PERTURBATIONS IN MOLECULES AND THE THEORY OF PREDISSOCIATION AND DIFFUSE SPECTRA[1]

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Abstract

It has been recognized for some time that, when the discrete vibration rotation absorption bands connected with transitions to a certain final electronic state of a molecule overlap the continuous region for the transitions to another final electronic state, some of the discrete bands may be diffuse, i.e., the rotation lines may be broad and blur into each other. The broadness of the lines has previously been assumed to be connected with the short life period of a molecule in a discrete state, when there is the possibility of its making a radiationless transition to a state of dissociation. In this paper a calculation is made of the width directly. One starts with a wave equation which represents approximately the state of a molecule, and which has continuous and discontinuous groups of eigenfunctions. Then the extra terms in the *exact* wave equation may be treated in the usual manner as a perturbation, and the perturbed eigenfunctions may be expressed as a linear function of the unperturbed ones. The energy range over which the properties of a given discrete state may influence the properties of the perturbed eigenfunctions is determined in terms of the perturbation matrix components, and from this is found the width of the line and the total absorption over its width.

I T HAS been recognized for some time that, when a molecule is raised by absorption of light to an excited state from which subsequent decomposition may occur, the resultant vibration bands may be diffuse, i.e., the rotation lines may be broad and blur into each other.[3] Several recent writers [4] have described the situation more specifically as follows. The molecule is originally in some initial state, with definite electronic, rotational, and vibrational quantum numbers. Through the absorption of radiation it jumps to a higher electronic state, changing at the same time its vibrational and rotational quantum numbers (the rotational in accordance with a selection principle). The upper electronic state has a certain dissociation limit; for smaller energies than the energy of dissociation there is a discrete set of vibration-rotation levels, for larger energies a continuous set. In the cases where predissociation occurs there are *two* higher electronic states to which the molecule might jump, and some of the discrete vibration-rotation levels of one of these electronic states have their energies in the continuous range for the other electronic state. The broadness of the lines has been connected with the short life period of a molecule in a discrete state, when there is the possibility of its making a radiationless transition

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[3] Henri and Teves, Nature **114**, 894 (1924).

[4] Bonhoeffer and Farkas, Zeits. Phys. Chem. **134**, 337 (1928); Kronig, Zeits. f. Physik **50**, 360 (1928).

to a state of dissociation. For example, Kronig[4] assumes that the bands will be diffuse if the life period of the molecule in its discrete state is shorter than its period of rotation. This assumption was originally made by Henri and Teves,[3] and a similar assumption was made by Wentzel[5] to explain the broadening of spectral lines. The work of Wentzel,[5] Fues,[6] and Kronig[4] supplies a means of calculating the life period on the basis of wave mechanics. It is the purpose of this paper to make a calculation of the width of the line directly in terms of the perturbation matrices without employing the assumption connecting width and life period. The total absorption over the line is also calculated. For the sake of simplicity we will consider only diatomic molecules.

To describe the molecule let us take as a first approximation a wave equation whose eigenvalues are such that they may be associated with the three electronic states (the initial state and the two final ones), and whose eigenfunctions in the region where the overlapping of discrete and continuous states occurs are of two distinct types, corresponding respectively to the discrete and continuous states. We write this approximate wave equation as follows:

$$(H-E)\psi=0 \tag{1}$$

where H is the usual Hamiltonian operator, E the energy, and ψ the wave function, the eigenfunctions (with the time left out) being designated, say, as ψ_n and the corresponding eigenvalues as E_n. Though the eigenfunctions, as stated, are of two distinct types, continuous and discrete, it will be found convenient to treat them all as if they belonged to discrete states (though still using the terms continuous and discrete to distinguish the two types). This may be done if we have the system enclosed in a box. The normalization will then be such that $\int\psi_n^2 d\tau=1$ (where $d\tau$ is a volume element, and the integration is to be taken over all allowable values of the coordinates) whether ψ_n belongs to a discrete or a continuous state.

If now we set up an equation to represent conditions *exactly* it may be considered as a perturbed form of Eq. (1), and, as the exact equation is linear in ψ, it may be written in the form[7]

$$(H-E+V)\psi=0 \tag{2}$$

where V is a perturbation function (or operator). Then this equation will have a series of eigenvalues E_n' with corresponding eigenfunctions ψ_n'. We shall see later that these eigenvalues form a continuous set (the distance between eigenvalues being determined by the size of the box) and the eigenfunctions, unlike the unperturbed eigenfunctions, are essentially of but one type, but their properties vary continuously with E_n'; and it is this

[5] Wentzel, Zeits. f. Physik **43,** 524 (1927).

[6] Fues, Zeits. f. Physik **43,** 726 (1927).

[7] Sometimes it cannot be put in this form, but the perturbation theory remains essentially unaltered. See, e.g., Kronig, Reference 4, p. 353; Slater, Proc. Nat. Acad. Sci., **13,** 423 (1927). These cases are included in our formulation if V operates specifically on each ψ_k in Eq. (4).

variation we wish to consider as it will show us how the perturbation produces the broadening of the lines.

