{array} \right|$$

are zero identically, and the other two determinants:

$$\begin{array}{c} l^\alpha \quad l^\beta \quad \dots \quad p^\beta \\ 1 \\ 2 \\ \vdots \\ n \end{array} \left| \begin{array}{c} \dots \\ \dots \\ \dots \\ \dots \end{array} \right| \quad \text{and} \quad \begin{array}{c} l^\beta \quad l^\alpha \quad \dots \quad p^\beta \\ 1 \\ 2 \\ \vdots \\ n \end{array} \left| \begin{array}{c} \dots \\ \dots \\ \dots \\ \dots \end{array} \right|$$

are identical up to a sign. To each of two identical orbital eigenfunctions, a distinct spin eigenfunction, i.e., either  $\alpha$  or  $\beta$ , must be attached; that is, “equivalent orbits” do not occur. The number of the possible multiplets is equal the number for  $n - 2a$  spins in the sense of §2.3, where  $a$  is the number of pairs with identical  $l, m, \dots, p$ . More than two each eigenfunctions with the same  $l, m, \dots, p$  do not occur.

For the calculations in §2.3 the initial assumption was that the separation between the different multiplets resulted from small spin interactions. Multiplets with identical multiplicity had the same energy. Now the separations between the multiplets are determined at the outset by the interaction of the electrons.—The rest of the calculation depends on the particular circumstances of the atoms under consideration.

Here it is useful to start with a particular term for an atom and to study which state of the whole system arises if in this term there is an electron in a given orbit. Such considerations lead to the following calculation:

The initial system has  $n - 1$  electrons and the antisymmetric eigenfunction

$$(30) \quad U(1, 2, \dots, n - 1).$$

Degeneracies are lifted by action of external fields. This function belongs to a particular value  $w = \sum_n m_s$  in the sense described in §2.3. We consider here a positive value for  $m$ , as there is always another stationary state with the eigenfunction  $W$  that belongs to the value  $\sum_n m_s = m - 1$ , and which, for vanishing multiplet splitting and vanishing external forces, has the same energy, i.e., belongs to the same multiplet.

At this point an electron with the eigenfunction  $k_n^\beta$  is inserted into the problem. So long as the interaction of this electron with atom is very small, there would be no degeneracy. The (antisymmetric!) eigenfunction for the whole system is:

$$(31) \quad \frac{1}{\sqrt{n}} \{ U(1, 2, \dots, n - 1) k_n^\beta + (-1)^n U(2, 3, \dots, n) k_1^\beta + (-1)^{2n} U(3, 4, \dots, n, 1) k_2^\beta + \dots \}.$$

When the multiplet splitting can be considered small in comparison to the interaction energy, degeneracy will result and the eigenfunction:

$$(32) \quad \frac{1}{\sqrt{n}} \{ W(1, 2, \dots, n - 1) k_n^\alpha + (-1)^n W(2, 3, \dots, n) k_1^\alpha + (-1)^{2n} W(3, 4, \dots, n, 1) k_2^\alpha + \dots \},$$

will belong to the same energy as the unperturbed system.

Resolution of the perturbation problem leads to a simple two member determinant, from which the energy splitting is easily determined if  $U$  and  $W$  are given. The energy splitting corresponds in large measure to a resonance of the electrons with the original atom. Simultaneously one of the two terms is a member of a multiplet of multiplicity  $r - 1$ , the other belongs to a multiplet of multiplicity  $r + 1$ , if the term of the initial system belongs to multiplet of multiplicity  $r$ .

Eqs. (31) and (32) indicate the situation of the multiplets in an atom in a relatively simple manner if the structure (and the relevant eigenfunctions) of the preceding atom (or ion) in the periodic chart is known.

The considerations presented herein should give a general overview of the physical problem and the mathematical methods for solution for atoms with many electrons. Perhaps the scheme given here is still insufficiently general. But, I wish to emphasize, the following results may be considered fully reliable: the division of all spectra into multiplets, splitting by effect of interaction between spin and orbit (Cosine Law and interval proportions!); separation of the various multiplets for the same electron quantum number depending on the resonance interaction; the term system for vanishing multiplet splitting comprises, as in Helium, non combinable subsystems.

