

A Class of Perturbations of Molecular Levels

G. H. DIEKE, *The Johns Hopkins University*

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By following Van Vleck and Kronig, the conditions for the occurrence of perturbations are investigated in detail for a simple case. Class A perturbations which are produced by the rotation of the molecule must have $\Lambda' = \Lambda \pm 1$. The vibrational levels cannot be perturbed in this case. There will be a constant shift between the rotational levels before and after the perturbations. When the electronic motion

can be described approximately by the precession of a constant angular momentum about the figure axis, the components of the perturbation matrix can be completely calculated. For class B perturbations $\Lambda = \Lambda'$. The vibrational levels may be perturbed and there is no constant shift between the levels for high and low values of J .

IF, in the regular sequence of rotational levels of a molecule, one or several of these levels are displaced from their expected positions, such a phenomenon is called a perturbation. Very often the lines originating from these perturbed rotational levels show also abnormal intensities. Since Kronig¹ showed first the general rules for the occurrence of such perturbations, several cases have been investigated and were shown in accordance with Kronig's theory to result from the interaction of two rotational levels with the same J of two electronic states which accidentally come very close together. However, except demonstrating that the occurrence of the perturbations found was in agreement with Kronig's general rules, not much has been done in a further theoretical analysis of such perturbations. Therefore it may be useful to investigate in detail a particularly simple case, and show that the magnitude of the perturbations and all its other characteristics can be correlated with other properties of the levels. This case has been chosen because it is the simplest representative of one of the two classes of perturbations, and because it gives a key to the understanding of some peculiarities of the molecular spectrum of hydrogen. It is, however, of sufficient importance to merit a special treatment. The general treatment follows closely that of Van Vleck and Kronig. The chief aim of this paper is to bring out clearly the conditions under which the different types of perturbations can occur so that a clear theoretical background is available for the discussion of some empirical perturbations which will be given in a subsequent paper.

§1. GENERAL ASSUMPTIONS

An electronic state of a diatomic molecule can be specified by a number of quantum numbers. If we were dealing with electrons in a central symmetric field of force, the total orbital angular momentum would be constant and to it would correspond a quantum number L . In a real molecule, the orbital momentum is not constant, and therefore L not a true quantum number, but for higher levels of light molecules the deviations from a central symmetric field of force are not large enough to cause any trouble. The projection Λ of L on the internuclear axis is constant, no matter whether L is a good quantum number or not, if we can disregard the influence of the spin which we shall do throughout this paper.² Besides L and Λ , there may be several other quantum numbers, but they are not important for the following and we represent them collectively by n . It is well known that the term symbols S , P , $D \dots$ and Σ , Π , Δ mean that L and Λ , respectively, have the values 0, 1, 2, \dots .³ Of course we have always $\Lambda \leq L$. All the $L+1$ states (L of them double) belonging to a given n and L but different Λ are called a *complex*. On the electron motion of the molecule is superimposed the vibration characterized by the quantum

² We restrict ourselves therefore to singlet states. The results, however, will be also applicable to many cases where the multiplicity is different from one, but the spin so loosely coupled to the rest of the molecule that its influence can be neglected. It would not be difficult to take into account the spin also in the general case, but the example would lose then much of its simplicity.

³ In order to avoid difficulties about the internal coupling of the electrons, we may assume that L and Λ come from a single electron only, that therefore the rest of the molecule is in an $s\Sigma$ state. Some of the results apply also in more general cases, but the one stated is by far the simplest and most important one.

¹ R. de L. Kronig, *Zeits. f. Physik* 50, 347 (1928).

number V and the rotation characterized by the total angular momentum J and its projection m on an axis fixed in space. As we are not dealing with external forces, m is of no importance to us. Any given energy level is now specified completely by n, L, Λ, V and J .

In order that we may have a perturbation two energy levels must come very close together. They will have to be rotational levels belonging to two different electronic states. But the close proximity of two levels is not sufficient for a perturbation. It is necessary that the matrix component $S_{\tau\tau'}$ of a perturbing potential S must be different from zero, and we shall say that two states can perturb each other when that is the case. Kronig gave some general rules which restrict the number of perturbing pairs considerably, the chief one of these restriction rules is that J must be the same for both levels, the others we shall have to deal with later.