The matrix component of the electric polarization P determining the probability of transition from one of the initial states,[8] ψ_0, to one of the final states is $\int \psi_0 P \psi_n' d\tau$. Since ψ_0 refers to a discrete state, in which there is no tendency for dissociation to occur, it will have appreciable values only if the distance between the nuclei r lies approximately within the limits of the classical range of vibration. Thus we are interested in the values of ψ_n' only for r of the order of molecular dimensions, since if r is large the integrand will be negligible anyhow. So we may now be more specific, and say that we wish to find out how ψ_n' (for such values of r) varies when E_n' varies in the neighborhood of a discrete state, for this will tell us over what range of energies a particular discrete state is of importance in determining the properties of the perturbed eigenfunctions.

APPLICATION OF PERTURBATION THEORY

The ψ_n form a complete orthogonal set, and it will be possible to expand the ψ_n' in terms of them, as a linear expression with constant coefficients, thus:

$$\psi_n' = \Sigma_k S_{kn} \psi_k \tag{3}$$

This sum is to be taken over both discrete and continuous unperturbed states. Substituting Eq. (3) into Eq. (2) gives

$$(H - E_n') \Sigma_k S_{kn} \psi_k + V \Sigma_k S_{kn} \psi_k = 0 \tag{4}$$

Now let us set

$$V \psi_k = \Sigma_i v_{ik} \psi_i \tag{5}$$

v_{ik} is the matrix component (without the exponential time factor) of V, and is given by

$$v_{ik} = \int \psi_i V \psi_k d\tau \tag{6}$$

Eq. (4) becomes, with the use of Eq. (5), and remembering that $H \psi_k = E_k \psi_k$,

$$\Sigma_k S_{kn} (E_k - E_n') \psi_k + \Sigma_k S_{kn} \Sigma_i v_{ik} \psi_i = 0 \tag{7}$$

Interchanging the dummy subscripts i and k and rearranging the last term, we get

$$\Sigma_k S_{kn} (E_k - E_n') \psi_k + \Sigma_k \psi_k \Sigma_i S_{in} v_{ki} = 0. \tag{8}$$

The coefficients of all ψ_k must be zero. Thus

$$S_{kn} (E_k - E_n') + \Sigma_i S_{in} v_{ki} = 0. \tag{9}$$

[8] Since there is no other electronic state for the initial state to interact with, it makes no essential difference whether we take a perturbed or unperturbed eigenfunction for the initial state.

There is an infinite number of these equations, each with an infinite number of terms, for every value of E_n'. Complete solution of the problem demands a simultaneous solution of these homogeneous equations for the S_{kn}, and a discovery of the values of E_n' which allow such a solution with the S_{kn} different from zero. We can, however, greatly reduce the complexity of the problem by means of two simplifying assumptions, and some approximations, which we now proceed to make and explain.

Assumptions and Approximations

To avoid circumlocution we shall begin by defining an isorotational set of quantum states as all those states which have the same nuclear-rotational quantum numbers. We shall designate quantities referring to states of specific isorotational sets by sub-subscripts; thus, $v_{k_m i_p}$ means that k refers to some state in the m isorotational set, and i refers to some state in the p isorotational set.

Our first simplifying assumption may then be stated thus:

$$v_{k_m i_p} = 0, \quad \text{unless} \quad m = p. \tag{10}$$

Looking at the matter from the point of view of Wentzel[5] and Kronig[4] we may express this by saying that we get no radiationless transitions in which the nuclear-rotational quantum numbers change. All the consequences of this assumption hold if the rotational quantum numbers change, but by a definite amount. Thus extended it is an assumption which is very probably true in all cases.[9]

We shall now consider the consequences of this assumption. Under it, the equations (9) break up into sets, which we may call isorotational sets of equations, thus:

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\begin{aligned}
S_{k_1 n}(E_{k_1} - E_n') + \Sigma_{i_1} S_{i_1 n} v_{k_1 i_1} = 0 \qquad (9_1) \\
S_{k_2 n}(E_{k_2} - E_n') + \Sigma_{i_2} S_{i_2 n} v_{k_2 i_2} = 0 \qquad (9_2) \\
\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot
\end{aligned}
\right\} \tag{9'}
$$

(9_1), (9_2), etc., each still represent an infinite number of equations. The values of E_n' which make possible a solution[10] of (9_1) (we designate these values as E_{n_1}', and call them an isorotational set of perturbed eigenvalues) will not in general[11] make possible a solution of (9_2) with values of the $S_{k_2 n}$

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[9] It is true, for example, in the case of the perturbations considered by Kronig (Reference 4, p. 361). It is also true if the coordinates giving the orientation of the line joining the nuclei are separable, and V does not depend on them. If it did not hold the selection principle governing the possible changes in the rotational quantum number on absorption of light would be destroyed. This would probably be the most important change, though the question might be investigated further; this, however, in the opinion of the writer, would not be a very fruitful thing to investigate.

