

# Stability of Polyatomic Molecules in Degenerate Electronic States

## II—Spin Degeneracy

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### INTRODUCTION

In a previous paper (Jahn and Teller 1937) the following theorem was established: A configuration of a polyatomic molecule for an electronic state having orbital degeneracy cannot be stable with respect to all displacements of the nuclei unless in the original configuration the nuclei all lie on a straight line. The proof given of this theorem took no account of the electronic spin, and in the present paper the justification of this is investigated. An extension of the theorem to cover additional degeneracy arising from the spin is established, which shows that if the total electronic state of orbital and spin motion is degenerate, then a non-linear configuration of the molecule will be unstable unless the degeneracy is the special twofold one (discussed by Kramers 1930) which can occur only when the molecule contains an odd number of electrons. The additional instability caused by the spin degeneracy alone, however, is shown to be very small and its effect for all practical purposes negligible. The possibility of spin forces stabilizing a non-linear configuration which is unstable owing to orbital degeneracy is also investigated, and it is shown that this is not possible except perhaps for molecules containing heavy atoms for which the spin forces are large. Thus whilst a symmetrical nuclear configuration in a degenerate orbital state might under exceptional circumstances be rendered stable by spin forces, it is not possible for the spin-orbit interaction to cause instability of an orbitally stable state.

### 1—GENERAL THEOREM FOR MOLECULES WITH SPIN

Just as before we must see how the symmetry of the molecular framework determines whether the energy of a degenerate electronic state with spin depends linearly upon nuclear displacements. This is again determined by

the existence of non-vanishing perturbation matrix elements which are linear in the nuclear displacements. These matrix elements are integrals involving the electronic wave functions with spin and the nuclear displacements, and we deduce as before from their transformation properties whether for a given molecular symmetry they can be different from zero.

We will see that if the molecule contains an even number of electrons then the transformation properties of the integrals involving the electronic wave functions with spin are identical with those of the corresponding case involving only orbital wave functions. Thus the previous theorem proven for orbital degeneracy holds also for spin degeneracy if there is an even number of electrons. For an odd number of electrons with spin, however, the transformation properties of the integrals differ owing to the two-valuedness of the spin wave functions. A special investigation is needed here and shows that in the case of an odd number of electrons with spin electronic states with twofold degeneracy can exist which are stable with respect to all nuclear displacements. This is in accordance with the results of Kramers and Wigner, who have shown that such twofold degeneracy cannot be split by any electrical forces. For electronic states which are more than twofold degenerate, however, we show that there always exist non-vanishing matrix elements which are linear in at least one set of non-totally symmetrical nuclear displacements, unless all the nuclei in the molecule lie on a straight line. Thus even if the degeneracy arises from the spin a non-linear polyatomic molecule cannot be stable in a degenerate electronic state, excepting this degeneracy be the special twofold one of Kramers and Wigner.

## 2—MATHEMATICAL FORMULATION AND GROUP-THEORETICAL CONSIDERATIONS

The linear matrix elements whose transformation properties we have to investigate are integrals of the form

$$\int \phi_{\rho}^* V_r \phi_{\sigma} d\tau,$$

where the  $\phi_{\rho}$ ,  $\phi_{\sigma}$  are electronic wave functions with spin and the  $V_r$  are functions of the electronic space co-ordinates alone. (A star is used in the following throughout to denote the conjugate complex.) The indices  $\rho$ ,  $\sigma$  refer to independent wave functions of the degenerate energy level and we denote as before the representation of the molecular symmetry group subtended by these functions by  $\Phi$ . The index  $r$  refers to the independent normal nuclear displacements and we denote the representation subtended



by the  $V_r$  by  $V$ . In the case of orbital degeneracy the wave functions  $\phi_\rho$  could be chosen real and the integrals transformed according to the representation  $V[\Phi^2]$ , where  $[\Phi^2]$  denotes the representation of the symmetrical product of  $\Phi$  with itself. It is our purpose to show that in the case of an even number of electrons with spin the integrals still transform according to the representation  $V[\Phi^2]$ , whilst in the case of an odd number of electrons with spin they transform according to the representation  $V\{\Phi^2\}$ , where  $\{\Phi^2\}$  denotes the representation of the antisymmetrical product of  $\Phi$  with itself.