We can distinguish two distinct classes of perturbations. For *class A* perturbations, the perturbing force is caused by the rotation of the molecule, whereas for *class B* the perturbing forces have a different origin. Class B might again be subdivided into several subclasses, but that is unnecessary here as this paper will deal almost exclusively with class A perturbations. An investigation of the exact nature of this type of perturbations will be the subject of the rest of the paper. At the same time it will become apparent that the same cause is responsible for irregularities in the Λ -doubling observed in several molecules. These irregularities usually are not called perturbations because they are of a more systematic character. The regular Λ -doubling is also closely connected with this kind of interaction.

§2. THE HAMILTONIAN OF A DIATOMIC MOLECULE

The necessary foundation for a detailed treatment of the perturbations have been given in a very thorough paper by Van Vleck⁴ and therefore it is best to start with a brief résumé of Van Vleck's results with the necessary modifications and simplifications. The principle is that first the complete wave equation of the rotating and

oscillating diatomic molecule is set up. This equation can only be solved if certain small terms in the Hamiltonian are omitted. After an approximate solution of the simplified wave equation has been obtained, the result can be corrected by introducing the neglected terms as perturbing potentials and calculating their influence by the method of perturbations. The influence of these small terms will be in general small except possibly when two unperturbed levels fall close together. In that case perturbations in the special sense defined at the beginning of this paper may result.

If the nuclei of the molecule are kept fixed, i.e., if the molecule is not vibrating nor rotating, the motion of the electrons is determined by a Hamiltonian $H^{(0)}$ and the wave equation

$$(\mathbf{H}^{(0)} - W^{(0)})\Phi = 0. \quad (1)$$

Φ is a function of the coordinates of the electrons, and $\mathbf{H}^{(0)}$, $W^{(0)}$ and Φ contain the internuclear distance r as a parameter. Φ is represented by as many quantum numbers as there are degrees of freedom. It depends in a very simple way on χ , the azimuth about the internuclear axis. We have

$$\begin{aligned} \Phi^+_{n, L, \Lambda} &= \varphi_{n, L, \Lambda} \cos \Lambda \chi, \\ \Phi^-_{n, L, \Lambda} &= \varphi_{n, L, \Lambda} \sin \Lambda \chi, \end{aligned} \quad (2)$$

in which φ is independent of χ . The energy belonging to Φ^+ and Φ^- is the same. For $\Lambda=0$ there is only one term Σ^+ with $\Phi^+_{n, L, \Lambda}$.⁵

If the molecule is left to rotate and vibrate freely, three degrees of freedom are added which are represented by the internuclear distance r , the angle θ which the internuclear axis makes with a fixed direction in space, and φ , the azimuth about this axis. If the very small motion which the center of gravity of the nuclei makes with respect to the center of gravity of the total mole-

⁵ Because of the degeneracy for the molecule with fixed nuclei, which is due to the fact that the energy is not changed if the sense of rotation of all the electrons is reversed any linear combination of Φ^+ and Φ^- would serve just as well. The particular form (2) is most useful because it must be taken if the degeneracy is removed by the interaction of electron motion and rotation. Φ^+ remains unchanged and Φ^- changes its sign when the sense of the electron motion is reversed. If there is more than one electron we may also have Σ^- terms. We prefer to write here Π^+ and Π^- , etc., rather than the more customary Π_c and Π_d because the latter, more empirical, designation does not always make it quite clear which of the two doublet components belongs to the $\cos \Lambda \chi$ and which to the $\sin \Lambda \chi$.

⁴ J. H. Van Vleck, Phys. Rev. 33, 467 (1929).

cule (electrons included) is neglected, the wave equation becomes

$$\left\{ \mathbf{H}^0 - \frac{\hbar^2}{8\pi^2\mu r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \text{ctg } \theta \left(\frac{\partial}{\partial \theta} - i\mathbf{M}_\xi \right) + \left(\frac{\partial}{\partial \theta} - i\mathbf{M}_\xi \right)^2 + \text{cosec}^2 \theta \left(\frac{\partial}{\partial \varphi} - i \sin \theta \mathbf{M}_\eta - i \cos \theta \mathbf{M}_\zeta \right)^2 \right] - W \right\} \psi = 0. \quad (3)$$

\mathbf{M}_ξ , \mathbf{M}_η and \mathbf{M}_ζ are operators corresponding to the ξ , η and ζ components of the angular momentum with respect to a coordinate system moving with the molecule. This equation is valid also if the spin is included, but in our case \mathbf{M} represents the *orbital* angular momentum only.