[10] These values are perfectly definite, and are later found.

[11] Actually the case we are considering is degenerate, and the rotation lines are multiple, but we could imagine the degeneracy removed by a very small external field. The procedure we follow will give us the broadening of a selected component of a rotation line, which is probably the same as that of any other of the components, since the perturbation matrices involving the various components of a given rotation level are probably all the same.

different from zero (etc.). Hence, corresponding to the various sets, E_{n_1}', E_{n_2}', etc., we get the following sets of equations for ψ_{n_1}', ψ_{n_2}', etc., respectively

$$\psi_{n_1}' = \Sigma_{k_1} S_{k_1 n_1} \psi_{k_1} \qquad (3_1)$$

$$\psi_{n_2}' = \Sigma_{k_2} S_{k_2 n_2} \psi_{k_2} \qquad (3_2)$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \qquad\qquad\qquad (3')$$

The ψ_{n_1}', ψ_{n_2}', etc., will not be related to each other, and each isorotational set will produce a distinct spectrum. In general the values of E_{n_1}' will not coincide but will interlace with the values of E_{n_2}', and hence the various spectra will be superimposed upon each other. The eigenfunction of any one of the discrete vibration rotation states will of course appear on the right hand side of only one of the isorotational sets (3'), i.e., the set corresponding to the appropriate rotational quantum numbers. Hence any apparent broadening of a line for which such a level is the final state in the transition will depend solely on the properties of one of the isorotational sets of ψ_n'. Hence we investigate the properties of one[11] such set, say the ψ_{n_1}'. The resultant of all the superimposed spectra will appear diffuse if a line is as wide as the distance between two rotation lines of the same vibration band.

This allows us to make another approximation which further simplifies matters. Since there is but one state per vibration band in any isorotational set of discrete states, the discrete states in the sum on the right hand side of (3_1) are a distance apart of the order of the heads of the vibration bands. Since this is ordinarily large compared to the distance between rotation lines it appears that we may neglect all the discrete states in that sum except one if we are interested in the broadening of some one line (as we will not be interested in the actual width of the line if it is so broad that the band is diffuse). The one discrete state which is of importance we distinguish by the subscript d_1.

We can also make an approximation regarding the continuous states which appear in the sum on the right hand side of (3_1). These states all have, of course, the same electronic as well as the same nuclear-rotational quantum numbers. Furthermore, (as will appear later—Eq. (21)) the $S_{k_1 n_1}$ will only be appreciable, in the expression for any ψ_{n_1}', if their E_{k_1} come in an extremely small energy range. Since the continuous ψ_{k_1} which contribute appreciably to any ψ_{n_1}' differ thus only in the vibrational quantum number and very slightly in that, it is safe to consider them all equal, say to ψ_{c_1}, as long as r is small.[12] The ψ_{c_1} thus obtained will depend upon the particular ψ_{n_1}' we are considering, but even here the change will be slight over an energy range equal to the energy between two rotation lines, and for our purposes we may neglect it.

We may thus write (3_1) (for small values of r) in the form

$$\psi_{n_1}' = S_{d_1 n_1} \psi_{d_1} + \psi_{c_1} \Sigma'_{k_1} S_{k_1 n_1}. \qquad (11)$$

[12] As we let r increase a difference in phase will develop between the eigenfunctions belonging to neighboring energy levels, and this may be expected to be the chief difference between these eigenfunctions.

where now the discrete term is separated out and not included in the sum, as indicated by the accent on the summation sign, and ψ_{c_1} is taken outside the summation sign. The purposes of this paper can be accomplished if we can find the values of $S_{d_1 n_1}$ and $\Sigma'_{k_1} S_{k_1 n_1}$ for different values of E_{n_1}' in the neighborhood of the discrete state. This concludes the discussion of our first assumption with the accompanying approximations and simplifications.

Our second simplifying assumption is that the integrand of Eq. (6) is appreciable only for small values[13] of r (molecular dimensions). Then remembering that for such values of r all continuous ψ_{k_1} are equal to the definite function ψ_{c_1}, we see that if s_1 and t_1 refer to two continuous states, we have

$$v_{s_1 t_1} = v_{s_1 s_1} = v_{c_1 c_1}$$

$$v_{d_1 s_1} = v_{d_1 c_1} \tag{12}$$

$$v_{s_1 d_1} = v_{c_1 d_1}.$$

If V is not an operator but only a multiplier we also have $v_{c_1 d_1} = v_{d_1 c_1}$; but if V is an operator this is not necessarily true, at least, *a priori*.

Later another simplifying assumption is made which concerns the size of $v_{c_1 c_1}$ (see Appendix I).