To establish this we make use of the properties of the symmetry operation of time reversal which have been investigated by Wigner (1932). He showed that for electrons with spin this operation has different properties according as the number of electrons in the system is even or odd, and it is this fact which gives rise to the different behaviour of the integrals in the two cases. We will further make use of the results of the fundamental work of Frobenius and Schur (1906) on the real representations of finite groups. They investigate the properties of representations which leave a certain form  $G$  invariant, and we will show that this form  $G$  has the same properties as the matrix ( $K$ ) representing the operation of time reversal. This enables us to write down almost at once the relations we need from the results of Frobenius and Schur.

Wigner shows that the operation  $K$  of reversing the time is a non-linear operator for the wave functions, acting as follows upon a linear combination of any two wave functions  $\phi$  and  $\psi$ :

$$K(a\phi + b\psi) = a^*K\phi + b^*K\psi.$$

He further shows that the operator  $K$  commutes with the operator  $R$  of any spatial rotation or reflexion (i.e. symmetry operation)

$$KR = RK.$$

Using any complete set of independent wave functions of an energy level the operator  $K$  can be represented by a matrix which we will denote by ( $K$ ). Owing to the non-linearity of  $K$  the operator  $K$  and its matrix ( $K$ ) do not obey the same commuting rules. Thus if

$$R\phi_\rho = \sum_\sigma R_{\sigma\rho} \phi_\sigma$$

and

$$K\phi_\rho = \sum_\sigma (K)_{\sigma\rho} \phi_\sigma,$$

we have

$$KR\phi_\rho = \sum_\sigma R_{\sigma\rho}^* K\phi_\sigma = \sum_\sigma \sum_\tau R_{\sigma\rho}^* (K)_{\tau\sigma} \phi_\tau$$

$$RK\phi_\rho = R \sum_\sigma (K)_{\sigma\rho} \phi_\sigma = \sum_\sigma \sum_\tau (K)_{\sigma\rho} R_{\tau\sigma} \phi_\tau,$$

from which we deduce, since  $KR = RK$

$$\sum_{\sigma} R_{\sigma\rho}^* (K)_{\tau\sigma} = \sum_{\sigma} (K)_{\sigma\rho} R_{\tau\sigma}$$

or

$$\{(K) R^*\}_{\tau\rho} = \{R(K)\}_{\tau\rho},$$

i.e.

$$(K) R^* = R(K).$$

(There is no need to distinguish between the operator  $R$  and its corresponding matrix since  $R$  is a linear operator.)

Now Wigner shows that if the number of electrons is even then

$$(a) \quad K^2 = +1,$$

whilst if the number of electrons is odd

$$(b) \quad K^2 = -1.$$

The relation

$$(K)R^* = R(K)$$

gives

$$(K)^2 R^*(K) = (K)R(K)^2,$$

from which we deduce in both cases

$$R^*(K) = (K) R$$

or (c)

$$R'(K) R = (K),$$

where  $R'$  denotes the transposed matrix and we have  $R^*R' = E$ , since  $R$  is unitary.

The relations (a), (b) and (c) are identical with those postulated by Frobenius and Schur for their invariant form  $G$ , and we can hence make use of their results directly by identifying our  $(K)$  with their  $G$ . They show that in case (a) i.e. when  $(K)^2 = E$  the independent vectors subtending the representation (or the wave functions of the energy level) can be so chosen that  $(K)$  is identical with the unit matrix  $E$  and the matrices  $R$  (and consequently the wave functions) can at the same time be chosen all real. Thus in the case of an even number of electrons with spin the results are the same as when there is no spin present and the linear matrix elements

$$\int \phi_{\rho}^* \phi_{\sigma} V_r d\tau = \int \phi_{\rho} \phi_{\sigma}^* V_r d\tau = \frac{1}{2} \int (\phi_{\rho} \phi_{\sigma} + \phi_{\sigma} \phi_{\rho}) V_r d\tau$$

subtend the representation  $V[\Phi^2]$  as described in the previous paper. In case (b), where  $(K)^2 = -E$ , Frobenius and Schur show that the independent vectors subtending the representation  $\Phi$ , which they show must now have an even number of dimensions (say  $2n$ ), can be chosen so that:



First, ( $K$ ) is the matrix

$$\begin{array}{|c|c|} \hline O & -E \\ \hline E & O \\ \hline \end{array},$$

where  $E$  and  $O$  denote the unit and zero  $n$ -dimensional matrices respectively. We may express this by putting

$$K\phi_\rho = \tilde{\rho}\phi_{-\rho},$$

where  $\tilde{\rho} = +1$  if  $\rho$  is positive and  $= -1$  if  $\rho$  is negative. (Positive values of  $\rho$  number the first  $n$  rows and columns of the representation, negative values the last  $n$  rows and columns.)

