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Stability of Polyatomic Molecules in Degenerate Electronic States. I. Orbital Degeneracy

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SUMMARY

The work of a previous paper on the elastic stability of a thin twisted strip has been corrected and extended to the consideration of the stability of the twisted strip when it is also subjected to a tension along its length. It is found that the strip becomes unstable at a definite value of the twist and that the instability is in the form of a number of loops superposed on the twisted strip in contrast to one loop in the case when no tension acts on the strip. The theory has been compared with experiment and satisfactorily good agreement between them is found.

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Stability of Polyatomic Molecules in Degenerate Electronic States

I—Orbital Degeneracy

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INTRODUCTION

In the following we investigate the conditions under which a polyatomic molecule can have a stable equilibrium configuration when its electronic state has orbital degeneracy, i.e. degeneracy not arising from the spin. We shall show that stability and degeneracy are not possible simultaneously unless the molecule is a linear one, i.e. unless all the nuclei in the equilibrium configuration lie on a straight line. We shall see also that the instability is only slight if the degeneracy is due solely to electrons having no great influence on the binding of the molecule.

* This research was carried out when the authors were working in the Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London.

We first note that if accidental degeneracy (i.e. degeneracy not caused by symmetry) is disregarded then a degenerate electronic state necessarily entails a symmetrical nuclear configuration. Thus in order to cover all cases we may first consider each possible type of symmetry separately and discuss what nuclear configurations are consistent with each symmetry. A given molecule will possess a continuous set of configurations consistent with one definite type of symmetry, and among these configurations there may be one with a minimum electronic energy. This configuration is then stable with respect to all totally symmetrical nuclear displacements (i.e. displacements which do not disturb the symmetry). We shall have to investigate its stability with respect to all other nuclear displacements.

Now a nuclear configuration cannot be stable if the electronic energy for neighbouring configurations depends linearly upon any one of the nuclear displacements. There may be reasons of symmetry, however, which preclude such a linear dependence, and we illustrate the occurrence and non-occurrence of this respectively by the two following examples. In these examples there is the added complication that the nuclear displacements in question cause a splitting of the degenerate electronic state into states with different energies. This complication will be the rule rather than the exception, since the displacements reduce the symmetry of the original configuration. A linear dependence upon a nuclear displacement of the energy of any one of these states formed by the splitting is then sufficient to cause instability.

1—TWO EXAMPLES

In our first example we consider the motion of a single electron in the field of three nuclei lying on a straight line. The states of the electron can then be classified as σ, π, δ, etc., states according as the component of the electron's orbital angular momentum along the nuclear axis is 0, ± 1, ± 2, etc. (in units of $h/2\pi$). The σ states are non-degenerate, whilst the π, δ and further states are each twofold degenerate, corresponding to the fact that the electron may move either clockwise or anticlockwise about the nuclear axis. If, now, one of the nuclei (say the middle one) is displaced through a distance d perpendicular to the axis, then the axial symmetry will be destroyed and the degeneracy removed. Each twofold degenerate state will split into two states, one symmetrical with respect to reflexions in the plane of the nuclei and the other antisymmetrical with respect to the same plane. These states will have different energies E_s and E_a. When the nuclear displacement is varied these states and their energies will change continuously, but their symmetry will remain and it is clear that when the displacement is $-d$ the states and energies will be the same as before. Thus the two energies E_s and E_a must be even functions of d, and all that is required for stability with respect to this nuclear displacement is that the function be positive in both cases (see fig. 1).

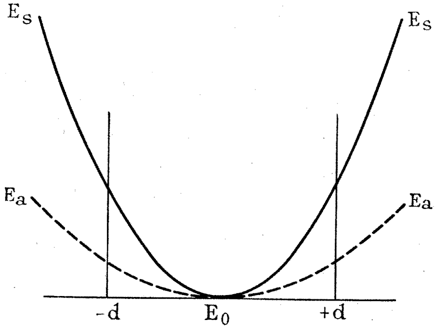

Fig. 1

In our second example we consider the motion of a single electron in the field of a plane square configuration of four identical nuclei. There is a similarity between the two examples in that, in the first example once the wave function on any half-plane through the axis is given, then it is determined by symmetry for all other such half-planes: a rotation through the angle θ multiplies the wave function by $e^{i\lambda\theta}$, where λ is the axial component of the orbital angular momentum. In the second example, on the other hand, the symmetry about the axis through the centre of the square, although considerably reduced, still determines the wave function completely on any four half-planes at right angles to each other, once the wave function has been given on any one of them. The function is again multiplied by $e^{i\lambda\theta}$, where here θ is restricted to the values $\pm\pi/2, \pi$ and λ can have the values 0, ± 1. The state with $|\lambda| = 1$ is again twofold degenerate. We will discuss the stability of the square configuration for this degenerate electronic state. Consider the two displaced configurations I and II depicted in fig. 2. These