A direct solution of (3) is obviously impossible. An approximate solution can be obtained by neglecting certain terms so that a separation of the variables is possible. We can write then

$$\psi = \Phi u(\varphi, \theta) R(r). \quad (4)$$

(4) is the solution of the approximate equation

$$(\mathbf{H}^{(0)} + \mathbf{H}^{(1)} + \mathbf{H}^{(2)} - W)\psi = 0, \quad (5)$$

whereas (3) is equivalent to

$$(\mathbf{H}^{(0)} + \mathbf{H}^{(1)} + \mathbf{H}^{(2)} + \mathbf{H}^{(3)} + \mathbf{H}^{(4)} - W)\psi = 0, \quad (6)$$

which contains the two extra terms $\mathbf{H}^{(3)}$ and $\mathbf{H}^{(4)}$

$$\mathbf{H}^{(1)} = -B[\text{ctg } \theta \partial/\partial \theta + \partial^2/\partial \theta^2 + \text{cosec}^2 \theta (\partial/\partial \varphi - i\Lambda \cos \theta)^2], \quad (7a)$$

$$\mathbf{H}^{(2)}\psi = -B\Phi u(\partial/\partial r)(r^2 \partial R/\partial r), \quad (7b)$$

$$\mathbf{H}^{(3)} = B i [\text{ctg } \theta (\mathbf{M}_\xi - i\mathbf{M}_\eta \mathbf{M}_\zeta - i\mathbf{M}_\zeta \mathbf{M}_\eta) + 2 \text{cosec } \theta \mathbf{M}_\eta \partial/\partial \varphi + 2\mathbf{M}_\xi \partial/\partial \theta], \quad (7c)$$

$$\mathbf{H}^{(4)}\psi = B \left[(\mathbf{M}_\xi^2 + \mathbf{M}_\eta^2) \Phi - 2r \frac{\partial \Phi}{\partial r} - r^2 \frac{\partial^2 \Phi}{\partial r^2} - \frac{2r^2}{R} \frac{\partial R}{\partial r} \frac{\partial \Phi}{\partial r} \right] R u, \quad (7d)$$

$B = \hbar^2/8\pi^2\mu r^2$ is also a function of r .

The procedure in solving (5) is as follows: First solve (1)

$$(\mathbf{H}^{(0)} - W^{(0)})\Phi = 0,$$

which gives the electronic energy W^0 and wave function Φ both containing the parameter r . Then solve

$$(\mathbf{H}^{(1)} - W^{(1)})u = 0, \quad (8)$$

from which we obtain the rotational energy

$$W^{(1)} = B[J(J+1) - \Lambda^2], \quad (9)$$

which also contains r as parameter and the rotational wave function⁶ $u(\varphi, \theta)$ which is independent of r . The next step is the solution of

$$[\mathbf{H}^{(2)} + W^{(1)}(r) + W^{(0)}(r) - W]R = 0. \quad (10)$$

This gives the vibrational eigenfunction R and the total energy W of the approximated molecule. We have reached now the same stage of approximation which is employed in the elementary theory of band spectra in which $W(r)$ is assumed to be given as a power series in $r - r_0$ (r_0 is the equilibrium distance). We have then the energy as function of the total angular momentum J and the vibrational quantum number V .

$$W = W_0 + \sum_{l, k} Y_{lk} (V + \frac{1}{2})^l [J(J+1) - \Lambda^2]^k. \quad (11)$$

This is for $\Lambda = 0$, the familiar expression for the energy of a rotating anharmonic oscillator.⁷

§3. OCCURRENCE OF CLASS A PERTURBATIONS

We can take care now of the terms $\mathbf{H}^{(3)}$ and $\mathbf{H}^{(4)}$ neglected so far by considering them as perturbing potentials. $\mathbf{H}^{(4)}$ is independent of the rotational coordinates and therefore any perturbations resulting from it will be of class B. We shall not be any further concerned with perturbations of this type in this paper. The matrix elements $H_{rr}^{(4)}$ are different from zero under almost

⁶ The $u(\varphi, \theta)$ are the well-known wave functions of the symmetrical top as (7a) represents the Hamiltonian of the symmetrical top.