And secondly, the matrices  $R_{\sigma\rho}$  for the rotations or reflexions  $R$  of the group

$$\phi'_\rho = \sum_\sigma R_{\sigma\rho} \phi_\sigma$$

can be so chosen that

$$R = \begin{array}{|c|c|} \hline A & B \\ \hline -B^* & A^* \\ \hline \end{array},$$

or

$$R_{\sigma\rho}^* = \tilde{\sigma}\tilde{\rho}R_{-\sigma, -\rho}.$$

Now from Wigner's results we deduce that since the  $V_r$  in his terminology are real (they do not involve the spins) we have the relation

$$(\phi_\rho, V_r \phi_\sigma) = (K\phi_\rho, KV_r \phi_\sigma)^*,$$

i.e.

$$\int \phi_\rho^* V_r \phi_\sigma d\tau = \int (K\phi_\sigma)^* V_r (K\phi_\rho) d\tau.$$

But from the above relations we find

$$\int (K\phi_\sigma)^* V_r (K\phi_\rho) d\tau = \int \tilde{\sigma}\phi_{-\sigma}^* V_r \tilde{\rho}\phi_{-\rho} d\tau.$$

Thus the integrals satisfy the relation

$$\int \phi_\rho^* \phi_\sigma V_r d\tau = \tilde{\rho}\tilde{\sigma} \int \phi_{-\sigma}^* \phi_{-\rho} V_r d\tau.$$

This relation can be written in the form

$$\int \phi_{-\rho}^* \phi_{\sigma} V_r d\tau = -\tilde{\rho} \tilde{\sigma} \int \phi_{-\sigma}^* \phi_{\rho} V_r d\tau$$

or

$$-\tilde{\rho} \int \phi_{-\rho}^* \phi_{\sigma} V_r d\tau = \tilde{\sigma} \int \phi_{-\sigma}^* \phi_{\rho} V_r d\tau.$$

Introducing the abbreviation

$$\psi_{\rho} = -\tilde{\rho} \phi_{-\rho}^*$$

we then have

$$\int \psi_{\rho} \phi_{\sigma} V_r d\tau = - \int \psi_{\sigma} \phi_{\rho} V_r d\tau = \frac{1}{2} \int (\psi_{\rho} \phi_{\sigma} - \psi_{\sigma} \phi_{\rho}) V_r d\tau.$$

Hence if we can show that the  $\psi_{\rho}$  transform according to the same representation  $\Phi$  as the  $\phi_{\sigma}$  we can conclude that the integrals transform according to the representation  $V\{\Phi^2\}$ .

Now from the transformation formulae

$$\phi'_{\rho} = \sum_{\sigma} R_{\sigma\rho} \phi_{\sigma}$$

follows, since

$$R_{\sigma\rho}^* = \tilde{\sigma} \tilde{\rho} R_{-\sigma, -\rho},$$

$$(\phi_{\rho}^*)' = \sum_{\sigma} R_{\sigma\rho}^* \phi_{\sigma}^*$$

$$= \tilde{\rho} \sum_{\sigma} \tilde{\sigma} R_{-\sigma, -\rho} \phi_{\sigma}^*$$

$$= \tilde{\rho} \sum_{\sigma} (-\tilde{\sigma}) R_{\sigma, -\rho} \phi_{-\sigma}^*,$$

so that

$$(\phi_{-\rho}^*)' = -\tilde{\rho} \sum_{\sigma} (-\tilde{\sigma}) R_{\sigma\rho} \phi_{-\sigma}^*$$

or

$$(-\tilde{\rho} \phi_{-\rho}^*)' = \sum_{\sigma} R_{\sigma\rho} (-\tilde{\sigma} \phi_{-\sigma}^*),$$

i.e.