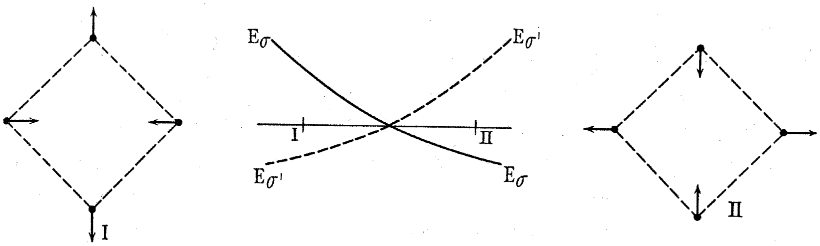

Fig. 2

may be regarded clearly as belonging to a positive and negative value of one and the same nuclear displacement. This nuclear displacement destroys the fourfold axial symmetry, replacing it by a twofold one. The degenerate state will split into two states ϕ_σ and $\phi_{\sigma'}$, the first having a node in the horizontal plane of symmetry σ and the second a node in the vertical plane σ'. Now it is clear that since the configurations I and II are geometrically congruent and the planes σ', σ in II correspond respectively to the planes σ, σ' in I, the energy of ϕ_σ for the configuration I must be the same as the energy of $\phi_{\sigma'}$ for the configuration II. Thus if E_σ, $E_{\sigma'}$ are the corresponding energies, we must have the relation

$$E_\sigma(\text{I}) = E_{\sigma'}(\text{II}).$$

Similarly

$$E_\sigma(\text{II}) = E_{\sigma'}(\text{I}).$$

Thus the two energy levels E_σ, $E_{\sigma'}$ have crossed over at the energy E_0 of the undisplaced configuration (see fig. 2). There is here thus no apparent reason of symmetry which precludes a linear dependence of the energy levels upon the nuclear displacement in the neighbourhood of E_0, and the square configuration therefore will not in general be a stable equilibrium configuration for the degenerate electronic state.

2—GENERAL THEOREM

In the above two examples we have seen how the type of molecular symmetry can determine whether the energy of a degenerate electronic state should depend linearly or not upon nuclear displacements. It is our purpose to study this influence for all possible types of symmetry. We do this by an application of group theory to perturbation calculation. We restrict ourselves in this paper to orbital degeneracy and reserve the consideration of the special effects due to spin degeneracy for a second paper. The electronic energy levels of the displaced configuration are the characteristic values of a perturbation matrix, the elements of which may be expressed as a power series in the nuclear displacements. Unless those perturbation matrix elements which are linear in the nuclear displacements all vanish, then at least one perturbed energy level will depend linearly upon a nuclear displacement. Now the elements of these matrices are integrals which are necessarily invariant with regard to the group of symmetry of the equilibrium configuration. The integrands, on the other hand, are products whose transformation properties are determined by those of the degenerate electronic wave functions and the nuclear displacements. From an investigation of these transformation properties it may be deduced whether the invariance of the integrals and the transformation properties of the integrands are compatible. Unless this is the case the integrals vanish. If, however, they are compatible the matrix elements depending linearly upon the nuclear displacements will be in general different from zero. It will be found that all linear matrix elements will necessarily vanish only when the nuclear configuration shows complete axial symmetry, i.e. only when all the nuclei in the molecule lie on a straight line. *All non-linear nuclear configurations are therefore unstable for an orbitally degenerate electronic state.* Thus if we know of a polyatomic molecule that the nuclei in the equilibrium configuration do not all lie on a straight line, then we know at the same time that its ground electronic state does not possess orbital degeneracy. We should exclude from our consideration, however, orbitally degenerate electronic states in which the degenerate electrons do not contribute appreciably to the molecular binding and are not perturbed therefore by nuclear displacements. Such is the case for the inner degenerate electronic shells of the paramagnetic rare earth ionic salts. If, apart from such instances, a non-linear molecule is paramagnetic, then we may conclude that this paramagnetism must be due to the action of the spin alone, for it is well known that a non-degenerate orbital state can possess neither a mean orbital angular momentum nor a mean orbital magnetic moment (cf. van Vleck 1932).

3—MATHEMATICAL FORMULATION AND GROUP-THEORETICAL CONSIDERATIONS

We shall have to consider nuclear configurations Q which can be obtained from the given symmetrical configuration Q_0 by adding a linear combination of a complete set of displaced configurations Q_r which may be chosen orthogonal to each other, to the translations and rotations and also to all the totally symmetrical displacements:

$$Q = Q_0 + \sum_r Q_r \eta_r.$$

Here the η_r are infinitesimally small quantities which we will call the (non-totally symmetrical) normal displacements of the configuration Q_0. It is to be noted that the η_r can be so chosen that they transform according to irreducible representations of the symmetry group of Q_0 (cf. Wigner 1930).

The energy operator $H(Q)$ for the electronic motion in the field of the nuclei fixed in the configuration Q can be expanded as a power series in the η_r:

$$H = H_0 + \sum_r V_r(q)\,\eta_r + \sum_{rs} V_{rs}(q)\,\eta_r \eta_s + \dots,$$

where the V_r, V_{rs} are functions of the electronic coordinates q alone, since the kinetic energy of the electrons is included in the energy operator H_0.