⁷ Except for terms of higher order (11) is identical with the approximate expression

$$W = W_0 + \omega_e (V + \frac{1}{2}) - x (V + \frac{1}{2})^2 + \dots + [B_e - \alpha (V + \frac{1}{2})][J(J+1) - \Lambda^2].$$

W_0 is the electronic energy, i.e., the eigenvalue of (1) for the value $r = r_0$ of the parameter and is independent of the masses of the nuclei. As can be easily seen from the derivation sketched above, the higher terms in J are of the form $[J(J+1) - \Lambda^2]^k$ and not simply $J^k(J+1)^k$, as is usually found. For most practical purposes, however, the difference is negligible. The coefficients Y_{lk} have been calculated to a high approximation by Dunham (Phys. Rev. **41**, 721 (1932)).

the same conditions as those of $\mathbf{H}^{(3)}$ (see below). The essential difference is that we must have $\Lambda' = \Lambda$ for $\mathbf{H}^{(4)}$ whereas we have $\Lambda' = \Lambda \pm 1$ for $\mathbf{H}^{(3)}$.⁸

In order to calculate the influence of $\mathbf{H}^{(3)}$, we have to know the matrix components

$$S_{\tau\tau'} = H^{(3)}_{\tau\tau'} = \int \psi_{\tau}^* S \psi_{\tau'} dv. \quad (12)$$

We write from now on S instead of $\mathbf{H}^{(3)}$ for the perturbing potential in order to avoid writing too many indices. The integration is extended over all the electronic coordinates, the internuclear distance r , and the rotational coordinates φ and θ . As Kronig showed first, and as can be verified easily, from (12) and (7c) by taking the nature of the wave functions into account, the matrix components $S_{\tau\tau'}$ are different from zero only if the two states τ and τ' fulfill the following conditions.

- (a) Both levels must have the same value of J .
- (b) Both levels must be positive or both negative.
- (c) If the two nuclei are identical, both levels must be even or both odd; furthermore, both must be symmetrical or both antisymmetrical.

These conditions are based entirely on the symmetry properties of the molecule and do not involve any further assumptions.

The integration in (12) over the rotational coordinates can be separated from that over the other coordinates, so that the integral can be split into two factors, one of which is independent of J . If we call it α then Van Vleck showed that

$$S_{\tau\tau'} = \alpha [(J + \frac{1}{2} - \bar{\Lambda})(J + \frac{1}{2} + \bar{\Lambda})]^{\frac{1}{2}}, \quad (13)$$

$$\alpha(n, L, \Lambda, V; n', L', \Lambda', V') = 2(BM_{\eta})_{n, L, \Lambda, V; n', L', \Lambda', V'}, \quad (14)$$

in which $2\bar{\Lambda} = \Lambda + \Lambda'$.

(13) and (14) are still quite general, but in order to go further it is convenient to consider some specialized cases.

1. Assume that the influence of the internuclear axis is comparatively weak. Then the angular momentum M has a constant magnitude L and precesses about the internuclear axis. Let us assume further that the angle which M makes

with the internuclear axis has no effect on the equilibrium position, i.e., that r_0 is independent of Λ . Then

$$M_{\eta}(n, L, \Lambda, V; n, L, \Lambda \pm 1, V) = \frac{1}{2} [L(L+1) - \Lambda(\Lambda \pm 1)]^{\frac{1}{2}} \quad (15)$$

and all other matrix components are zero. In that case α is zero except when $n = n'$, $L = L'$, $V = V'$, and $\Lambda' = \Lambda \pm 1$.

$$\alpha(n, \Lambda, V; n, \Lambda \pm 1, V) = B_V [L(L+1) - \Lambda(\Lambda \pm 1)]^{\frac{1}{2}}. \quad (16)$$

This gives the regular Λ -doubling, as levels which differ only by the quantum number Λ , can never come accidentally close together. Perturbations, therefore, cannot occur.

2. Assume that the motion is still a regular precession of the constant angular momentum about the figure axis, but that the equilibrium internuclear distance r_0 depends on Λ . In that case (15) still holds true, but

$$B_{VV'} = \int RBR'r^2 dr$$

is not even approximately diagonal as R' belongs to a different equilibrium distance than R . We have here a case very similar to that found when the Franck-Condon principle is applied to the matrix components of the electric moment. As long as the equilibrium distance is affected only slightly by the value of Λ the nondiagonal elements of B will be small compared with the elements diagonal in V .