### 3. THE RESONANCE EFFECT IN THE THEORY OF SPECTRAL BANDS

In this theory of band spectra, in contrast the old theory, Quantum Mechanics introduces a substantial difference only in so far as oscillation and rotation quantum numbers

take on half integer values[19] (For exact quantum mechanical calculations, see: [20–24]). Although, this result is sufficient to represent a large collection of observed band spectra, there are still others for which it is insufficient.

In many bands a intensity variation is observed such that successive lines of a rotational band alternately appear strong and weak, in some other bands every other line is absent altogether[25, 26]. This empirical fact, as is known, has been the occasion of a representation of these bands in terms of a quarter quantum number. No matter how well such a scheme has succeeded[27], it contradicts the correspondence principle for which a change in the rotation quantum number is given by  $p \rightarrow p \pm 1/2$ . These anomalous bands are observed only for two atom molecules with identical nuclei<sup>7</sup>. Thus, it is reasonable to relate the intensity variation with a resonance between the nuclei<sup>8</sup>, a study of which we undertake below.

The eigenfunction for the whole molecule is comprised of the product of four eigenfunctions, of which the first is for the electron orbital motions, the second for the nuclear oscillations, the third for motion of the center of gravity and the fourth for nuclear rotation. Again, the terms are divided into two systems, one of which constitutes eigenfunctions symmetric in the coordinates, the other changes sign under exchange of nuclei. HUND[31] gives thorough analysis of the first factor of these eigenfunctions which belongs to the electron orbital motion in molecules. From his work we conclude, that, disregarding degeneracies, the electron functions are always either symmetric or antisymmetric in the coordinates of the nuclei. The oscillation eigenfunction is—insofar as it depends on a single variable: the distance from the nucleus—certainly symmetric in the coordinates of the nucleus. Likewise, the eigenfunction for translation of the center of gravity surely is symmetric in the coordinates of the nucleus. As the independent variable from which the eigenfunctions for rotation of the molecule depend, let us chose the angle  $w$  about the axis of the angular momentum  $p$  of the nucleus, that is, the angle that the line connecting the nuclei makes with the node line—here a fixed line in the plane in which the molecule rotates. The angular momentum  $p$  is a whole number, the energy is proportional to  $(p + 1/2)^2$  up to an additive constant. The eigenfunction belonging to a particular value of  $p$ , is then (unnormalized):

$$(33) \quad e^{ipw}.$$

Exchanging the nuclei then implies changing  $w$  by an amount  $\pi$ . Thus, all rotation functions, Eq. (33) for even number  $p$ 's are symmetric and for odd  $p$ 's antisymmetric in the coordinates of the nuclei. Such considerations can also be carried out with SCHRÖDINGER's wave functions, that is with the polar angles  $\vartheta, \phi$ , but, the calculations are a bit more complicated. Finally, we obtain the following term system:

A. Symmetric system	B. Antisymmetric system
Symmetric eigenfunctions and $p = 0, 2, 4, \dots$	Symmetric eigenfunctions and $p = 1, 3, 5, \dots$
Antisymmetric eigenfunctions and $p = 1, 3, 5, \dots$	Antisymmetric eigenfunction and $p = 0, 2, 4, \dots$

<sup>7</sup>MECKE[28] and SLATER[29] have assumed that the intensity variation relates to the symmetry of the nuclei. Both of their considerations differ substantially from ours. SLATER's arguments agree with ours with respect to the correspondence principle.

<sup>8</sup>See also: [30].

This introduction corresponds to the distribution of terms for Helium into the para- and ortho-helium systems.