Let E_0 be the energy level of the degenerate electronic state and ϕ_ρ a complete set of orthogonal wave functions such that

$$H_0\phi_\rho = E_0\phi_\rho.$$

In the configuration Q this energy level either may be split up into a number of different energy levels E_α or it may be merely displaced (i.e. the degeneracy may not be removed). The configuration Q_0 can be stable with respect to all nuclear displacements only if each of these energy levels E_α has a minimum for $Q = Q_0$. We denote the contribution to the perturbed energy E_α arising from the linear terms $\sum_r V_r\eta_r$ by E^I_α, putting

$$E_\alpha = E_0 + E^I_\alpha + \dots.$$

Perturbation theory shows that the perturbation energies E^I_α are the characteristic values of a perturbation matrix having the following elements:

$$M_{\rho\sigma} = \Sigma\eta_r \int \phi^*_\rho V_r \phi_\sigma d\tau.$$

Now it is clear that if E is a characteristic value of this matrix for a given set of values of the η_r, then $-E$ is a characteristic value for the configuration obtained by changing the sign of all the η_r. Thus unless the characteristic values of this matrix all vanish (in which case the matrix itself must vanish) the configuration Q_0 cannot possibly be a stable one.

If the representation of the symmetry group of the configuration Q_0 which is subtended by the products $\phi^*_\rho V_r \phi_\sigma$ does not contain the identical representation, then the integrals $\int \phi^*_\rho V_r \phi_\sigma d\tau$ will vanish, for these integrals are necessarily invariant with respect to the symmetry operations. If this condition does not hold, then the integrals in general will not vanish. Now the normal displacements η_r may be chosen so that the V_r transform according to irreducible representations V of the group of symmetry. The degenerate wave functions ϕ_ρ will also subtend a representation Φ of the group of symmetry, which representation will be in general irreducible. An exception occurs here, as Wigner (1932) has shown, when the degeneracy arising from the invariance of the wave equation with respect to time reversal is considered; this may cause an "accidental" degeneracy so that the wave functions of the energy level subtend a representation which is the sum of two irreducible representations. For our purpose, however, this double representation Φ may be treated as though it were a single one. It may then be shown that if we restrict ourselves to orbital degeneracy (i.e. if we do not consider the spin wave functions) the representation Φ and consequently the wave functions ϕ_ρ can be chosen always real. The products $\phi_\rho V_r \phi_\sigma$ are linearly independent except that of course

$$\phi_\sigma V_r \phi_\rho = \phi_\rho V_r \phi_\sigma.$$

They will therefore transform according to the product representation $V[\Phi^2]$, where $[\Phi^2]$ denotes the representation of the symmetrical product of Φ with itself (cf. Weyl 1928). Thus if there exists a normal displacement (other than a totally symmetrical one) for which $V[\Phi^2]$ contains the identical representation, the symmetrical configuration Q_0 will not be stable.

We may illustrate these general considerations by applying them to the two examples discussed in the introduction. In the first example the group of symmetry for a general position of the nuclei on the axis is C_∞^v. The degenerate irreducible representations are all two-dimensional, and there is an infinite series of them, denoted by $E_1, E_2, \ldots, E_k, \ldots$. It can be shown (cf. Tisza 1933) that the representation of the symmetrical product of E_k is given by

$$[E_k^2] = A_1 + E_{2k},$$

where A_1 is the unit representation. Placzek (1934) has shown that for linear nuclear configurations all non-totally symmetrical vibrations are of the type E_1. One finds

$$E_1[E_k^2] = E_1(A_1 + E_{2k}) = E_1 + E_{2k+1} + E_{2k-1},$$

so that the product $V[\Phi^2]$ never contains the identical representation A_1 for any non-totally symmetrical vibration and any degenerate electronic state Φ. Thus, as has already been seen above, there is no reason of symmetry why the linear nuclear configuration should not be stable in any of the degenerate states. In the second example the reverse is the case. Here the group of symmetry is D_4^h, and there are only two degenerate representations, viz. E_g and E_u, g and u referring to even and odd representations with respect to inversion in the centre of symmetry. These representations are both two-dimensional. The considerations of Wigner (1930) show that the square configuration possesses non-totally symmetrical displacements of types B_{1g}, B_{1u}, B_{2g} and E_u. Since it can be shown that

$$[E_g^2] = [E_u^2] = A_{1g} + B_{1g} + B_{2g},$$

and since $B_{1g}^2 = B_{2g}^2 = A_{1g}$, we see that $B_{1g}[E_g^2]$, $B_{1g}[E_u^2]$, $B_{2g}[E_g^2]$ and $B_{2g}[E_u^2]$ all contain the identical representation A_{1g}. Hence normal displacements of the type B_{1g} or B_{2g} render the square configuration unstable for a degenerate electronic state of either type. One verifies easily that the nuclear displacement considered in the example is of the type B_{2g}.

4—PROOF OF GENERAL THEOREM

Excluding the groups of complete axial symmetry, we have to show, for all configurations and any degenerate one-valued representation of the group of symmetry, that a symmetrical nuclear configuration necessarily possesses non-totally symmetrical normal displacements transforming according to irreducible representations V such that $V[\Phi^2]$ contains the identical representation. This is equivalent to showing that $[\Phi^2]$ in its reduced form contains at least one of the representations V.

