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PERTURBATIONS IN MOLECULES AND THE THEORY OF PREDISSOCIATION AND DIFFUSE SPECTRA. II

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Abstract

Further consideration is given to the problems which arise when the continuum of one electronic state of a diatomic molecule occurs in the same range as the discrete states of another electronic state. In the finding of electronic states and the potential curves which go with them certain approximations must be made; a better approximation can then be obtained by quantum mechanical perturbation theory. The discrete states are broadened, and this will appear, inasmuch as spectral lines involving these states are broadened. In this paper the shape of the broadened spectral lines is found, certain properties of the perturbation matrix are considered, and a wave packet is set up or rather one such as would be set up by nature is used to give all the details of a radiationless transition from a discrete state to the overlying continuum.

Shape of a Spectral line in Cases of Predissociation

THE simple result obtained in the preceding paper[2] for the shape of the absorption line in the case of radioactive decay and other similar processes, suggests that it would be well to try to obtain an explicit result for the shape of the line in the case of predissociation, for purposes of comparison. The shape of line could of course be calculated from the expressions in the first paper with the above title[3] (hereafter referred to as (I)), but it turns out that these can be somewhat simplified.

In this paper it was shown that the absorption coefficient over a broadened spectral line (see Abstract above) as a function of $E-E_1$ (called $-E$ in (I)) where E is the energy of the light absorbed and E_1 the energy of the center of the line, is proportional to K^2, where

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

where ϵ is the distance between unperturbed continuous levels[4] (the system being in a box) and where β is a parameter given by the equation[5]

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[1] National Research Fellow.

[2] Rice, Phys. Rev. preceding paper in this issue.

[3] Rice, Phys. Rev. **33,** 748 (1929).

[4] ϵ can of course be varied arbitrarily by varying the size of the box, but in any given problem can be regarded as a constant. None of the results depend on it in any essential particular, and it will always cancel out of expressions for things which are experimentally determinable. Nevertheless it has been found very convenient to treat the system as if contained in a box, so the continuous levels really become a very close-spaced set of discrete ones, and we shall continue to do so.

[5] (I), Eq. (26), since $v_{cd}=v_{dc}$ (see Rice, Phys. Rev., **34,** 1459 (1929), especially footnote 19).

$$E - E_1 = -2\beta A v_{cd}^2 \tag{2}$$

where $A = (\pi/2\epsilon\beta)\ [2\cot(2\pi\beta/\epsilon) - \cot(\pi\beta/\epsilon)]$ and v_{cd} is the component of the perturbation matrix giving the interaction between the discrete level and the continuous levels. Now A is easily reduced to the form $-(\pi/2\epsilon\beta)\tan(\pi\beta/\epsilon)$, hence (2) becomes

$$E - E_1 = (v_{cd}^2\pi/\epsilon)\tan(\pi\beta/\epsilon) \tag{3}$$

Eq. (1) can also be further reduced as follows. A was originally expressed as an infinite series,[6]

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

which is equal to

$$\frac{1}{2\beta}\left(\frac{1}{\epsilon/2 + \beta} + \frac{1}{3\epsilon/2 + \beta} + \cdots - \frac{1}{\epsilon/2 - \beta} - \frac{1}{3\epsilon/2 - \beta} - \cdots\right).$$

From this and (1) we see that K^{-2} is equal to $-2d(\beta A)/d\beta = (\pi/\epsilon)^2\sec^2(\pi\beta/\epsilon)$. Disregarding the constant factor, the absorption coefficient is given as a function of β/ϵ by $(K\pi/\epsilon)^2 = [\sec^2(\pi\beta/\epsilon)]^{-1} = [1 + \tan^2(\pi\beta/\epsilon)]^{-1}$. By (3) this becomes

$$(K\pi/\epsilon)^2 = 1/[1 + 4(E - E_1)^2 w^{-2}] \tag{4}$$

where $w = 2\pi v_{cd}^2/\epsilon$ is the width of the line. Hence the shape of the broadened discrete line is the same in the case of predissociation as in the case of radioactive decay or dissociation by rotation.