The band systems that arise from combinations of these terms are distinguished from the usual band systems by the following characteristics. There is for a particular electron transition only either a null branch ( $p \rightarrow p$ ), or a  $P$ - and  $Q$ -branch ( $p \rightarrow p \pm 1$ ). The first of these is the case when the electron transition is between terms of the same type (i.e., symmetric $\leftrightarrow$ symmetric, or antisymmetric $\leftrightarrow$ antisymmetric), the second occurs between dissimilar types (symmetric $\leftrightarrow$ antisymmetric).

Hereafter there are various cases to distinguish among. To begin, let us take it, that the nuclei are spherically symmetric, i.e., beyond the degrees of freedom considered here, there are no others, such as, say, an eigenrotation. Then the above two systems do not combine in any way, so that one must consider, in analogy to electron and light quanta statistics, that only one of the two term systems occurs in nature. In the first instance, one would tend to consider the antisymmetric system  $B$  in order to complete the analogy with electron statistics. One cannot be certain, however, and in the following considerations it will turn out not to matter which system is selected. If only one of the two systems is available, then there will arise rotation bands by cause of combinations such that every other line is absent. If, for example, the antisymmetric system gives the final solution, then there is for a transition from symmetric to symmetric electron functions only a null branch for the transitions:  $5 \rightarrow 5$ ,  $3 \rightarrow 3$  and  $1 \rightarrow 1$ . Similarities are seen in the bands for helium (atomic weight 4) and oxygen (atomic weight 16), and these nuclei seem particularly stable, closed structures and have no eigenrotation. The exclusion of one of the two solutions, that is, the reduction of the statistical weight by a factor of 2, plays a role, as is well known, in the derivation of statistical chemical constants for diatomic molecules.

As a further example, let us consider, that the two nuclei of the molecule of interest have an eigenrotation, similar to two electrons, and of the size  $s = 1/2$ , and that the system is antisymmetric. For this case the term system given above given is fully analogous to that of the helium atom<sup>9</sup>. Both systems, i.e., the para- and ortho-system arise; and, they exhibit very weak interactions. In system  $A$  the nuclear spins are antiparallel, in  $B$ , parallel. All terms in system  $B$  have, therefore, statistical weight 3, while those of  $A$ , have statistical weight 1. In a particular band—the null branch, say, which belongs to electron [orbital] transitions symmetric $\leftrightarrow$ symmetric—all lines occur; the lines for ...,  $5 \rightarrow 5$ ,  $3 \rightarrow 3$ , and  $1 \rightarrow 1$  are three times as intensive (all other factors, temperature say, that affect intensity being equal), as the lines ...,  $4 \rightarrow 4$ ,  $2 \rightarrow 2$ , and  $0 \rightarrow 0$ . If the angular momentum is larger than  $1/2$ , then the relationship between the statistical weights approaches unity.

Examples of such an intensity variation have been seen to appear in  $N_2^+$ , and maybe also for  $H_2$ [32]. It is satisfying, that the nitrogen nucleus (3 Helium nuclei + 2 hydrogen nuclei + 1 electron) and the hydrogen nucleus all possess eigenrotation.

A rather different sort of intensity variation arises if the nuclei have no further degrees of freedom, but still various isotopes, that is, various types of nuclei with the same total charge. In this case all molecules, within which the nuclei are distinguishable, would have the usual spectra of emissions, whereas all other molecules should have the type of band structure discussed above, for which every other line is absent. The total spectrum then would be a mixture of these two variants. Such, however, seems experimentally unobserved.

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<sup>9</sup>I thank F. HUND for bringing this to my attention.

The considerations described herein as presented in §2.2 could be extended easily to molecules with identical nuclei. Such a study, because of the diversity of experimental results, is initially only of theoretical interest. But as there is for the molecules considered §2.2 rather more comprehensible substitution groups with concrete meaning, a special example will be worked out here.

We consider a tricotomic molecule, consisting of three identical atoms, arranged as an isosceles triangle (See Fig. 1).