Now Wigner (1930) has shown how to calculate for any given nuclear configuration how many normal displacements of each irreducible type occur. In order to apply this calculation of Wigner to all possible symmetrical molecules we note that any symmetrical configuration must contain sets of equivalent nuclei whose positions are transformed into one another by the various symmetry operations. For any given group of symmetry there are various possible kinds of such equivalent sets according as the points lie on no symmetry element or on one, two or more of them. We have applied the method of Wigner to all possible sets of equivalent points for the various groups of symmetry, and the results of our calculations are tabulated in Table I.

In this table the notation of Placzek (1934), Mulliken (1933), Lennard-Jones (1934) and Tisza (1933) is used for the groups and their irreducible representations. Column I gives the designation of the group, columns II and III give the reduction into irreducible constituents of the translations and rotations respectively, column IV gives a designation to the various kinds of equivalent points for each group, column V gives the number of equivalent points in each individual set, column VI gives the symmetry elements, if any, on which these points lie, whilst the last column VII gives the reduction into irreducible constituents for the whole set of nuclear displacements inclusive of translations, rotations and normal displacements for a "molecule" consisting of the equivalent points given in column IV. By subtracting the translations and rotations from this last column we find what types of normal displacements occur. This subtraction has not been carried out in the table, since for any molecule more than one set of equivalent points may occur (i.e. more than one row of the table is required, or the same row required more than once), whilst the subtraction of the translation and rotation has of course only to be carried out once. The table will be useful not

TABLE I

I	II	III	IV	V	VI	VII
C^v_∞	A_1+E_1	E_1	a	1	All	A_1+E_1
$C^{vi}_\infty = D^h_\infty$	$A_{1u}+E_{1u}$	E_{1g}	a	2	C_∞, σ_v	$A_{1g}+A_{1u}+E_{1g}+E_{1u}$
			b	1	All	$A_{1u}+E_{1u}$
C_{2p+1}	$A+E_1$	$A+E_1$	a	$2p+1$	None	$3(A+E_1+\ldots+E_p)$
			b	1	C_{2p+1}	$A+E_1$
C_{2p}	$A+E_1$	$A+E_1$	a	$2p$	None	$3(A+B+E_1+\ldots+E_{p-1})$
			b	1	C_{2p}	$A+E_1$
D_{2p+1}	A_2+E_1	A_2+E_1	a	$2(2p+1)$	None	$3(A_1+A_2)+6(E_1+E_2+\ldots+E_p)$
			b	$2p+1$	C_2	$A_1+2A_2+3(E_1+E_2+\ldots+E_p)$
			c	2	C_{2p+1}	$A_1+A_2+2E_1$
			d	1	All	A_2+E_1
D_{2p}	A_2+E_1	A_2+E_1	a	$4p$	None	$3(A_1+A_2+B_1+B_2)+6(E_1+E_2+\ldots+E_{p-1})$
			b	$2p$	C_2	$A_1+2A_2+B_1+2B_2+3(E_1+E_2+\ldots+E_{p-1})$
			c	$2p$	C_2'	$A_1+2A_2+2B_1+B_2+3(E_1+E_2+\ldots+E_{p-1})$
			d	2	C_{2p}	$A_1+A_2+2E_1$
			e	1	All	A_2+E_1
C^i_{2p+1} $=S_{2(2p+1)}$	A_u+E_{1u}	A_g+E_{1g}	a	$2(2p+1)$	None	$3(A_g+A_u+E_{1g}+E_{1u}+\ldots+E_{pg}+E_{pu})$
			b	2	C_{2p+1}	$A_g+A_u+E_{1g}+E_{1u}$
			c	1	All	A_u+E_{1u}
$C^i_{2p} = C^h_{2p}$	A_u+E_{1u}	A_g+E_{1g}	a	$4p$	None	$3(A_g+A_u+B_g+B_u+E_{1g}+E_{1u}+\ldots+E_{p-1,g}+E_{p-1,u})$
			b	$2p$	σ_h	$2A_g+A_u+\begin{cases} B_g+2B_u \text{ } (p \text{ odd}) \\ 2B_g+B_u \text{ } (p \text{ even}) \end{cases}+E_{1g}+2E_{1u}+2E_{2g}+E_{2u}$ $+\ldots+\begin{cases} 2E_{p-1,g}+E_{p-1,u} \text{ } (p \text{ odd}) \\ E_{p-1,g}+2E_{p-1,u} \text{ } (p \text{ even}) \end{cases}$
			c	2	C_{2p}	$A_g+A_u+E_{1g}+E_{1u}$
			d	1	All	A_u+E_{1u}