OTHER PROPERTIES OF THE PERTURBATION MATRIX—NORMALIZATION CONSIDERATIONS

We will also need other properties of the v's which depend upon the normalization of the unperturbed eigenfunctions. The unperturbed Eq. (1) will be taken of such a form that we may set $\psi_k = \Theta_k R_k$ where Θ_k depends only on the electronic and nuclear-rotational coordinates, (except that r enters as a parameter) while the only variable which enters R_k is the distance of the nuclei, r (though R_k depends also on the quantum numbers involved in Θ_k); also, if $F_k = r R_k$ we may write[14]

$$\frac{d^2 F_k}{dr^2} + \left[\frac{8\pi^2 M}{h^2}(E_k - U) - \frac{\sigma}{r^2} \right] F_k = 0. \tag{13}$$

Here M is the reduced mass, h Planck's constant, E_k the unperturbed eigenvalue, as before, U a function of r (the potential energy), and σ a constant depending on the quantum numbers involved in Θ_k. We shall suppose that Θ_k is so normalized that $\int \Theta_k^2 d\tau' = 1$ where $d\tau'$ includes all the coordinates except r. Then the final normalization depends on the equation $\int_0^{r_1} R_k^2 r^2 dr = 1$, or $\int_0^{r_1} F_k^2 dr = 1$, where r_1 is the largest possible value of r. We may vary

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[13] In the case of $v_{d_1 s_1}$ or $v_{s_1 d_1}$ (or $v_{d_1 d_1}$) this depends only on the properties of ψ_{d_1}, but in the case of $v_{s_1 s_1}$ or $v_{s_1 t_1}$ it depends on V. If the statement is true of $v_{s_1 t_1}$ but not of $v_{s_1 s_1}$ (as would occur if V were constant for large values of r, on account of the orthogonal properties of the continuous eigenfunctions) the theory can be worked through without change (see end Appendix I). A case of this type seems to arise from the perturbations considered by Kronig and Slater.[7] This will be further investigated.

[14] See, e.g., Born and Oppenheimer, Ann. d. Physik **84**, 457 (1927); Kronig, Reference 4, p. 347.

r_1 as a very idealized way of finding the effect of changing the size of the box in which the system is contained. Θ_k and the discrete F_k will of course not be affected by the box.

σ involves directly quantum numbers and their squares,[15] and for moderate values of these quantum numbers the term σ/r^2 will be small compared to the first term in the square brackets in Eq. (13) even for r of the order of molecular dimensions, if $E_k - U$ is of the order of 0.1 volt electron. The term involving σ may therefore be neglected under these conditions. Also for values of r ranging from r_1 to only slightly greater than a molecular diameter, U may be taken as equal to a constant U_1. Eq. (13) will then become

$$d^2F_k/dr^2 + (8\pi^2M/h^2)(E_k - U_1)F_k = 0. \tag{14}$$

If E_k is greater than U_1 (as for a continuous state) the solution is $a \sin\{(2\pi/h)[2(E_k - U_1)M]^{1/2}r + \phi\}$ where a and ϕ are constants. Since r_1 will be very much larger than the order of molecular dimensions, and can in fact be made as large as we please by increasing the size of the box, we may take this solution as holding over all except a negligible portion of the range of r. The normalization then makes $a = 2^{1/2}r_1^{-1/2}$, similarly to the case of a freely moving particle in a box. So if ψ_k corresponds to one of the continuous states it may be said to vary as $r_1^{-1/2}$. If ψ_k belongs to a discrete state it is of course independent of r_1.

We may at this point also consider the difference in energy between adjacent continuous states of the same isorotational set. We will have essentially the same energy levels as if U were constant for all values of r, and the energy difference, ϵ, between two adjacent energy levels is the same as for a component of the translational motion of a freely moving particle in a box.

$$\epsilon = (h/r_1)[(E_k - U_1)/2M]^{1/2}. \tag{15}$$

The dependence of various quantities in which we are interested on r_1, as given above, or deduced with the aid of Eq. (6), may be summarized as follows:

$$\begin{array}{ll} \psi_{c_1} \propto r_1^{-1/2} & v_{c_1c_1} \propto r_1^{-1} \\ \psi_{d_1} \propto r_1^{0} & v_{d_1c_1} \propto v_{c_1d_1} \propto r_1^{-1/2} \\ \epsilon \propto r_1^{-1} & v_{d_1d_1} \propto r_1^{0} \end{array} \tag{16}$$

DEVELOPMENT OF THE EQUATIONS

Remembering Eqs. (12), we can write Eq. (9_1) for the case $k_1 = d_1$ in the form

$$S_{d_1n_1}(E_{d_1} - E_{n_1}' + v_{d_1d_1}) + v_{d_1c_1}\Sigma'_{i_1}S_{i_1n_1} = 0 \tag{17}$$

(The accent on the summation sign has the same meaning as before—Eq. (11)). Taking the coefficients of the two definite continuous states s_1 and t_1 we may also write from Eq. (9_1)

[15] See, e.g., Fues, Ann. d. Physik **80**, 371 (1926); Kronig, Reference 4, p. 349.