$$\psi'_{\rho} = \sum_{\sigma} R_{\sigma\rho} \psi_{\sigma},$$

so that the  $\psi_{\rho} = -\tilde{\rho} \phi_{-\rho}^*$  do transform according to the representation  $\Phi$ . One verifies then easily that

$$\psi'_{\rho} \phi'_{\sigma} - \psi'_{\sigma} \phi'_{\rho} = \sum_{\alpha} \sum_{\beta} \frac{1}{2} (R_{\rho\alpha} R_{\sigma\beta} - R_{\rho\beta} R_{\sigma\alpha}) (\psi_{\rho} \phi_{\sigma} - \psi_{\sigma} \phi_{\rho}),$$

so that the spur of the representation subtended by the products

$$\psi_\rho \phi_\sigma - \psi_\sigma \phi_\rho$$

is given by

$$\begin{aligned} \sum_\alpha \sum_\beta \frac{1}{2} (R_{\alpha\alpha} R_{\beta\beta} - R_{\alpha\beta} R_{\beta\alpha}) &= \frac{1}{2} \left( \sum_\alpha R_{\alpha\alpha} \sum_\beta R_{\beta\beta} - \sum_\alpha R_{\alpha\alpha}^2 \right) \\ &= \frac{1}{2} \{ \chi^2(R) - \chi(R^2) \}. \end{aligned}$$

This is the spur of the antisymmetrical product representation  $\{\Phi^2\}$ .

We have thus shown that the integrals  $\int \psi_\rho \phi_\sigma V_r d\tau$  and consequently the integrals  $\int \phi_\rho^* \phi_\sigma V_r d\tau$  transform according to the representation  $V\{\Phi^2\}$ , for an odd number of electrons with spin.

### 3—PROOF OF GENERAL THEOREM FOR MOLECULES WITH SPIN

We have seen that if the molecule contains an even number of electrons with spin the results obtained in Part I apply without modification. Thus we need consider only molecules containing an odd number of electrons. For these the electronic wave functions with spin transform according to two-valued irreducible representations of the group of symmetry and for the purpose of establishing our theorem we list below in Table I the two-valued irreducible representations of all the point groups. The two-valued

TABLE I—TWO-VALUED IRREDUCIBLE REPRESENTATIONS OF THE POINT GROUPS

$D_\infty^r$	$E$	$R$	$2C(\phi)$	$C_2$
$C_{\infty v}^r$	$E$	$R$	$2C(\phi)$	$\sigma_v$
$E'_{\frac{1}{2}}$	2	-2	$2 \cos \frac{\phi}{2}$	0
$E'_{\frac{3}{2}}$	2	-2	$2 \cos \frac{3\phi}{2}$	0
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
$E'_{\frac{2l+1}{2}}$	2	-2	$2 \cos \frac{2l+1}{2} \phi$	0
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

$$(0 < \phi < 4\pi)$$



TABLE I—(continued)

$D'_{2p+1}$	$E$	$R$	$2C$	...	$2C^p$	$2C^{p+1}$	...	$2C^{2p}$	$2pC_2$	$2pC'_2$
$C'_{2p+1, v}$	$E$	$R$	$2C$	...	$2C^p$	$2C^{p+1}$	...	$2C^{2p}$	$2p\sigma_v$	$2p\sigma'_v$
$B'_1$	1	-1	-1	...	$(-1)^p$	1	...	$(-1)^{p+1}$	$i$	$-i$
$B'_2$	1	-1	-1	...	$(-1)^p$	1	...	$(-1)^{p+1}$	$-i$	$i$
$E'_1$	2	-2	$-2\cos\omega$	...	$(-1)^p 2\cos p\omega$	$2\cos\omega$	...	$(-1)^{p+1} 2\cos p\omega$	0	0
$E'_2$	2	-2	$-2\cos 2\omega$	...	$(-1)^p 2\cos 2p\omega$	$2\cos 2\omega$	...	$(-1)^{p+1} 2\cos 2p\omega$	0	0
$\vdots$	$\vdots$	$\vdots$	$\vdots$		$\vdots$	$\vdots$	...	$\vdots$	$\vdots$	$\vdots$
$E'_p$	2	-2	$-2\cos p\omega$	...	$(-1)^p 2\cos p^2\omega$	$2\cos p\omega$	...	$(-1)^{p+1} 2\cos p^2\omega$	0	0