D^i_{2p+1} $= D^d_{2p+1}$	$A_{2u}+E_{1u}$	$A_{2g}+E_{1g}$	a	$4(2p+1)$	None	$3(A_{1g}+A_{1u}+A_{2g}+A_{2u})+6(E_{1g}+E_{1u}+\ldots+E_{pg}+E_{pu})$
			b	$2(2p+1)$	σ_d	$2A_{1g}+A_{1u}+A_{2g}+2A_{2u}+3(E_{1g}+E_{1u}+\ldots+E_{pg}+E_{pu})$
			c	$2(2p+1)$	C_2	$A_{1g}+A_{1u}+2A_{2g}+2A_{2u}+3(E_{1g}+E_{1u}+\ldots+E_{pg}+E_{pu})$
			d	2	C_{2p+1}, σ_d	$A_{1g}+A_{2u}+E_{1g}+E_{1u}$
			e	1	All	$A_{2u}+E_{1u}$
$D^i_{2p}=D^h_{2p}$	$A_{2u}+E_{1u}$	$A_{2g}+E_{1g}$	a	$8p$	None	$3(A_{1g}+A_{1u}+A_{2g}+A_{2u}+B_{1g}+B_{1u}+B_{2g}+B_{2u})$ $+6(E_{1g}+E_{1u}+\ldots+E_{p-1,g}+E_{p-1,u})$
			b	$4p$	σ	$2A_{1g}+A_{1u}+A_{2g}+2A_{2u}+\left\{\begin{matrix}B_{1g}+2B_{1u}+2B_{2g}+B_{2u}\ (p \text{ odd})\\ 2B_{1g}+B_{1u}+B_{2g}+2B_{2u}\ (p \text{ even})\end{matrix}\right.$ $+3(E_{1g}+E_{1u}+\ldots+E_{p-1,g}+E_{p-1,u})$
			c	$4p$	σ'	$2A_{1g}+A_{1u}+A_{2g}+2A_{2u}+\left\{\begin{matrix}2B_{1g}+B_{1u}+B_{2g}+2B_{2u}\ (p \text{ odd})\\ B_{1g}+2B_{1u}+2B_{2g}+B_{2u}\ (p \text{ even})\end{matrix}\right.$ $+3(E_{1g}+E_{1u}+\ldots+E_{p-1,g}+E_{p-1,u})$
			d	$4p$	σ_h	$2A_{1g}+A_{1u}+2A_{2g}+A_{2u}+\left\{\begin{matrix}B_{1g}+2B_{1u}+B_{2g}+2B_{2u}\ (p \text{ odd})\\ 2B_{1g}+B_{1u}+2B_{2g}+B_{2u}\ (p \text{ even})\end{matrix}\right.$ $+2E_{1g}+4E_{1u}+4E_{2g}+2E_{2u}+\ldots+\left\{\begin{matrix}4E_{p-1,g}+2E_{p-1,u}\ (p \text{ odd})\\ 2E_{p-1,g}+4E_{p-1,u}\ (p \text{ even})\end{matrix}\right.$
			e	$2p$	σ_h, C_2, σ	$A_{1g}+A_{2g}+A_{2u}+\left\{\begin{matrix}B_{1u}\ (p \text{ odd})\\ B_{1g}\ (p \text{ even})\end{matrix}\right\}+B_{2g}+B_{2u}$ $+E_{1g}+2E_{1u}+2E_{2g}+E_{2u}+\ldots+\left\{\begin{matrix}2E_{p-1,g}+E_{p-1,u}\ (p \text{ odd})\\ E_{p-1,g}+2E_{p-1,u}\ (p \text{ even})\end{matrix}\right.$
			f	$2p$	σ_h, C'_2, σ'	$A_{1g}+A_{2g}+A_{2u}+B_{1g}+B_{1u}+\left\{\begin{matrix}B_{2u}\ (p \text{ odd})\\ B_{2g}\ (p \text{ even})\end{matrix}\right.$ $+E_{1g}+2E_{1u}+2E_{2g}+E_{2u}+\ldots+\left\{\begin{matrix}2E_{p-1,g}+E_{p-1,u}\ (p \text{ odd})\\ E_{p-1,g}+2E_{p-1,u}\ (p \text{ even})\end{matrix}\right.$
			g	2	C_{2p}, σ, σ'	$A_{1g}+A_{2u}+E_{1g}+E_{1u}$
			h	1	All	$A_{2u}+E_{1u}$
C^h_{2p+1} $= S_{2p+1}$	$A''+E'_1$	$A'+E''_1$	a	$2(2p+1)$	None	$3(A'+A''+E'_1+E''_1+\ldots+E'_p+E''_p)$
			b	$2p+1$	σ_h	$2A'+A''+2E'_1+E''_1+2E'_2+E''_2+\ldots+2E'_p+E''_p$
			c	2	C_{2p+1}	$A'+A''+E'_1+E''_1$
			d	1	All	$A''+E'_1$

TABLE I—(*continued*)