$$S_{s_1 n_1}(E_{s_1} - E_{n_1}') + v_{c_1 d_1} S_{d_1 n_1} + v_{c_1 c_1} \Sigma'_{i_1} S_{i_1 n_1} = 0 \tag{18}$$

$$S_{t_1 n_1}(E_{t_1} - E_{n_1}') + v_{c_1 d_1} S_{d_1 n_1} + v_{c_1 c_1} \Sigma'_{i_1} S_{i_1 n_1} = 0 \tag{19}$$

Subtracting Eq. (19) from Eq. (18) we get

$$S_{s_1 n_1}(E_{s_1} - E_{n_1}') = S_{t_1 n_1}(E_{t_1} - E_{n_1}') = K \tag{20}$$

where K is a quantity which will be determined later by the normalization of ψ'_{n_1}. Thus

$$\Sigma'_{i_1} S_{i_1 n_1} = \Sigma'_{i_1} K/(E_{i_1} - E_{n_1}'). \tag{21}$$

The difference between successive values of E_{i_1} in this sum is ϵ. This may be taken as a constant for the range for energies we will find it necessary to consider (i.e., approximately the energy between two adjacent rotation lines). Now let us take the smallest positive value of $E_{i_1} - E_{n_1}'$ in the sum as α. Then the smallest negative value is $-(\epsilon - \alpha)$. α can of course vary between 0 and ϵ. Now let us set $\alpha = \epsilon/2 + \beta$, where β can vary between $-\epsilon/2$ and $\epsilon/2$. Thus if β is zero the perturbed energy is halfway between two unperturbed energies. Eq. (21) becomes

$$\Sigma'_{i_1} S_{i_1 n_1} = \frac{K}{\epsilon/2 + \beta} + \frac{K}{3\epsilon/2 + \beta} + \cdots - \frac{K}{\epsilon/2 - \beta} - \frac{K}{3\epsilon/2 - \beta} - \cdots \tag{22}$$

Combining the positive and negative terms pair by pair[16] the series can be written

$$\Sigma'_{i_1} S_{i_1 n_1} = 2\beta K \left(\frac{1}{\beta^2 - (\epsilon/2)^2} + \frac{1}{\beta^2 - (3\epsilon/2)^2} + \cdots \right) \tag{23}$$

The series in parentheses is equal[17] to $(\pi/2\epsilon\beta)[2\cot(2\pi\beta/\epsilon) - \cot(\pi\beta/\epsilon)]$ which we shall designate as A. Then we may write from Eq. (17).

$$S_{d_1 n_1} E + 2\beta K A v_{d_1 c_1} = 0 \tag{24}$$

where $E = E_{d_1} - E_{n_1}' + v_{d_1 d_1}$. And from Eqs. (18) and (20), assuming that $v_{c_1 c_1}$ is small compared to ϵ (an assumption which will be justified later—see Appendix I—and which will make all terms containing $v_{c_1 c_1}$ negligible unless β is very close to $-\epsilon/2$ or $\epsilon/2$) we get

$$S_{d_1 n_1} v_{c_1 d_1} + K = 0 \tag{25}$$

From Eqs. (24) and (25) we get

$$E = 2\beta A v_{d_1 c_1} v_{c_1 d_1} \tag{26}$$

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[16] It is necessary to combine the terms to make the series converge. If, however, we take into account the variation of ϵ with E_{i_1} and the fact that $E_{i_1} - E_{n_1}'$ has a lower limit, the series in Eq. (22) converges without combining terms. It converges very slowly, and this might leave some doubt as to whether we are justified in writing such sums as $\Sigma'_{i_1} \psi_{i_1} S_{i_1 n_1}$ as $\psi_{c_1} \Sigma'_{i_1} S_{i_1 n_1}$. It seems all right, however, when one remembers that ψ_{i_1} is an oscillating function, not only of r when E_{i_1} is fixed, but also of E_{i_1} when r is fixed, which, of course, considerably increases the rapidity of convergence of the sum. The same reasoning applies to $\Sigma'_{i_1} v_{d_1 i_1} S_{i_1 n_1}$ which equals $\Sigma'_{i_1} \int \psi_{d_1} V \psi_{i_1} d\tau S_{i_1 n_1} = \int d\tau \psi_{d_1} V \Sigma'_{i_1} \psi_{i_1} S_{i_1 n_1}$.