$$\omega = \frac{2\pi}{2p+1}$$

$B'_1$  and  $B'_2$  are conjugate complex, taken together they give

$E'_0$	2	-2	-2	...	$2(-1)^p$	2	...	$2(-1)^{p+1}$	0	0
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$D'_{2p}$	$E$	$R$	$2C$	$2C^2$	...	$C^p$	$2C^{p+1}$	...	$pC_2$	$pC'_2$
$C'_{2p, v}$	$E$	$R$	$2C$	$2C^2$	...	$C^p$	$2C^{p+1}$	...	$p\sigma_v$	$p\sigma'_v$
$S'_{2p, v}$	$E$	$R$	$2S$	$2S^2$	...	$S^p$	$2S^{p+1}$	...	$p\sigma_v$	$pC_2$
$E'_{\frac{1}{2}}$	2	-2	$2\cos\frac{\omega}{2}$	$2\cos\omega$	...	0	$2\cos\frac{\omega}{2}$	...	0	0
$E'_{\frac{3}{2}}$	2	-2	$2\cos\frac{3\omega}{2}$	$2\cos 3\omega$	...	0	$-2\cos\frac{3\omega}{2}$	...	0	0
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$		$\vdots$	$\vdots$		$\vdots$	$\vdots$
$E'_{\frac{2p-1}{2}}$	2	-2	$2\cos\frac{2p-1}{2}\omega$	$2\cos(2p-1)\omega$	...	0	$-2\cos\frac{2p-1}{2}\omega$	...	0	0

$$\omega = \frac{2\pi}{2p}$$

$T^r$	$E$	$R$	$4C_3$	$4C_3^2$	$4C_3^4$	$4C_3^5$	$6C_2$
$E'_1$	2	-2	1	-1	-1	1	0
$E'_2$	2	-2	$\epsilon^*$	$-\epsilon$	$-\epsilon^*$	$\epsilon$	0
$E'_3$	2	-2	$\epsilon$	$-\epsilon^*$	$-\epsilon$	$\epsilon^*$	0

$$\epsilon = e^{\frac{2\pi i}{3}}$$



TABLE I—(continued)

 $E'_2$  and  $E'_3$  are conjugate complex, taken together they give

$G'$	4	-4	-1	+1	+1	-1	0
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$O^r$	$E$	$R$	$8C_3$	$8C_3^2$	$6C_4$	$12C_2$	$6C_4$	$6C_4^3$
$T_d^r$	$E$	$R$	$8C_3$	$8C_3^2$	$6S_4$	$12\sigma$	$6S_4$	$6S_4^3$
$E'_1$	2	-2	1	-1	0	0	$\sqrt{2}$	$-\sqrt{2}$
$E'_2$	2	-2	1	-1	0	0	$-\sqrt{2}$	$\sqrt{2}$
$G'$	4	-4	-1	1	0	0	0	0

$I^r$	$E$	$R$	$12C_5$	$12C_5^2$	$12C_5^3$	$12C_5^4$	$20C_3$	$20C_3^2$	$30C_2$
$E'_1$	2	-2	$\frac{1-\sqrt{5}}{2}$	$\frac{-1-\sqrt{5}}{2}$	$\frac{1+\sqrt{5}}{2}$	$\frac{-1+\sqrt{5}}{2}$	1	-1	0
$E'_2$	2	-2	$\frac{1+\sqrt{5}}{2}$	$\frac{-1+\sqrt{5}}{2}$	$\frac{1-\sqrt{5}}{2}$	$\frac{-1-\sqrt{5}}{2}$	1	-1	0
$G'$	4	-4	1	-1	1	-1	-1	1	0
$I'$	6	-6	-1	1	-1	1	0	0	0