We have now

$$\alpha(n, L, \Lambda, V, n, L, \Lambda \pm 1, V') = [B_{VV'} + (r_0' - r_0) \int BR'R(\partial\Phi/\partial r)_{r=r_0} \Phi dv] \times [L(L+1) - \Lambda(\Lambda \pm 1)]^{\frac{1}{2}}. \quad (17)$$

$B_{VV'}$ can be completely calculated if the rotational and vibrational structure of the two perturbing states is known. In general it will be small compared with (16) if $V \neq V'$, and the term in $r_0' - r_0$ will be small compared to $B_{VV'}$ and can be neglected in first approximation.

It may happen now that the levels of n, L, Λ, V and $n, L, \Lambda \pm 1, V'$ come very close together. For instance in H_2 we have that the $p\Pi$ levels lie several thousand cm^{-1} above the corresponding

⁸ In contrast to $\mathbf{H}^{(3)}$ there are also diagonal elements in $\mathbf{H}^{(4)}$. Their significance has been discussed elsewhere. (G. H. Dieke, Phys. Rev. 47, 661 (1935)).

$p\Sigma$ levels and a high vibrational level of $p\Sigma$ can come very close to a low vibrational level of $p\Pi$. The magnitude and character of the perturbations in such a case can then be completely predicted. It is also apparent that if the rotational states of two such vibrational levels do not actually cross over (see §4) but are close enough that they influence each other notwithstanding the small value of α , irregularities in the Λ -doubling must occur which do not have the character of typical perturbations. From what was said above, we must expect such irregularities to be more pronounced when the equilibrium distance is much affected by the value of Λ .

3. In heavy molecules the motion may be different from a regular precession of a constant angular momentum about the figure axis. In that case (15) does not hold any more and neither the restriction $n'=n$ nor $L=L'$ can be used any longer. However, the restriction $\Lambda'=\Lambda\pm 1$ will still hold true as long as the dependence on the azimuth χ about the internuclear axis is given by (2), i.e., as long as everything is symmetrical about the internuclear axis. As soon as this symmetry is disturbed, e.g., by the rotation of the molecule, deviations from the Λ -restriction rule must be expected.⁹ Levels can perturb each other now even though their L or n are different. A calculation of the perturbation matrix is then only possible with a more detailed knowledge of the wave function. Very often we can know that the deviations from the motion under 2 cannot be very large, and in that case we can be sure that the interaction elements which are absent in case 2 will be small now.

§4. THE PERTURBATIONS AS FUNCTIONS OF J

We shall investigate now a little more in detail the influence of the perturbation due to $\mathbf{H}^{(3)}$ on the rotational energy levels. We saw that ordinarily the elements of the perturbation matrix are large only when the two levels perturbing each other have all quantum numbers identical except that their value of Λ differs by ± 1 . Such states are far apart except for the

⁹ This disturbance of the symmetry about the internuclear axis which results in the L -decoupling will be much more effective in the cases 1 and 2 and therefore the deviations from the Λ -restriction rule will be more pronounced in these cases. A case where this happens is given in §5.

higher levels of light molecules. But even in the latter case there can be no crossing over. (By crossing over is meant that if the levels of the first state are below those of the second state for small values of J , they are above them for large values of J . For intermediate values then they must come very close together and cross over.) We do not have perturbations in the proper sense in this case, but the regular Λ -doubling which is called L -decoupling, when it is very large owing to the proximity of the two states. Although these phenomena are due to exactly the same causes as the real perturbations and there are transition cases between them, they are distinguished from them, because they seem more systematic in character, whereas the real perturbations seem always erratic at a first glance. The reason for this is that the perturbing matrix elements are so much smaller that their influence is not felt, except when the two perturbing states are very close together.