I	II	III	IV	V	VI	VII
D^h_{2p+1} $= D^v_{2p+1}$	$A''_2+E'_1$	$A'_2+E''_1$	a	$4(2p+1)$	None	$3(A'_1+A''_1+A'_2+A''_2)+6(E'_1+E''_1+\ldots+E'_p+E''_p)$
			b	$2(2p+1)$	σ_v	$2A'_1+A''_1+A'_2+2A''_2+3(E'_1+E''_1+\ldots+E'_p+E''_p)$
			c	$2(2p+1)$	σ_h	$2A'_1+A''_1+2A'_2+A''_2+4E'_1+2E''_1+\ldots+4E'_p+2E''_p$
			d	$2p+1$	σ_h, σ_v, C_2	$A'_1+A'_2+A''_2+2E'_1+E''_1+\ldots+2E'_p+E''_p$
			e	2	C_{2p+1}	$A'_1+A''_2+E'_1+E''_1$
			f	1	All	$A''_2+E'_1$
C^v_{2p+1}	A_1+E_1	A_2+E_1	a	$2(2p+1)$	None	$3(A_1+A_2)+6(E_1+\ldots+E_p)$
			b	$2p+1$	σ	$2A_1+A_2+3(E_1+\ldots+E_p)$
			c	1	All	A_1+E_1
C^v_{2p}	A_1+E_1	A_2+E_1	a	$4p$	None	$3(A_1+A_2+B_1+B_2)+6(E_1+\ldots+E_{p-1})$
			b	$2p$	σ	$2A_1+A_2+2B_1+B_2+3(E_1+\ldots+E_{p-1})$
			c	$2p$	σ'	$2A_1+A_2+B_1+2B_2+3(E_1+\ldots+E_{p-1})$
			d	1	All	A_1+E_1
S_{4p}	$B+E_1$	$A+E_{2p-1}$	a	$4p$	None	$3(A+B+E_1+\ldots+E_{2p-1})$
			b	2	C_{2p}	$A+B+E_1+E_{2p-1}$
			c	1	All	$B+E_1$
$S^v_{4p}=D^d_{2p}$	B_1+E_1	A_2+E_{2p-1}	a	$8p$	None	$3(A_1+A_2+B_1+B_2)+6(E_1+E_2+\ldots+E_{2p-1})$
			b	$4p$	σ_v	$2A_1+A_2+2B_1+B_2+3(E_1+E_2+\ldots+E_{2p-1})$
			c	$4p$	C_2	$A_1+2A_2+2B_1+B_2+3(E_1+E_2+\ldots+E_{2p-1})$
			d	2	C_{2p}	$A_1+B_1+E_1+E_{2p-1}$
			e	1	All	B_1+E_1
T	F	F	a	12	None	$3A+3E+9F$
			b	6	C_2	$A+E+5F$
			c	4	C_3	$A+E+3F$
			d	1	All	F
T_d	F_2	F_1	a	24	None	$3A_1+3A_2+6E+9F_1+9F_2$
			b	12	σ	$2A_1+A_2+3E+4F_1+5F_2$
			c	6	C_2, σ	$A_1+E+2F_1+3F_2$
			d	4	C_3, σ	$A_1+E+F_1+2F_2$
			e	1	All	F_2

$T_h = i \times T$	F_u	F_g	a	24	None	$3A_g+3A_u+3E_g+3E_u+9F_g+9F_u$
			b	12	σ	$2A_g+A_u+2E_g+E_u+4F_g+5F_u$
			c	8	C_3	$A_g+A_u+E_g+E_u+3F_g+3F_u$
			d	6	C_2, σ	$A_g+E_g+2F_g+3F_u$
			e	1	All	F_u
O	F_1	F_1	a	24	None	$3A_1+3A_2+6E+9F_1+9F_2$
			b	12	$6C_2$	$A_1+2A_2+3E+5F_1+4F_2$
			c	8	$3C_2$	$A_1+A_2+2E+3F_1+3F_2$
			d	6	$3C_2$, C_4	$A_1+E+3F_1+2F_2$
			e	1	All	F_1
$O_h = i \times O$	F_{1u}	F_{1g}	a	48	None	$3(A_{1g}+A_{1u}+A_{2g}+A_{2u})+6(E_g+E_u)+9(F_{1g}+F_{1u}+F_{2g}+F_{2u})$
			b	24	σ_h	$2(A_{1g}+A_{2g})+A_{1u}+A_{2u}+4E_g+2E_u+4(F_{1g}+F_{2g})+5(F_{1u}+F_{2u})$
			c	24	σ_d	$2A_{1g}+A_{1u}+A_{2g}+2A_{2u}+3E_g+3E_u+4F_{1g}+5F_{1u}+5F_{2g}+4F_{2u}$
			d	12	C_2^d, σ_h, σ_d	$A_{1g}+A_{2g}+A_{2u}+2E_g+E_u+2F_{1g}+3F_{1u}+2F_{2g}+2F_{2u}$
			e	8	C_3, σ_d	$A_{1g}+A_{2u}+E_g+E_u+F_{1g}+2F_{1u}+2F_{2g}+F_{2u}$
			f	6	C_2^v, C_4, σ_h, σ_d	$A_{1g}+E_g+F_{1g}+2F_{1u}+F_{2g}+F_{2u}$
			g	1	All	F_{1u}
I	F_1	F_1	a	60	None	$3A+9(F_1+F_2)+12G+15H$
			b	30	C_2	$A+5(F_1+F_2)+6G+7H$
			c	20	C_3	$A+3(F_1+F_2)+4G+5H$
			d	12	C_5	$A+3F_1+F_2+2G+3H$
			e	1	All	F_1
$I_h = i \times I$	F_{1u}	F_{1g}	a	120	None	$3(A_g+A_u)+9(F_{1g}+F_{1u}+F_{2g}+F_{2u})+12(G_g+G_u)+15(H_g+H_u)$
			b	60	σ	$2A_g+A_u+4F_{1g}+5F_{1u}+4F_{2g}+5F_{2u}+6(G_g+G_u)+8H_g+7H_u$
			c	30	C_2, σ	$A_g+2F_{1g}+3F_{1u}+2F_{2g}+3F_{2u}+3(G_g+G_u)+4H_g+3H_u$
			d	20	C_3, σ	$A_g+F_{1g}+2F_{1u}+F_{2g}+2F_{2u}+2(G_g+G_u)+3H_g+2H_u$
			e	12	C_5, σ	$A_g+F_{1g}+2F_{1u}+F_{2u}+G_g+G_u+2H_g+H_u$
			f	1	All	F_{1u}