irreducible representations of the crystallographic groups  $D_2$ ,  $D_4$ ,  $D_6$  and  $O$  have been tabulated by Bethe (1929), and we have followed his method in calculating the characters of the representations of the general groups  $D_{2p}$ ,  $D_{2p+1}$ . The characters of the two-valued irreducible representations of the icosahedral group  $I$  (and of the groups  $T$  and  $O$ ) have been given already by Frobenius (1899). For completeness we include also the axial groups  $D_\infty$ ,  $C_{\infty v}$ , but following Tisza (1933) and Bethe we do not include the groups which are the direct product of the inversion or a reflexion with a group already listed, since the representations of the new group can be written down at once. In accordance with Bethe's method we introduce a new symmetry  $R$  commuting with all the symmetry elements and which denotes a complete rotation through  $2\pi$  about any axis of the molecule. This element is added to the original symmetry group to form the new "double" group which we designate by an index  $r$  added to the symbol of the simple group. It is to be noted that the double group is not simply the direct product of  $R$  with the original group since the relations between the elements of the latter are also altered (e.g. in  $D_{2p}^r$  we have  $C_2^2 = R$ , whilst in  $D_{2p}$   $C_2^2 = E$ ,  $C_2$

denoting a rotation through  $\pi$  about one of the twofold axes). The two-valued representations of the symmetry group are then one-valued representations of the double symmetry group and their characters can be calculated in the usual way.

In order to establish the theorem we have to investigate whether a molecule of a given symmetry possesses at least one set of non-totally symmetrical normal displacements transforming according to a representation  $V$  such that  $V\{\Phi^2\}$  contains the identical representation,  $\Phi$  being any two-valued representation of the corresponding group of symmetry.  $V$  is excluded from being the identical representation, because, as before, the molecular configuration is always taken to be stable with respect to all totally symmetrical displacements. Now it is easy to show (see below) that the antisymmetrical product of any two-dimensional representation is the unit representation, so that  $V\{\Phi^2\}$  can never contain the identical representation for any two-dimensional representation when  $V$  itself is not the unit representation. Thus we need list the antisymmetrical product of only those two-valued representations which are more than two-dimensional and these are listed in Table II.

TABLE II

Group	Antisymmetrical product of more than twofold degenerate two-valued representations
$T$	$\{G'^2\} = A + E + F$
$T_h$	$\{G'_g\} = \{G'_u\} = A_g + E_g + F_g$
$T_d$ and $O$	$\{G'^2\} = A_1 + E + F_2$
$O_h$	$\{G'_g\} = \{G'_u\} = A_{1g} + E_g + F_{2g}$
$I$	$\{G'^2\} = A + H$
	$\{I'^2\} = A + G + 2H$
$I_h$	$\{G'_g\} = \{G'_u\} = A_g + H_g$
	$\{I'_g\} = \{I'_u\} = A_g + G_g + 2H_g$

The above mentioned property of the two-dimensional representations is established as follows. The character of any group element  $R$  in the antisymmetrical product is given by

$$\{\chi^2\}(R) = \frac{1}{2}(\chi^2(R) - \chi(R^2)),$$

and when  $R$  is a two-dimensional matrix

$$R = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix},$$



then

$$R^2 = \begin{pmatrix} a_{11}^2 + a_{12}a_{21} & (a_{11} + a_{22})a_{12} \\ (a_{11} + a_{22})a_{21} & a_{12}a_{21} + a_{22}^2 \end{pmatrix}.$$

Thus

$$\chi(R) = a_{11} + a_{22},$$

$$\chi^2(R) = a_{11}^2 + a_{22}^2 + 2a_{11}a_{22},$$

$$\chi(R^2) = a_{11}^2 + a_{22}^2 + 2a_{12}a_{21}.$$

Consequently

$$\{\chi^2\}(R) = a_{11}a_{22} - a_{12}a_{21} = \text{Det}(R).$$

Now the determinant of the two-dimensional matrices is always +1, since they can be expressed as the product of the matrix of a pure rotation with that of the inversion, the determinant of both of which is +1, the inversion being the matrix

$$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Thus a twofold degeneracy cannot produce instability for a molecule containing an odd number of electrons with spin.

Making use of the list of normal displacements of all possible symmetrical molecules given in Table I of Part I it is easy to verify that the general theorem is true as formulated above. Thus, for example, the antisymmetrical product of the more than twofold degenerate two-valued representations  $G'$ ,  $I'$  of the group  $I$  always contain the representation  $H$  and molecules of the symmetry  $I$  always possess at least one set of normal displacements transforming according to  $H$ . Hence  $H\{G'^2\}$ ,  $H\{I'^2\}$  always contain the identical representation, and the symmetrical molecular configuration must be unstable in any more than twofold degenerate electronic state, if the molecule contains an odd number of electrons with spin.