SOME PROPERTIES OF THE EIGENFUNCTIONS AND PERTURBATIONS

In previous work on the rate of predissociation[7] it has never as yet been possible to follow the wave of dissociating molecules in the same way as in the preceding paper we have followed the wave of departing alpha particles in the case of radioactivity or the dissociating molecules in the case of dissociation by rotation. We are now in a position to do this in the case of predissociation. First we must consider certain properties of the eigenfunctions and perturbations involved.

To get the unperturbed eigenfunctions we first hold the distance, r, between the nuclei fixed, and solve the wave equation for the electrons and the rotation of the nuclei. We can write this equation in the following form

$$(H_\Theta - U_m)\Theta_m = 0 \tag{5}$$

H_Θ is the Hamiltonian[8] with respect to the electrons and the rotation, Θ_m

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[6] See (I), Eq. (23), and text just after (23).

[7] Wentzel, Phys. Zeits. **29,** 333 (1928); Kronig, Zeits. f. Physik **50,** 360 (1928); Rice, Phys. Rev. **34,** 1451 (1929).

[8] We use the following system of coordinates. We refer everything to a set of axes which pass through the center of gravity of the *system as a whole.* But in the case of the nuclei we use

is an eigenfunction, U_m an eigenvalue with quantum numbers designated collectively as m. We then set up arbitrarily the following wave equation for a function $F_{m,\,k}$ of r:

$$\begin{gathered} d^2F_{m,k}/dr^2 + \kappa^2(E_{m,k} - U_m)F_{m,k} = 0 \\ \kappa^2 = 8\pi^2 M/h^2 \end{gathered} \tag{6}$$

where M is the reduced mass, h Planck's constant $E_{m,k}$ an eigenvalue of (6), U_m being the eigenvalue (a function of r) previously found from (5).

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instead of the six rectangular coordinates, the three coordinates of the center of gravity of the *nuclei*, the two coordinates ϕ and θ giving the direction of the line joining the nuclei, and r. The coordinates of the center of gravity of the two nuclei are counted among the electronic and rotational coordinates. Now if r is so large that interaction between the two atoms forming the molecule is negligible (a case which will later be of importance) then the potential energy function for any given ϕ and θ will depend on $x_1-\alpha rl$, $y_1-\alpha rm$, $z_1-\alpha rn$, $x_2-\alpha rl$, $\cdots$, where l, m, and n are the direction cosines of the line joining the nuclei, α is a constant depending on the relative masses of the two nuclei and on which nucleus the electron in question is (αr being the distance to the given nucleus from the center of gravity of the nuclei), and $x_1y_1z_1x_2$, $\cdots$, are the coordinates of the electrons, and also on the coordinates of the center of gravity of the *nuclei*, but not otherwise on r than as noted above, provided the coordinates of the system have values at all probable. Therefore the eigen-function Θ_m will depend upon r only in like manner. From this we see that any function of Θ_m and its derivatives when integrated over all coordinates except r, ϕ, θ will very approximately be independent of r. For we can always substitute the variables $x_1-\alpha rl$ for the original variables, and $d(x_1-\alpha rl)$ for dx_1 for constant r. Further integration over ϕ and θ of course leaves the expression independent of r.