merely in establishing our theorem but also in showing what normal displacements any given molecule possesses. Tables for this purpose restricted to the crystallographic point groups have already been published by Placzek (1934) and further tables for special molecules have been given by Bright Wilson (1934).

Now in order to establish our theorem for each group of symmetry we must investigate what is the minimum number of points from which a molecule of the corresponding symmetry can be composed. For instance, if we want to construct a molecule of the symmetry T it will not be sufficient to take six atoms and place them on the twofold axes (the points (*b*) in Table I), for this configuration would have the higher symmetry O_h. To this end we list in Table II the minimum number of the different kinds of points which are necessary and sufficient to produce each of the various groups of symmetry. In this table an entry such as 2(*a*) means that two complete sets of points of the type (*a*) have to be taken to produce the necessary symmetry. Types which are not listed can never produce the symmetry no matter how many complete sets of such a type are taken, e.g. the type (*b*) for the group T.

TABLE II

Group	Minimum points required to produce symmetry of group
C^v_∞	2(*a*)
C^{vi}_∞	(*a*)
C_{2p+1}	2(*a*)
C_{2p}	2(*a*)
D_{2p+1}	(*a*)
D_{2p}	(*a*)
C^i_{2p+1}	(*a*)
C^i_{2p}	2(*a*), 2(*b*) or (*a*)+(*b*)
D^i_{2p+1}	(*a*) or (*b*)
D^i_{2p}	(*a*), (*b*), (*c*), (*d*), (*e*) or (*f*)
C^h_{2p+1}	2(*a*), 2(*b*) or (*a*)+(*b*)
D^h_{2p+1}	(*a*), (*b*), (*c*) or (*d*)
C^v_{2p+1}	2(*a*), 2(*b*), (*a*)+(*b*), (*a*)+(*c*) or (*b*)+(*c*)
C^v_{2p}	2(*a*), 2(*b*), 2(*c*), (*a*)+(*b*), (*a*)+(*c*), (*a*)+(*d*), (*b*)+(*c*), (*b*)+(*d*) or (*c*)+(*d*)
S_{4p}	2(*a*)
S^v_{4p}	(*a*) or (*b*)
T	(*a*)
T_d	(*a*), (*b*) or (*d*)
T_h	(*a*) or (*b*)
O	(*a*)
O_h	(*a*), (*b*), (*c*), (*d*), (*e*) or (*f*)
I	(*a*)
I_h	(*a*), (*b*), (*c*), (*d*) or (*e*)