#### 4—MAGNITUDE OF THE SPIN EFFECTS\*

In considering quantitatively the effects arising from the spin we shall have to compare the order of magnitude of the changes produced by the nuclear displacements in the electrostatic interaction energy and in the spin-orbit interaction (multiplett splitting) respectively.

Consider first a non-degenerate orbital state in which a certain symmetrical nuclear configuration is stable when only the electrostatic interaction is con-

\* The considerations of this paragraph are due to Dr E. Teller.

sidered. The electrostatic energy in its dependence upon any one normal coordinate  $d$  may then be approximated by a parabola:

$$\epsilon = \alpha d^2.$$

The constant  $\alpha$  may be estimated from the binding energy  $\epsilon_0$ : if  $r$  denotes a distance of the order of the equilibrium nuclear distances we will have

$$\epsilon_0 = \alpha r^2 \quad \text{or} \quad \alpha = \frac{\epsilon_0}{r^2}.$$

Suppose now that this non-degenerate orbital state has spin degeneracy. For the symmetrical equilibrium configuration the spin-orbit interaction will produce a splitting into the various levels of a multiplett. Since the orbital state is non-degenerate and possesses therefore no magnetic moment this multiplett splitting will be small, of the order of

$$\epsilon_1 = \frac{I^2}{\Delta E},$$

where  $I$  denotes the spin-orbit interaction operator and  $\Delta E$  the energy difference between orbital states for which it has non-vanishing matrix elements. Because of the symmetry the lowest level of this multiplett may still be degenerate. Suppose this degeneracy is more than twofold: then according to our theorem for small nuclear displacements there will be a linear splitting of the ground state. The question is whether this dependence of the spin-orbit interaction upon nuclear displacements can cause any appreciable instability of the original equilibrium configuration. To judge of this we must compare its order of magnitude with that of the electrostatic perturbation described by the parabola above. The spin-orbit interaction in its dependence upon the normal co-ordinate  $d$  may be approximated by the linear relation

$$\epsilon = \beta d.$$

The constant  $\beta$  may again be estimated by considering a distance  $r$  of the order of the atomic equilibrium distances. The process of bringing the atoms together will not change the spin-orbit interaction by an amount greater than the total multiplett splitting and we may therefore put

$$\epsilon_1 = \beta r \quad \text{or} \quad \beta = \frac{\epsilon_1}{r}.$$

We find therefore for the electrostatic perturbation

$$\epsilon = \frac{\epsilon_0}{r^2} d^2$$



and for the spin-orbit perturbation

$$\epsilon = \frac{\epsilon_1}{r} d,$$

and we see that whilst for small distances  $d$  the latter perturbation is greater than the first, at large distances the reverse is the case. Thus each of the energy levels into which the multiplett levels are split may be approximated for large distances by parabolas which will have their minimum slightly displaced from the original minimum (see fig. 1). By equating the two

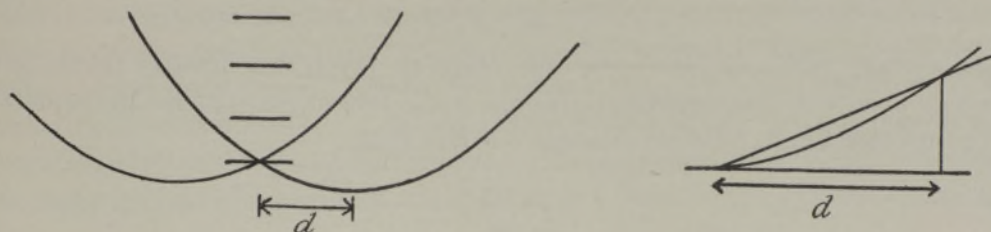


FIG. 1

perturbation energies we find a distance  $d$  which will give a rough estimate of the change in the equilibrium distances which can be caused by the spin-orbit interaction. We find

$$d = \frac{\epsilon_1}{\epsilon_0} r,$$

which is a very small fraction of the equilibrium distance. If we take the binding energy  $\epsilon_0$  as  $1 \text{ V} = 8000 \text{ cm.}^{-1}$  and the multiplett splitting  $\epsilon_1$  as  $1 \text{ cm.}^{-1}$ , the distance  $d$  will have the order of  $10^{-4} \text{ \AA}$ . This shows that the change of configuration involved is in general so small that it will be covered even by the zero-point amplitude of the nuclear vibrations. Thus for all practical purposes the spin in this case produces no instability.