If we are interested in the perturbations of a given state we can restrict ourselves, therefore, on the influence of only those states able to interact with it which are very close. Except for rare cases of coincidence we have, therefore, to consider only one pair of interacting states and shall differentiate them by indices 1 and 2. As the changes in the energy due to the perturbations may be of the order of the distance between the perturbing levels, we must apply the perturbation theory for semidegenerate states. If we call ϵ the energy shift due to the perturbations and δ the energy difference between the unperturbed levels we have

$$\begin{vmatrix} S_{11}-\epsilon & S_{12} \\ S_{21} & S_{22}+\delta-\epsilon \end{vmatrix} = 0 \quad (18)$$

or in the case of class A perturbations for which $S_{11}=S_{22}=0$

$$\epsilon = \delta/2 \pm (|S_{12}|^2 + \delta^2/4)^{1/2}.$$

If δ is taken positive and ϵ' and ϵ'' are the roots with the negative and positive sign of the square root, respectively, the perturbed energies are

$$W_1 + \epsilon' \quad \text{and} \quad W_1 + \epsilon'' = W_2 + \epsilon'' - \delta = W_2 - \epsilon'.$$

The perturbations of the two levels are of equal

magnitude and opposite sign, so that the levels seem to repel each other. For $\delta \gg |S_{12}|$ we have

$$\epsilon' = - |S_{12}'|^2 / \delta. \quad (19)$$

The maximum disturbance occurs when the unperturbed levels coincide. In this case $\epsilon_0 = \pm |S_{12}|$.

The wave functions belonging to the two perturbed levels are linear combinations of the unperturbed ones

$$\begin{aligned} \psi_1' &= a_{11}\psi_1 + a_{12}\psi_2, \\ \psi_2' &= a_{21}\psi_1 + a_{22}\psi_2, \end{aligned} \quad (20)$$

and the coefficients a_{ij} are the solutions of the linear equations

$$\begin{aligned} (S_{11} - \epsilon)a_{11} + S_{12}a_{12} &= 0, \\ S_{21}a_{11} + (S_{22} + \delta - \epsilon)a_{22} &= 0. \end{aligned}$$

As in all similar cases the values of the coefficients are for the limiting cases

$$\begin{aligned} a_{11} = a_{22} = 1; \quad a_{12} = a_{21} = 0 \quad \text{for } \delta \gg |S_{12}|, \\ a_{11} = a_{12} = a_{21} = -a_{22} = 1/\sqrt{2} \quad \text{for } \delta = 0. \end{aligned}$$

The first of these relations means that when the two states do not perturb each other appreciably, the perturbed states are identical with the unperturbed ones. When the interaction is not negligible either perturbed state acquires because of (20) the properties of both unperturbed states. For $\delta = 0$ these properties are shared in equal parts. The amplitudes of the electric moment become

$$\begin{aligned} P_1' &= \int \psi_1'^* P \psi_1' dv = a_{11}P_1 + a_{12}P_2, \\ P_2' &= \int \psi_2'^* P \psi_2' dv = a_{21}P_1 + a_{22}P_2, \end{aligned}$$

from which it follows that the intensities are proportional to

$$\begin{aligned} I_1 &= a_{11}^2 I_1 + a_{12}^2 I_2 + 2a_{11}a_{12}I_{12}, \\ I_2 &= a_{21}^2 I_1 + a_{22}^2 I_2 + 2a_{21}a_{22}I_{12}, \end{aligned} \quad (21)$$

in which $I_1 = |P_1|^2$, $I_2 = |P_2|^2$ and I_{12} the real part of $P_1^* P_2$. Always we have, as the matrix of the a_{ij} is a unitary matrix,

$$I_1' + I_2' = I_1 + I_2,$$

but the intensities of the two individual lines

may have any value between 0 and $I_1 + I_2$ depending on the particular value of the a_{ij} and of P_1 and P_2 .

As is well known everything in this paragraph so far applies equally well to any kind of interaction. We shall apply this now to our special case for which the perturbation matrix is given by (13).

We can write with sufficient approximation

$$W_i = A_i + B_i J(J+1) \quad (22)$$

or $\delta = A_2 - A_1 + (B_2 - B_1)J(J+1) = a + bJ(J+1)$.

If a is positive b must be negative to have a perturbation. For large δ this gives (18)

$$\epsilon' = \alpha^2 \frac{(J + \frac{1}{2} - \bar{\Lambda})(J + \frac{1}{2} + \bar{\Lambda})}{a + bJ(J+1)}. \quad (23)$$

Let us simplify matters still further by restricting ourselves to Σ , Π perturbations for which $\bar{\Lambda} = \frac{1}{2}$. Then

$$\epsilon' = \alpha^2 J(J+1) / (a + bJ(J+1)). \quad (24)$$

If a is sufficiently large the perturbation is negligible for small values of J . For $J=0$ it is exactly zero which can be seen also without any calculation, as there is a level with $J=0$ only for the Σ state which cannot interact with any level of the Π state. For large values of J we have $\epsilon' = -\alpha^2/b$.

