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DELOCALIZED EXCITATION AND EXCITATION TRANSFER

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INSTITUTE OF MOLECULAR BIOPHYSICS and
DEPARTMENT OF CHEMISTRY

Contents

Delocalized Excitation and Excitation Transfer*

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DELOCALIZED EXCITATION AND EXCITATION TRANSFER

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I. INTRODUCTION

1. Empirical aspects. There are many systems consisting of well defined components, where the ground state properties are essentially additive but not those of the excited electronic states. Examples for this behavior can be found among atomic or molecular vapors, solutions of not too low concentrations, molecular crystals or polymers with aromatic or unsaturated groups not in conjugation. Proteins and nucleic acids, chloroplasts, crystalline and liquid scintillators are further examples, and the functions of these systems depend largely on this non-additivity of their excited state properties.

For such systems, absorption spectra as well as luminescence and photochemical properties may be quite different from those of their components. The reason for this is that in excited states the electronic excitation is not completely localized within one or the other of these components. The excitation may be completely delocalized and spread out over the whole system or, in a less drastic way, it may be localized only temporarily, but transferred from one component of the system to another.

From a phenomenological point of view, three different cases of such behavior are distinguished easily. This may be illustrated with the aid of some characteristic examples. References may be found in earlier publications[1].

Case A. This is one where major alterations occur in the absorption spectra. Typical examples are those of dimers which can be recognized often in the more concentrated solutions of a number of dyes, such as thionine or the rhodamines. A peculiar example is that of the Scheibe-Jelley-polymers from pseudo-isocyanine and related dyes. But also the more intense absorption

regions of molecular crystals like that corresponding to the 2500 Å-absorption of the anthracene molecule belong into this group. In all these examples the vibronic envelopes of the spectra are completely different from those of the component spectra, even if the absorption region is approximately the same. Such profound alterations are obviously the result of a fairly strong interaction between the components and it is natural to speak here of a strong coupling case. As we shall see later, this strong coupling results from a quite complete delocalization of electronic excitation over the components of the system.

Case B. There are other examples where less profound alterations exist in the absorption spectra. The vibronic envelope is then retained, but the individual vibronic levels of the components are split in a characteristic way. This has been observed with some 'double-molecules' like diphenyl-methane and is a quite common effect in the weaker absorption regions of molecular crystals as, for instance, the 3600 Å absorption of anthracene. In the latter case, the effect has been named 'Davydov-splitting'. Obviously, these effects are also due to some kind of interaction between the components, but of a lesser magnitude. It has become customary to speak here of a weak coupling case. One may expect that the delocalization of electronic excitation will be less strong than in the forgoing case.

Case C. There is, however, a third case which should be not overlooked. Many systems show no or at least no essential alterations in their absorption spectra if compared with those of their components, but nevertheless have quite different luminescence and photochemical properties. This occurs, for instance, in dye solutions at moderate concentrations, where no essential association exists. While there the absorption and fluorescence spectra and even the fluorescence quantum efficiences may be the same as in the more diluted solutions,

the fluorescence polarization is often much less. Likewise, in mixed solutions, the fluorescence or phosphorescence emission originates, independent of the absorbing component, from that one with the lower excited state. Recently, some very interesting demonstrations of this effect have been given by Kuhn et.al.[2] with dye layers, separated by inert molecular sheets more than 100 Å thick.

Obviously, in this case too, there exists some coupling between the excited states of the different molecules, but of even lesser magnitude than in the foregoing case B. In a revision of an earlier proposal[3], we shall call case C now the case of very weak coupling. As the degree of delocalization has to be still less in this case, it will be reasonable to regard the electronic exitation as temporarily completely localized and to interpret the observed effects in terms of an excitation transfer.

When speaking of delocalized excitation or of excitation transfer, one should keep in mind that these conceptions are more or less complementary. The first one is concerned with the stationary states of the system and should be the adequate one in discussing band splittings, absorption intensities and related effects. The second one is by its nature concerned with non-stationary states and should therefore allow a better description of experiments where the process of electronic excitation and its final effect can be located in different parts of the system.

This justifies to some extent our preference of the term delocalized excitation in cases A and B and of excitation transfer in case C. However, also in systems belonging to the first two cases excitation transfer experiments are possible and should be described so in the appropriate manner. We shall see that this is indeed possible, but that some ambiguity in defining such terms as transfer rate cannot be avoided here.

It is only in the very weak coupling case C that such terms can be defined unequivocally. On the other hand, it would be unreasonable here to speak of delocalized excitation.

Some objections might be - and indeed have been[4] - raised against our empirical distinction between cases B and C, because it can be applied only to spectra with well resolved vibronic structure whereas it is useless in cases of continuous spectra. The solution of this difficulty is simple but surprising: For systemswith continuous spectra there is no weak coupling case B at all, but the strong coupling case A changes directly into the very weak coupling one. Even for systems with broad vibronic levels, which are quite common in solutions at room temperature, the so called weak coupling case is very closely limited and it scarcely deserves its name as a separate case. The justification for this will be given later in chapter IV.