Note added in proof: Since Footnote 8 may not be clear it may be well to explain it in more detail. The reason that Θ_m involves r only in the form $x_1-\alpha rl$ when r is large is as follows. A partial differentiation with respect to x_1 is the same as a partial differentiation with respect to $x_1-\alpha rl$. So if in finding our eigenfunction we first hold ϕ and θ fixed as well as r we get an eigenfunction depending only on $x_1-\alpha rl$, etc., and the coordinates of the center of gravity of the nuclei. We call this eigenfunction N and will omit subscripts. For the dependence on ϕ and θ we multiply by a spherical harmonic, Y. The NY form a complete orthogonal set in terms of which the Θ_m can be expanded. The perturbation matrix components are found in much the same way as the others (v_{ss} and v_{st}) in this paper, and are due to the fact that the terms

$$\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

in the Hamiltonian must operate on the whole expression NY instead of just on Y, since l m, and n which are involved in N depend on ϕ and θ. We have

$$\partial N/\partial\theta = -\,\alpha r\,(\partial l/\partial\theta)\,\partial N/\partial\,(x_1 - \alpha rl),$$

and correspondingly for the second derivative, etc. Wherever the second partial derivatives of N with respect to $x_1-\alpha rl$, etc., occur a factor r^2 cancels the r^{-2} in the perturbation operator, and subsequent integration over x_1, etc., removes the dependence on r in the way discussed near the end of footnote 8. The terms in a perturbation matrix component involving only a first derivative of N will contain r to the minus first power, hence will be small for large r. Therefore, for large r, the coefficients of the of NY's in the expression for Θ_m will not involve r and Θ_m will depend on r only as stated.

Another remark we should like to make is this. The coordinates of the actual distance of an electron to its nucleus (if X_0, etc., are the coordinates of the center of gravity of the nuclei) are $x_1-\alpha rl-X_0$ and the potential energy depends more directly on this quantity than on $x_1-\alpha rl$, but this does not matter for our purposes.

As the unperturbed eigenfunction we use $\Theta_m F_{m,k}/r$. This is the usual procedure for molecules, it being generally conceded that it gives the energy levels of molecules to a good approximation.[9]

The unperturbed eigenfunction obviously obeys the equation:

$$(F_{m,k}/r)(H_\Theta - U_m)\Theta_m - \kappa^{-2}(\Theta_m/r)d^2F_{m,k}/dr^2 - (\Theta_m/r)(E_{m,k} - U_m)F_{m,k} = 0 \quad (7)$$

Since H_Θ and $E_{m,k}$ and U_m contain no derivatives with respect to r we may write

$$H_\Theta(\Theta_m F_{m,k}/r) - \kappa^{-2}(\Theta_m/r)d^2F_{m,k}/d^2r - E_{m,k}(\Theta_m F_{m,k}/r) = 0 \quad (8)$$

The actual Hamiltonian for the system, however, is

$$H = H_\Theta - \kappa^{-2}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right). \quad (9)$$

The actual wave equation, therefore, if it operates on $\Theta_m F_{m,k}/r$ contains the extra terms[10]

$$-\kappa^{-2}\left[(F_{m,k}/r)(\partial^2\Theta_m/\partial r^2) + (2/r)(\partial\Theta_m/\partial r)(dF_{m,k}/dr)\right]. \quad (10)$$

Now to get the real solution of the wave equation we can expand in terms of the $\Theta_m F_{m,k}/r$ which form an orthogonal set.[10] We can treat the $\Theta_m F_{m,k}/r$ as solutions of equations like (8) and use the extra terms in setting up a perturbation matrix, (10) being considered as the result of an operator acting in a special way on $\Theta_m F_{m,k}/r$.

Now in the case of predissociation we expand the perturbed eigenfunction in terms of a $\Theta_m F_{m,k}/r$ belonging to a discrete state,[11] which we will call simply ψ_d, and a set of continuous ones, which belong to another electronic level, and which we designate as $\Theta_c F_{c,i}/r$ where i runs over the set of continuous states. It is to be noted that the continuous property arises from the $F_{c,i}$'s, as Θ_c for all r's is a discrete eigenfunction of (5).