[17] Knopp, "Unendliche Reihen," p. 197 (Springer, 1922).

and $S_{d_1 n_1} = -K/v_{c_1 d_1}.$ (27)

We will now see if we can find from Eq. (26) what series of values E_{n_1}' may take. Now if l_1 represents the nearest continuous state with energy greater than E_{n1}' we may write

$$E = E_{d_1} - E_{l_1} + \epsilon/2 + \beta + v_{d_1 d_1}.$$ (28)

If we substitute this in Eq. (26) we see that Eq. (26) may be regarded as an equation in β (and hence in E_{n_1}'). We must, however, find the roots that satisfy the condition $-\epsilon/2 < \beta < \epsilon/2$. But we see that as we let β go from $-\epsilon/2$ to $\epsilon/2$ there is a monotonic change in the right hand side of Eq. (26), which passes from $+\infty$ to $-\infty$ or from $-\infty$ to $+\infty$, according as $v_{d_1 c_1}$ and $v_{c_1 d_1}$ are or are not of the same sign. As we let β go from $-\epsilon/2$ to $\epsilon/2$ there is also a monotonic change in the right hand side of Eq. (28), which changes by ϵ. Thus E from Eq. (26) and E from Eq. (28) will coincide at least at one point which lies within a range of ϵ. If $v_{d_1 c_1}$ and $v_{c_1 d_1}$ are of the same sign it is at once evident that there can be but one such point. But even if they are not of the same sign, since the value of E from Eq. (26) is entirely independent of r_1 (with β a given fraction of $\epsilon/2$), while the range, through which the right hand side of Eq. (28) varies, is ϵ, and hence is inversely proportional to r_1, it is seen that we can make this range so small as to include only one point of coincidence of the two calculated values of E. This means that there will be only one allowable value of β and hence only one perturbed state whose nearest unperturbed continuous state on the greater energy side is the particular state E_{l_1}. Likewise there will be but one perturbed state whose nearest unperturbed continuous state on the lower energy side is any particular such state. So between each two adjoining states of the unperturbed continuous series there is one perturbed state.[18] These perturbed states approach the unperturbed states as E grows large, and in such a way that the number of perturbed states is equal to the total number of unperturbed states (including both the continuous states and the discrete state) if $v_{d_1 c_1}$ and $v_{c_1 d_1}$ have the same sign. If $v_{d_1 c_1}$ and $v_{c_1 d_1}$ have opposite signs the total number of perturbed states is two less. It may be objected that the above considerations are not valid, because by our approximations we have deliberately excluded the regions where β is close to $-\epsilon/2$ or $\epsilon/2$, and that roots of the equation may lie in these regions, where the term in $v_{c_1 c_1}$ may be of importance; but the arguments, which to prevent interruption of the continuity of the article are presented in Appendix II, show this not to be the case. It is also true that strictly the above conclusions do not apply when the magnitude of E is very large, for then β is necessarily close to either $\epsilon/2$ or $-\epsilon/2$. But that the qualitative character of the conclusions should be altered in these regions seems very unlikely.

[18] As we pass to the limit, letting r_1 become infinite, it is seen that E becomes continuous and β/ϵ becomes a continuous monotonic function of E ("since the value of E from Eq. (26) is entirely independent of r_1 with β a given fraction $\epsilon/2$") given by Eq. (26), β/ϵ increasing in absolute value from 0 to $\frac{1}{2}$ as E increases in absolute value from 0 to ∞. This fact is implied in the deduction of Eq. (34).

Let us return now to the final evaluation of $S_{d_1 n_1}$ from Eq. (27). The value of K will be determined by the normalization equation $\int \psi_{n_1}'^2 d\tau = 1$. Now

$$\psi_{n_1}' = S_{d_1 n_1}\psi_{d_1} + \Sigma'_{i_1}S_{i_1 n_1}\psi_{i_1} \tag{29}$$

and

$$\int \psi_{n_1}'^2 d\tau = S_{d_1 n_1}{}^2 + \Sigma'_{i_1}S_{i_1 n_1}{}^2 = 1 \tag{30}$$

since $\int \psi_{d_1}{}^2 d\tau = \int \psi_{i_1}{}^2 d\tau = 1$ and $\int \psi_{i_1}\psi_{m_1}d\tau = \int \psi_{d_1}\psi_{i_1}d\tau = 0$ where m_1 is a continuous state different from i_1. Now from Eqs. (20), (27), and (30) and the definition of β we get

$$K^2/v_{c_1 d_1}{}^2 + K^2\left(\frac{1}{(\epsilon/2+\beta)^2} + \frac{1}{(3\epsilon/2+\beta)^2} + \cdots\right.$$
$$\left. + \frac{1}{(\epsilon/2-\beta)^2} + \frac{1}{(3\epsilon/2-\beta)^2} + \cdots\right) = 1. \tag{31}$$

But $v_{c_1 d_1}$ does not decrease as fast as ϵ when we increase the size of the box, by (16). Hence, for β any given fraction of $\epsilon/2$, we can imagine the size of the box to be so great that the first term in Eq. (31) is negligible. Then we find

$$K = \left(\frac{1}{(\epsilon/2+\beta)^2} + \frac{1}{(3\epsilon/2+\beta)^2} + \cdots + \frac{1}{(\epsilon/2-\beta)^2} + \frac{1}{(3\epsilon/2-\beta)^2} + \cdots\right)^{-1/2} \tag{32}$$

We are enabled to evaluate $S_{d_1 n_1}$ and $\sum_{i_1}'S_{i_1 n_1}$, but it is not necessary to write them out. But it may be noted that the ratio of $S_{d_1 n_1}\psi_{d_1}$ to $\psi_{c_1}\Sigma'_{i_1}S_{i_1 n_1}$ (small values of r) varies as $1/E$ (see Eq. (17)) and, as is to be expected, does not depend on r_1. Also ψ_{n_1}' varies as $r_1^{-1/2}$, as is to be expected, for any given E. These facts may be readily verified with the aid of (16).