There is the further possibility that although the lowest state of the multiplett is stable and does not split yet its energy level for small nuclear displacements should intersect the perturbed energy level of a higher state of the multiplett thereby becoming unstable. It follows however at once from the above considerations that such an intersection of the parabolas from different levels of the multiplett is impossible. Thus in no case can the spin forces produce instability of an orbitally stable non-degenerate state.

Let us consider now a degenerate orbital state and ask whether a nuclear configuration which is unstable when the orbital motion alone is considered can be rendered stable when the spin is introduced. The multiplett splitting is here greater, being proportional to the spin-orbit interaction operator  $I$ .

Suppose now that the lowest state of the multiplett is stable for the symmetrical configuration in question, being either non-degenerate or only two-fold degenerate. Because of the orbital instability the energy of some of the higher states of the multiplett will show a linear dependence upon the nuclear displacement  $d$ :

$$\epsilon = \beta d.$$

For large displacements  $r$  this perturbation will be of the order of the binding energy  $\epsilon_0$  (energy between different multipletts):

$$\epsilon_0 = \beta r$$

and we may easily estimate the distance  $d$  at which this linearly perturbed energy level will intersect the parabola of the lowest state of the multiplett. We find (see fig. 2) that this distance is less than

$$d = \frac{\epsilon_1}{\epsilon_0} r,$$

and is thus again a small fraction of the equilibrium distances (we may take  $\epsilon_1 = 100 \text{ cm.}^{-1}$ ), being, however, greater than the corresponding distance discussed for the non-degenerate state. Thus a symmetrical nuclear configuration might under exceptional circumstances be rendered stable in a degenerate orbital electronic state, if the spin-orbit interaction is large of the order of the binding energy, but it is not possible for the spin-orbit interaction to cause instability of an orbitally stable state.

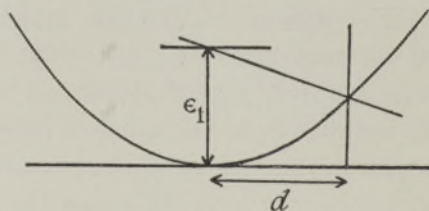


FIG. 2

## 5—CONCLUSION

In conclusion, let us discuss briefly the applicability of our theorem to crystals. Bethe (1929) has discussed the splitting of the degenerate states of an atom when placed in the symmetrical field of a crystal and had discussed also the further splitting which occurs when the crystal symmetry is reduced. The question could also be discussed by treating the whole crystal as a single molecule and applying our theorem. The question then arises why the



orbitally degenerate inner shells which occur in the paramagnetic crystals, e.g. in the rare earth ionic salts, do not cause instability of the crystal lattice. Two reasons may be given for this. First, we may show by quite similar reasoning to that used above that the linear splitting of the levels of the inner shells is so much smaller than the binding energy of the crystal which arises from the electrostatic interaction of the outer electrons, that the change of equilibrium configuration involved is negligibly small. Secondly, we should note that this linear splitting of the inner levels has the same order of magnitude as the perturbation arising from the exchange of these inner electrons between different atoms of the crystal, i.e. from the possibility of the electrons being propagated through the crystal. These translational effects have been treated neither by Bethe nor by us in our theorem. Their treatment would involve a consideration of the whole space group of the crystal, whereas Bethe and we ourselves have explicitly restricted ourselves to those groups of symmetry which leave one point of the system invariant.

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#### SUMMARY

It is shown that a polyatomic molecule cannot possess a stable non-linear nuclear configuration in an electronic state having spin degeneracy unless this degeneracy is the special twofold one which can occur only when the molecule contains an odd number of electrons. Instability caused by the spin alone is shown to be of secondary importance compared with the orbital effects discussed in a previous paper. Table I gives the irreducible two-valued representations of all the point groups and will be useful in discussion of the electronic states of polyatomic molecules containing an odd number of electrons with spin.

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