TABLE III

Group	Symmetrical product of degenerate representations
C_{∞}^{v}	$[E_k^2] = A_1 + E_{2k} \quad (k = 1, 2, \ldots)$
C_{∞}^{vi}	$[E_{kg}^2] = [E_{ku}^2] = A_{1g} + E_{2k,g} \quad (k = 1, 2, \ldots)$
C_{2p+1}	$[E_k^2] = A + E_{2k}$ for $k \leqq p/2$
	$= A + E_{2p+1-2k}$ for $k > p/2 \quad (k = 1, 2, \ldots, p)$
C_{2p}	$[E_k^2] = A + E_{2k}$ for $k < p/2$
	$= A + 2B$ for $k = p/2$
	$= A + E_{2p-2k}$ for $k > p/2 \quad (k = 1, 2, \ldots, p-1)$
D_{2p+1} and C_{2p+1}^{v}	$[E_k^2] = A_1 + E_{2k}$ for $k \leqq p/2$
	$= A_1 + E_{2p+1-2k}$ for $k > p/2 \quad (k = 1, \ldots, p)$
D_{2p} and C_{2p}^{v}	$[E_k^2] = A_1 + E_{2k}$ for $k < p/2$
	$= A_1 + B_1 + B_2$ for $k = p/2$
	$= A_1 + E_{2p-2k}$ for $k > p/2 \quad (k = 1, \ldots, p-1)$
C_{2p+1}^{i}	$[E_{kg}^2] = [E_{ku}^2] = A_g + E_{2k,g}$ for $k \leqq p/2$
	$= A_g + E_{2p+1-2k,g}$ for $k > p/2 \quad (k = 1, \ldots, p)$
C_{2p}^{i}	$[E_{kg}^2] = [E_{ku}^2] = A_g + E_{2k,g}$ for $k < p/2$
	$= A_g + 2B_g$ for $k = p/2$
	$= A_g + E_{2p-2k,g}$ for $k > p/2 \quad (k = 1, \ldots, p-1)$
D_{2p+1}^{i}	$[E_{kg}^2] = [E_{ku}^2] = A_{1g} + E_{2k,g}$ for $k \leqq p/2$
	$= A_{1g} + E_{2p+1-2k,g}$ for $k > p/2 \quad (k = 1, \ldots, p)$
D_{2p}^{i}	$[E_{kg}^2] = [E_{ku}^2] = A_{1g} + E_{2k,g}$ for $k < p/2$
	$= A_{1g} + B_{1g} + B_{2g}$ for $k = p/2$
	$= A_{1g} + E_{2p-2k,g}$ for $k > p/2 \quad (k = 1, \ldots, p-1)$
C_{2p+1}^{h} and D_{2p+1}^{h}	$[E_k'^2] = [E_k''^2] = A' + E_{2k}'$ for $k \leqq p/2$
	$= A' + E_{2p+1-2k}'$ for $k > p/2 \quad (k = 1, \ldots, p)$
S_{4p}	$[E_k^2] = A + E_{2k}$ for $k < p$
	$= A + 2B$ for $k = p$
	$= A + E_{4p-2k}$ for $k > p \quad (k = 1, \ldots, 2p-1)$
S_{4p}^{v}	$[E_k^2] = A_1 + E_{2k}$ for $k < p$
	$= A_1 + B_1 + B_2$ for $k = p$
	$= A_1 + E_{4p-2k}$ for $k > p \quad (k = 1, \ldots, 2p-1)$
T	$[E^2] = A + E$
	$[F^2] = A + E + F$
T_d and O	$[E^2] = A_1 + E$
	$[F_1^2] = [F_2^2] = A_1 + E + F_2$
T_h	$[E_g^2] = [E_u^2] = A_g + E_g$
	$[F_g^2] = [F_u^2] = A_g + E_g + F_g$
O_h	$[E_g^2] = [E_u^2] = A_{1g} + E_g$
	$[F_{1g}^2] = [F_{1u}^2] = [F_{2g}^2] = [F_{2u}^2] = A_{1g} + E_g + F_{2g}$
I	$[F_1^2] = [F_2^2] = A + H$
	$[G^2] = A + G + H$
	$[H^2] = A + G + 2H$
I_h	$[F_{1g}^2] = [F_{1u}^2] = [F_{2g}^2] = [F_{2u}^2] = A_g + H_g$
	$[G_g^2] = [G_u^2] = A_g + G_g + H_g$
	$[H_g^2] = [H_u^2] = A_g + G_g + 2H_g$

We require, further, the symmetrical products of the various degenerate representations. These may be taken from the work of Tisza (1933), for they are identical with the representations subtended by the first overtones of the corresponding normal vibrations. For convenience we tabulate in Table III these symmetrical product representations for all degenerate representations.

Using Tables I, II and III, our general theorem will be verified easily. For instance, according to Table II the group of symmetry O_h can be produced by one complete set of equivalent points of any of the types (*a*), (*b*), (*c*), (*d*), (*e*) or (*f*). But from Table I we see that each of these sets of points has normal displacements of the type E_g, and according to Table III, $E_g[\Phi^2]$ always contains the identical representation for any degenerate representation Φ of the group O_h. We must, of course, always remember that displacements of the type A_{1g} (or A_1 or A or A_g) must not be made use of, since the molecular configurations considered are always taken to be stable with respect to all totally symmetrical displacements.

5—CONCLUSION

In concluding we would like to point out again that the forces which tend to destroy the symmetrical configuration, and which we have shown exist in cases of orbital degeneracy, will be important only if the degenerate electrons participate strongly in the binding of the molecule. The effect may be small both if the degenerate electrons are in inner atomic shells or if they are in highly excited states. Spin degeneracy may also produce similar effects, but these, too, will be small, since the coupling of spin and nuclear motion will depend upon the interaction of the spin with the orbital motion of the electrons, which interaction, at least for light elements, is small. Furthermore, a general theorem of Kramers (1930) and Wigner (1932) shows that for molecules containing an odd number of electrons there is a twofold spin degeneracy which cannot be split by any electrical forces. Such twofold spin degeneracy cannot therefore produce any instability of the molecular configuration. It can be shown, however, that with the exception of this one type of degeneracy all degenerate electronic states of non-linear molecules are unstable whether the degeneracy is due to electronic orbits or to spin. The proof of this statement, together with a more detailed discussion of the order of magnitude of splitting, will be given in a second paper.

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SUMMARY

It is shown that orbital electronic degeneracy and stability of the nuclear configuration are incompatible unless all the atoms of a molecule lie on a straight line. The proof is based on group theory and is therefore valid only if accidental degeneracy is disregarded. If the electrons causing the degeneracy are not essential for molecular binding, only a slight instability will result. Table I, which is needed to prove the theorem, can also be used to obtain the number of proper vibrations of a given symmetry type for any polyatomic molecule.

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