The perturbed eigenfunction, ψ'_n may thus be written as a linear function of the unperturbed, thus:[12]

$$\psi_n' = S_{dn}\psi_d + \Theta_c \textstyle\sum_i S_{in}F_{c,i}/r. \quad (11)$$

For large values of r the first term of (11) gives no appreciable contribution, hence for this case

$$\psi_n' = \Theta_c \textstyle\sum_i S_{in}F_{c,i}/r = \Theta_c F_n'/r \quad (12)$$

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[9] Born and Oppenheimer, Ann. d. Physik **84,** 457 (1927).

[10] Perturbations of this nature were first set up in practically this form by Slater, Proc. Nat. Acad. Sci. **13,** 423 (1927), which should be seen for details. Our formulation differs only in that we have put the r part of the eigenfunction in the form $F_{m,k}/r$.

[11] Only one discrete state is to be considered, for we assume as throughout that any other discrete states which interact with the set of continuous states we are interested in are so far away in the term spectrum that their effect may be neglected. Also, of course we consider that the given discrete state interacts with only one set of continuous ones. See (I) pp. 751–2.

[12] (I), Eq. (29) It has been, unfortunately, necessary to change the notation somewhat.

where $F_n' = \sum_i S_{in} F_{c,i}$. The perturbed wave equation may be written

$$(H - E_n')\psi_n' = 0 \tag{13}$$

where E_n' is the corresponding eigenvalue.

This gives, for large r, using (9) and (12)

$$H_\Theta(\Theta_c F_n'/r) - \kappa^{-2}(\Theta_c/r)d^2F_n'/dr^2 - E_n'(\Theta_c F_n'/r) - \kappa^{-2}(F_n'/r)\partial^2\Theta_c/\partial r^2 - \kappa^{-2}(2/r)(\partial\Theta_c/\partial r)(dF_n'/dr) = 0. \tag{14}$$

We now proceed to reduce (14) to an equation in F_n'. To do this we first multiply through by r, then by Θ_c and integrate over all values of the electronic and rotational coordinates. (We call the volume element $d\tau'$.) We remember that $\int\Theta_c H_\Theta \Theta_c d\tau' = U_c$ and note that[13] $2\int\Theta_c(\partial\Theta_c/\partial r)d\tau' = \int(\partial\Theta_c^2/\partial r)d\tau' = (d/dr)\int\Theta_c^2 d\tau' = d1/dr = 0$, since the Θ_m are an orthogonal set. Further we set $\kappa^{-2}\int\Theta_c(\partial^2\Theta_c/\partial r^2)d\tau' = I_c$. Eq. (14) thus becomes

$$d^2F_n'/dr^2 + \kappa^2(E_n' + I_c - U_c)F_n' = 0 \tag{15}$$

For large distances, r, the integral I_c must be independent of r, because for large distances r the molecule is separated into atoms which do not interact appreciably. Θ_c will always be affected the same way by a displacement, dr, regardless of what r is, provided it is large enough (see footnote 8). Eq. (15) shows us that F_n' satisfies a wave equation of the usual type for a problem of one degree of freedom, and hence is a sinusoidal function of the usual type.

Concerning the Perturbation Matrix and the Perturbation Problem

Before we proceed further we must introduce some considerations about the perturbation matrix. The diagonal matrix component for a given continuous state is by (10) remembering that the r part of the volume element is r^2dr (we substitute c for m in (10)—also we write s for k to correspond to the notation used in previous papers—unfortunately we cannot make the correspondence complete, as in this paper it has been necessary to use two subscripts):

$$v_{ss} = -\kappa^{-2}\int_0^\infty F_{c,s}^2 dr \int \Theta_c(\partial^2\Theta_c/\partial r^2)d\tau' - 2\kappa^{-2}\int_0^\infty F_{c,s}r(dF_{c,s}/dr)\,dr \int \Theta_c(\partial\Theta_c/\partial r)d\tau'$$

For the method of setting up this expression Slater's article[10] can be consulted. The last term vanishes since $\int\Theta_c(\partial\Theta_c/\partial r)d\tau' = 0$ as noted above. Remembering the definition of I_c we find

$$v_{ss} = -\int_0^\infty F_{c,s}^2 I_c dr.$$

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[13] Kronig, l. c., p. 355.