We have therefore the following picture: Let us assume that the two states cross over near a certain value J_0 of J . For $J \ll J_0$ the influence of the perturbation is negligible. The rotational levels are represented by the ordinary quadratic formula (21). The vibrational level which is obtained by extrapolation to $J=0$, can therefore never show any perturbation.

For very large values of J the influence of the perturbation does not disappear, however large the distance between the unperturbed levels may become. The reason for this is that the perturbing forces are originated by the rotation of the molecule itself and increase with increasing angular velocity. For large J the interaction results in the constant term α^2/b in the energy so that also in this case the rotational levels are represented by a simple quadratic formula. They are shifted however by the constant amount α^2/b with respect

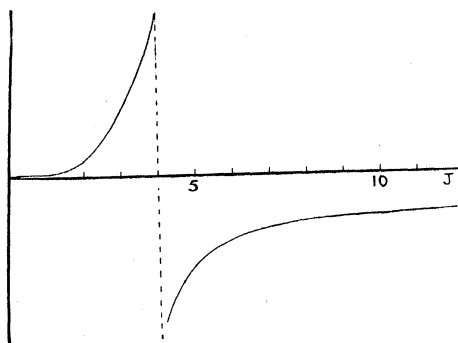
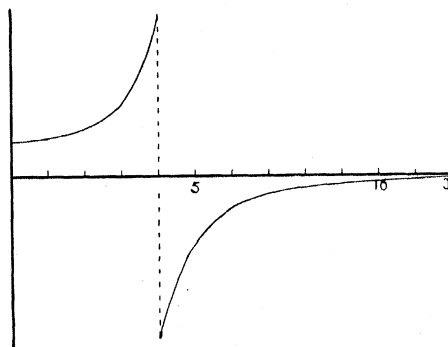
FIG. 1. Class A perturbation. Maximum at $J=4$.

FIG. 2. Class B perturbation. It has a maximum of the same magnitude and at the same place as the perturbation in Fig. 1.

to the levels for low J . In the vicinity of J_0 the levels show strong deviations from the quadratic formula and the lines originating from them may have abnormal intensities.

The occurrence of the constant shift of magnitude α^2/b for large J may be used as a criterion for differentiating between class A and class B perturbations. (See Figs. 1 and 2.) For class B perturbations there is no such constant shift, and the influence of the perturbation disappears completely for large J .

Also for small J the two classes, as we saw above, may show a pronounced difference. Class A perturbations are small for small J and must be completely absent, e.g., in the $J=0$ Σ level. The vibrational levels which are obtained by extrapolating the rotational states to $J=0$ can therefore never be perturbed. For class B perturbations there are no such restrictions and as in Fig. 2, the vibrational level can be perturbed.

§5. COMPARISON WITH EXPERIMENTAL DATA

Unfortunately the empirical material for testing the results of the preceding paragraph is extremely limited. There are only a few cases known in which both perturbing levels have been investigated. Of these, most represent more com-

plicated cases. The best examples are the perturbations between the $p^3\Pi$ and $p^3\Sigma$ levels of the hydrogen molecule. They will be treated fully elsewhere. The numerous perturbations found in the levels of the CO molecule are complicated by the fact that several perturbations come close together and make accurate calculations impossible.

The perturbations of the He_2 levels¹⁰ offer an interesting example. They are perturbations between $ns\Sigma$ and $nd\Sigma$ levels. As $\Lambda'=\Lambda$ one might think that these perturbations must be of class B . But the fact that there seems to be a constant displacement between the levels with low J values and those with high J values suggests that we may have here nevertheless class A perturbations. This seems to contradict the Λ restriction rule. But as the $d\Sigma$ levels show almost complete L -decoupling, their wave function is a linear combination of the ψ 's of a $d\Sigma$, $d\Pi$ and $d\Delta$ state each depending on χ according to (2). The $d\Pi$ part can produce perturbations with the $s\Sigma$ levels. Because of the L -decoupling of $d\Sigma$ the exact dependence on J is somewhat different from the case treated in §4 and the experimental data are too meager to warrant going further into this.

¹⁰ G. H. Dieke, Phys. Rev. **38**, 646 (1931).