The eigenfunctions for translation and oscillations are always symmetric in the nuclei; we consider first only the rotation in the plane of the triangle. Let the momentum be  $p$  and the eigenfunction belonging to it is again  $e^{ip\omega}$ , if  $\omega$ , as above, denotes the angle about the axis of  $p$ . There must be now, according to §2.2, three non combinable term systems:  $\Gamma_1, \Gamma_\varepsilon, \Gamma_{\varepsilon^2}$  ( $\varepsilon = e^{2\pi i/3}$ ) which have the characteristic, that the eigenfunctions are multiplied with 1, possibly  $\varepsilon^2$ , if these eigenfunctions are subjected to the substitution  $S(1\ 2\ 3)$ .

The cyclical substitution  $(1\ 2\ 3)$  signifies now a rotation of the molecules of  $2\pi/3$ , that is an increase in  $\omega$  of  $2\pi/3$ . Moreover, there are states of the molecule for which the sequence of the nuclei on the circle in Fig. 1 is not  $1\ 2\ 3$ , but  $1\ 3\ 2$ . The substitution  $(1\ 3\ 2)$  here signifies a rotation of  $4\pi/3$ . In addition the band terms in this permutation can be divided into three systems  $\Gamma_1, \Gamma_\varepsilon, \Gamma_{\varepsilon^2}$  from which in full analogy to Table 1 (p. 8):

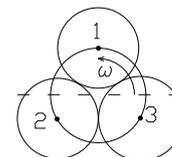


Fig. 1

$\Gamma_1$	$\Gamma_\varepsilon$	$\Gamma_{\varepsilon^2}$
Order 1 2 3 $p \equiv 0 \pmod{3}$	Order 1 2 3 $p \equiv 1 \pmod{3}$	Order 1 2 3 $p \equiv 2 \pmod{3}$
Order 1 3 2 $p \equiv 0 \pmod{3}$	Order 1 3 2 $p \equiv 2 \pmod{3}$	Order 1 3 2 $p \equiv 1 \pmod{3}$

Table 6

As in Table 2 (p. 8), each term of  $\Gamma_\varepsilon$  has the same energy, as do the terms in  $\Gamma_{\varepsilon^2}$ ; the energy<sup>10</sup> is proportional to  $p^2$ . If the nuclei as a system of points is symmetric, and only the symmetric (or antisymmetric) solutions remain, then only one term in the system  $\Gamma_1$  remains and in the rotation spectrum only every third line appears, the other two are always absent. For other degrees of freedom of the nuclei corresponding intensity variations arise.

From these considerations nothing substantial is changed, if general rotations of the triangle molecule are taken into account. The angle  $\omega$  remains a cylindrical coordinate and  $p$  remains constant. Another quantum rotation number is added, representing the whole angular momentum, the corresponding bands overlay those considered above without distortion.

The above calculations always concerned a resonance of the nuclei, this is justified for the sake of the analogy to the considerations of §2.2. But one should not imagine that resonance implies complex oscillatory phenomena, the nuclei follow identical orbits (with different phases) and change places with a distinct frequency. They do so simply by cause of rotation and the resonance frequency is just the rotation rate. These considerations provide an explanation for a paradox, that can be problematic for the understanding of term distributions. At first it seems remarkable, that also (for pointwise symmetric nuclei) within the antisymmetric system, so that no equivalent orbits can arise, that simple rotations

<sup>10</sup>Compare with ref. [22].

are possible, for which obviously the nuclei follow “equivalent” orbits. The solution to this puzzle is to be found in the fact, that the expression “equivalent orbits” is defined above only for the marginal case of vanishing interaction. If the nucleus is bound by an exterior force onto a particular point and then released adiabatically, the rotation with antisymmetric eigenfunctions certainly does not go over to “equivalent orbits” of both nuclei.—The selection here of antisymmetric systems on the basis of a prohibition for equivalent orbits cannot be effortlessly replaced.

Empirical proof of these ideas thus far has been found only for dichotomic molecules. One may hope that an examination of this empirical material will lead to important conclusions from the point of view of nuclear resonance.

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