Now I_c approaches a constant value for large r. Let us call this value I_{c1}. Then $I_c = I_c' + I_{c1}$ where I_c' differs from zero only for small r, and there will be of the order of I_{c1}. From the orthogonal properties of the $F_{c,s}$ we see that

$$v_{ss} = -\int_0^\infty F_{c,s}{}^2 I_c' dr - I_{c1}. \tag{16}$$

In similar manner, for two different continuous states s and t belonging to the same electronic-rotational state c, we get, remembering the orthogonal properties of the $F_{c,s}$

$$v_{st} = -\int_0^\infty F_{c,s} F_{c,t} I_c' dr.$$

Therefore the contributions to v_{st} come from a range in which r is small, and our previous deductions that v_{st} is small enough to be neglected are valid.[14] The same deductions hold for the first term of the right of (16). Hence, very approximately

$$v_{ss} = -I_{c_1} \tag{17}$$

The method of handling cases where v_{ss} is not small has already been indicated.[14] In fact, it consists simply in adding v_{ss} (which is practically independent of s) to the corresponding energy $E_{c,s}$ and proceeding exactly as before. Now suppose instead of (6) we write (for the case $m=c$ and $k=s$)

$$d^2F_{c,s}/dr^2 + \kappa^2(E_{c,s} - U_c - v_{ss})F_{c,s} = 0 \tag{18}$$

Then $E_{c,s}+v_{ss}$ takes the place of $E_{c,s}$ ($m=c$, $k=s$) as eigenvalue in Eq. (6). We could therefore take (18) as the unperturbed equation for the electronic-rotational state c, and otherwise disregard v_{ss}. This is the most convenient way of handling the problem, for the relations between the eigenvalues of (18) and the perturbed eigenvalues E_n' will be just the same as the relation between the eigenvalues of (6) and the E_n' *would have been* were v_{ss} actually 0, and this relationship has been deduced in the previous work.

The relationship is as follows. Between every two eigenvalues of (18) lies a value E_n'. Let us denote as $E_{c,n}$ the eigenvalue of (18) which is just above the particular value E_n'. Then from the original definition[15] of the quantity β which appeared earlier in the paper

$$E_{c,n} - E_n' = \beta + \epsilon/2. \tag{19}$$

THE WAVE PACKET FOR THE DISSOCIATING MOLECULES

Now it has been shown[16] that the wave packet for the dissociation from the discrete state into the overlying continuum is given by

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[14] (I), Appendix I. Correction, Phys. Rev. **34,** 1462.

[15] (I), p. 755.

[16] Rice, Phys. Rev. **34,** 1451 (1929).

$$\psi = \sum_n S_{dn} \psi_n' \exp\left(-2\pi i E_n' t/h\right) \tag{20}$$

where $S_{dn} = K/v_{cd}$. For values of r large compared to atomic sizes, we have from (12), (4), and (20)

$$\psi = \frac{\epsilon \Theta_c}{\pi v_{cd} r} \sum_n \frac{F_n' \exp\left(-2\pi i E_n' t/h\right)}{[1 + 4(E_n' - E_1)^2/\omega^2]^{1/2}} \cdot \tag{21}$$

We shall now find the relation between the F_n' and the eigenfunctions $F_{c,s}$ of Eq. (18). The latter may be written in the following form for large r

$$F_{c,s} = \sin\left\{\kappa(E_{c,s} - U_c - v_{ss})^{1/2} r + \zeta_s\right\} \tag{22}$$

where ζ_s is a phase constant. The condition that $F_{c,s} = 0$ at $r = r_1$ where r_1 is the largest value r can take (the system being in a box) requires

$$\sin\left\{\kappa(E_{c,s} - U_c - v_{ss})^{1/2} r_1 + \zeta_s\right\} = 0. \tag{23}$$