The Width of the Line

In the case to which we wish particularly to apply the above considerations the spectrum appears to consist of a series of discrete but more or less diffuse vibration rotation lines, possibly in some of the vibration bands completely blurred into each other, superimposed upon a continuous spectrum. The fact that the discontinuous spectrum shows up over the continuous indicates that the former is chiefly responsible for the absorption i.e., for the purpose of determining the absorption we may write

$$\psi_{n_1}' = S_{d_1 n_1}\psi_{d_1} \tag{33}$$

$S_{d_1 n_1}$ will have a maximum when β is zero, hence by Eq. (26) when $|E|$ is zero.[18] It will have decreased to $2^{-1/2}$ times its maximum value when $|\beta|$ is equal to $\epsilon/4$ by Eqs. (27) and (32). Thus when $|\beta|$ is $\epsilon/4$ the matrix component of the polarization will have $2^{-1/2}$ its maximum value and the absorption $1/2$ its maximum value. So the half-absorption width, w, of the

line will be the magnitude of E, obtained by substituting $\epsilon/4$ for β in Eq. (26), multiplied by 2, and is given by

$$w = \left|\ 2\pi v_{d_1c_1} v_{c_1d_1}/\epsilon\ \right| \tag{34}$$

Using Eq. (15) this becomes

$$w = \left|\ 2\pi(r_1/h) v_{d_1c_1} v_{c_1d_1}[2M/(E_{d_1} - U_1)]^{1/2}\ \right| \tag{35}$$

We write in E_{d_1} since the energy is approximately that. This is assuming that the normalization is so affected that $F_{c_1} = (2/r_1)^{1/2}\sin\{(2\pi/h)[2(E_{d_1} - U_1)M]^{1/2}r + \phi\}$ as we have done throughout. It is rather more usual, however, to set

$$F_{c_1} = (2/h)^{1/2}[2M/(E_{d_1} - U_1)]^{1/4}\sin\{(2\pi/h)[2(E_{d_1} - U_1)M]^{1/2}r + \phi\}$$

If this is done Eq. (35) would be written

$$w = \left|\ 2\pi v_{d_1c_1}' v_{c_1d_1}'\ \right| \tag{36}$$

where $v_{d_1c_1}'$ and $v_{c_1d_1}'$ are what would be obtained by using the latter expression for F_{c_1}. Kronig[4] did not actually calculate the width, but what he has done is approximately equivalent to taking it equal to $4\pi^2 v_{c_1d_1}'^2$, which is the same as (36) except for the factor 2π, as $|v_{1c_1d}| = |v_{1dc_1}|$ (see below).

The Total Absorption

The absorption due to one of the energy states E_{n_1}' is proportional to the square of the matrix component of the electrical polarization (see following Eq. (2)). By Eq. (33) the square of this matrix component is $(S_{d_1n_1}\int\psi_0 P\psi_{d_1}d\tau)^2$ The total absorption over the width of the broad line is thus seen to be proportional to $\sum_{n_1}(S_{d_1n_1}\int\psi_0 P\psi_{d_1}d\tau)^2 = P_{0d_1}{}^2\sum_{n_1}S_{d_1n_1}{}^2$. The sum is unity if the perturbed and unperturbed eigenfunctions both form complete orthogonal sets, so the total absorption is unchanged by interaction with the continuum. We may now convert the sum to an integral, writing

$$\sum_{n_1}S_{d_1n_1}{}^2 = \int_{-\infty}^{\infty} S_{d_1n_1}{}^2 \frac{dE}{\epsilon}$$

since dE/ϵ is the number of states in the energy range dE. We find the integral by Eqs. (27), (32), and (26) to be $|v_{d_1c_1}/v_{c_1d_1}|$. So this ratio is unity.

In this paper no attempt will be made to apply the theory to any special cases. Professor G. E. Gibson and I[19] hope shortly to apply it to the diffuse spectrum of iodine monochloride, which has been observed by him. I also hope to apply similar ideas to the theory of unimolecular reactions.

One of the problems which must be considered is the question of what the perturbations which cause the diffuseness are due to, a problem which resolves itself into a proper choice of the unperturbed eigenfunctions. On this problem Kronig[4] has made a good start.

[19] Gibson and Rice, Nature **123**, 347 (1929).

I wish to express my thanks to Professor Gibson for having directed my attention to this problem.