But the quantum condition in the neighborhood of $r = 0$ requires that ζ_s should be the same[17] for all s. At any rate this will be practically true over a range of energies greater than the small breadth, w, of the broadened discrete state It would always be exactly true if U_c were constant for small r, as well as large, (i.e. if (22) actually held for small r), and the smallest value r could take were 0. Now since F_n' obeys the equation (15) we have for large r

$$F_n' = \sin\left\{\kappa(E_n' - U_c - v_{ss})^{1/2} r + \zeta_n'\right\} \tag{24}$$

F_n' must be 0 at $r = r_1$ so

$$\sin\left\{\kappa(E_n' - U_c - v_{ss})^{1/2} r_1 + \zeta_n'\right\} = 0 \tag{25}$$

Eq. (25) will obviously be satisfied if

$$\zeta_n' = \zeta_s + \kappa(E_{c,n} - U_c - v_{ss})^{1/2} r_1 - \kappa(E_n' - U_c - v_{ss})^{1/2} r_1 \tag{26}$$

(see Eq. (23) and see also just before Eq. (19) for definition of $E_{c,n}$). Now as the difference between the quantities $(E_{c,n} - U_c - v_{ss})^{1/2}$ and $(E_n' - U_c - v_{ss})^{1/2}$ is very small[18] we may write it as $\frac{1}{2}(E_{c,n} - E_n')\ (E_{c,n} - U_c - v_{ss})^{-1/2}$ or, by (19) as $\frac{1}{2}(\beta + \epsilon/2)\ (E_{c,n} - U_c - v_{ss})^{-1/2}$. Now $\epsilon = 2\pi\kappa^{-1}(E_{c,n} - U_c - v_{ss})^{1/2} r_1^{-1}$. So we see that

$$\begin{aligned} \zeta_n' = \zeta_s + \pi\beta/\epsilon + \pi/2 &= \zeta_s + \pi/2 + \tan^{-1}\left\{(E_n' - E_1)\epsilon/\pi v_{cd}^2\right\} \\ &= \zeta_s + \pi/2 + \tan^{-1}\left\{2(E_n' - E_1)/w\right\} \end{aligned} \tag{27}$$

by (3) and remembering that $w = 2\pi v_{cd}^2/\epsilon$. We thus get an expression for ζ_n' which can be used in evaluating F_n'. Now

$$\sin\left\{x + \tan^{-1} y\right\} = (\sin x + y \cos x)\ (1 + y^2)^{-1/2}.$$

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[17] Or differ only by multiples of π. We can choose that they should be all the same.

[18] It may be made as small as we please by making r_1 large.

Using this formula we get from (24), (27), and (21)

$$\psi = \frac{\epsilon\Theta}{\pi v_{cd} r}\sum_n$$

$$\frac{[\sin\{\kappa(E_n'-U_c-v_{ss})^{1/2}r+\zeta_s+\pi/2\}+[2(E_n'-E_1)/w]\cos\{\kappa(E_n'-U_c-v_{ss})^{1/2}r+\zeta_s+\pi/2\}]\exp(-2\pi iE_n\,t/h)}{1+4(E_n'-E_1)^2/w^2}.$$

The sum over n can be converted to an integral with respect to E_n', and then, except for the factor $1/r$, which merely means that here we have taken all three dimensions of space into account, and so have a spherical wave, the part which involves r has exactly the same form as Eq. (23) of the preceding paper. We thus have a wave of dissociating particles of exactly the same type as before, with exponential decrement with time bearing the same relation to the width of the discrete state, in fact the same in all details. There is thus a complete analogy in results between these two different types of decompositions. Also the part of the wave for small r can be handled as in the preceding paper, since for small r the eigenfunctions will not vary appreciably over a small range of energies.

I wish to express my thanks to Professor Heisenberg for his interest in this work, and helpful discussion.