APPENDIX I

We have left to the end the task of showing that $v_{c_1 c_1}$ is small compared to ϵ. Actually we shall simply show that we may have a completely diffuse band spectrum even though $v_{c_1 c_1}$ is very small compared to ϵ. In order to have a completely diffuse spectrum we must have two adjacent lines blur into each other, which means that w must be of the order of the separation of two rotation states, $h^2 j/4\pi^2 M r_0$, where j is the rotational quantum number, and r_0 is of the order of molecular dimensions. Let us give j the value $8\pi^3$, which is fairly large. We then have $w = 2\pi h^2/M r_0$ or, from Eq. (34), $v_{d_1 c_1} v_{c_1 d_1} = \epsilon h^2/M r_0$. As the magnitudes of $v_{d_1 c_1}$ and $v_{c_1 d_1}$ are equal we have $v_{d_1 c_1} \sim (\epsilon h^2/M r_0)^{1/2}$. But since $v_{d_1 c_1} = \int \psi_{d_1} V \psi_{c_1} d\tau$ and $v_{c_1 c_1} = \int \psi_{c_1} V \psi_{c_1} d\tau$ the ratio of $v_{d_1 c_1}$ to $v_{c_1 c_1}$ will be of the order of the average value of ψ_{d_1} in the region where the above integrand is different from zero to the corresponding average value of ψ_{c_1}. (We assume that both integrands are different from zero only for small values of r.) This ratio will be approximately equal to the corresponding average of F_{d_1} divided by that of F_{c_1}. Now if the vibrations of the nuclei take place over a distance comparable to r_0, then $F_{d_1} \sim r_0^{-1/2}$ while $F_{c_1} \sim r_1^{-1/2}$. Hence, by Eq. (15), $v_{c_1 c_1}/\epsilon \sim h^{1/2} [M(E_{d_1} - U_1)]^{-1/4}$. Taking M as the mass of the hydrogen atom and $E_{d_1} - U_1$ as 0.1 volt electron we get $v_{c_1 c_1}/\epsilon \sim 10^{-4}$.

If the possibility mentioned in Footnote 13 is true, then $v_{s_1 s_1}$ is not small compared to ϵ, but the argument still applies to $v_{s_1 t_1}$. (It will be remembered that s_1 and t_1 refer to two continuous states; and $v_{s_1 s_1}$ may be regarded as independent of s_1 and $v_{s_1 t_1}$ of s_1 and t_1 though now $v_{s_1 s_1} \neq v_{s_1 t_1}$.) It is not hard to see that this is all that is needed to make the considerations which result in Eqs. (26) and (27) (and also the considerations of Appendix II, below) valid. For, from Eq. (9₁), by taking $k_1 = s_1$, we get $S_{s_1 n_1}(E_{s_1} - E_{n_1}' + v_{s_1 s_1} - v_{s_1 t_1}) + v_{s_1 d_1} S_{d_1 n_1} + v_{s_1 t_1} \sum'_{i_1} S_{i_1 n_1} = 0$, which is to be used instead of Eq. (18), and similarly for Eq. (19). We then set $S_{s_1 n_1}(E_{s_1} - E_{n_1}' + v_{s_1 s_1} - v_{s_1 t_1}) = K$. Since $v_{s_1 t_1}$ is small everything follows as before.

APPENDIX II

We wish to get a little more exact expression than Eq. (26) for the case that β is very close to $-\epsilon/2$ or $\epsilon/2$. We shall treat only the former case, as the latter is very similar. If β is close to $-\epsilon/2$ we can neglect every term except $K/(\epsilon/2+\beta)$ in Eq. (22). Substituting this in Eq. (18) and going through the same derivation as for Eq. (26) except that we do not neglect the term which is multiplied by $v_{c_1 c_1}$ we arrive at the expression

$$E = 2\beta A v_{d_1 c_1} v_{c_1 d_1} / [1 + v_{c_1 c_1}/(\epsilon/2 + \beta)] \tag{37}$$

If $v_{c_1 c_1}$ is of the same order as $\epsilon/2+\beta$ this gives for E a result which is of the same order as is given by Eq. (26). But $v_{c_1 c_1}$ will not be of the order of $\epsilon/2+\beta$ unless $\epsilon/2+\beta$ is very small in magnitude (see Appendix I), and E will then be much larger than the energy width of the spectral line. If $v_{c_1 c_1} = -(\epsilon/2+\beta)$, then E calculated from Eq. (37) would be infinite. If $|v_{c_1 c_1}|$ is considerably greater than $|\epsilon/2+\beta|$ then Eq. (37) reduces approximately (since A will be approximately $1/2\beta(\epsilon/2+\beta)$) to

$$E = v_{d_1 c_1} v_{c_1 d_1} / v_{c_1 c_1}.$$

But by comparing with Eq. (34) it is seen that this is a very large value compared to the width of the line. Therefore it appears that if there are any inaccuracies in the qualitative description of the positions of the new (perturbed) energy levels, which we have given above, they lie outside the range of energies we are particularly interested in; but it seems very unlikely that there could be qualitative errors for great values of E. The exact determination of this question would involve considerable reexamination of the simplifications and approximations we have made, and we will not attempt it.

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