II. FORMAL EXCITON THEORY

2. General formulations. The theory of delocalized electronic states goes under the name of exciton theory. This theory is based on an original conception by Frenkel[5] and has later been developed further essentially by Davydov[6] and others. In the present chapter, only the basic developements of this theory will be presented. In this connection no special references will be given, but the reader may refer to Davydov's monograph[7] or to other comprehensive articles.

We consider a system of N molecules with fixed distances and with their internal nuclear coordinates fixed in their equilibrium positions. The electronic coordinates, including spin, of the n^{th} molecule shall be symbolized by q_n. The electronic Hamiltonian of the system is then

$$\mathcal{H} = \sum_{n=1}^{N} \mathcal{H}_n + \sum_{n=1}^{N} \sum_{m>n}^{N} V_{mn} \qquad (2.1)$$

where $\mathcal{H}_n$, which operates on the q_n only, is the Hamiltonian of the free molecule n, and $V_{m,n}(q_m, q_n)$ is the intermolecular interaction potential between the molecules m and n. In zero order approximation, the ground state of the system can be described by the product wave function

$$\Phi_G = \prod_{n=1}^{N} \varphi_n \qquad (2.2)$$

where $\varphi_n = \varphi_n(q_n)$, supposed to be real, is the ground state eigenfunction of the free molecule n. Here and later we neglect orbital overlap between different molecules and do not trouble with antisymmetrization. The first order ground state energy becomes

$$W_G = \sum_{n=1}^{N} W_n^o + \sum_{n=1}^{N} \sum_{m>n}^{N} V_{mn} \qquad (2.3)$$

w_n^o is the ground state energy of the n^{th} free molecule and

$$V_{mn} = \langle \varphi_m \varphi_n | \mathcal{V}_{mn} | \varphi_m \varphi_n \rangle \qquad (2.4)$$

the matrix element representing the Coulombic interaction between m and n.

The singly excited states of the system can be described in terms of N locally excited configurations

$$\varphi_\ell' \prod_{n \neq \ell} \varphi_n \qquad (2.5)$$

where φ_l' is an excited state wave function of the free molecule l which belongs to the energy w_l'. We suppose these states to be non-degenerate so that the φ_l' too can be taken real, and their energies sufficiently different from those of other states. The zero order eigenfunctions $\bar{\Phi}_k$ are then linear combinations of the locally excited configurations

$$\bar{\Phi}_k = \sum_\ell c_{k\ell} \varphi_\ell' \prod_{n \neq \ell} \varphi_n \qquad (2.6)$$

They represent the <u>exciton</u> states of the system. The coefficients c_{kl} together with the corresponding energy values W_k can be obtained by solution of the eigenvalue problem

$$\langle \bar{\Phi}_j^* | \mathcal{H} | \bar{\Phi}_k \rangle = W_k \delta_{jk} \qquad (2.7)$$

With the Hamilton operator as defined in (2.1), this can be expressed by the additional interaction matrix elements

$$V_{mn}' = \langle \varphi_m' \varphi_n | \mathcal{V}_{mn} | \varphi_m' \varphi_n \rangle \qquad (2.8)$$

and

$$U_{mn} = \langle \varphi_m' \varphi_n | \mathcal{V}_{mn} | \varphi_m \varphi_n' \rangle \qquad (2.9)$$

$V'_{m,n}$ represents the Coulombic interaction between the excited molecule m and the unexcited one n. $U_{m,n}$ is the resonance integral between the configurations with m and with n excited. This resonance integral is the main source of the effects we are concerned with here. It can be interpreted as the pseudo-Coulombic interaction energy between the '<u>transition-charge</u>'-<u>densities</u> $\varphi_m' \varphi_n$ and $\varphi_m \varphi_n'$.

3. Dimers. Instead of treating the general case we shall restrict ourselves to two characteristic cases. The first one is that of a dimer, the components a and b of which may be dissimilar. Our Hamiltonian is then simply

$$\mathcal{H} = \mathcal{H}_a + \mathcal{H}_b + T_{ab} \tag{3.1}$$

and there are only two singly excited states. Their wave functions can be written

$$\Phi_+ = \cos x\ \varphi_a'\varphi_b + \sin x\ \varphi_a\varphi_b' \tag{3.2}$$

$$\Phi_- = \sin x\ \varphi_a'\varphi_b - \cos x\ \varphi_a\varphi_b' \tag{3.3}$$

They are already normalized and mutually orthogonal, so that the eigenvalue problem (2.7) only requires that

$$\langle \Phi_+ | \mathcal{H} | \Phi_- \rangle = 0$$

This can be satisfied by specifying the parameter α so that

$$\operatorname{tg} 2x = \frac{2U}{W_{a'b} - W_{ab'}}, \qquad 0 \le x \le \frac{\pi}{2} \tag{3.4}$$

Here U is the resonance integral from (2.9) in which the indices have been dropped. $W_{a'b}$ is the energy of the configuration $\varphi_a'\ \varphi_b$:

$$W_{a'b} = W_a' + W_b^0 + V_{a'b}' \tag{3.5}$$

and $W_{ab'}$ has a similar meaning. The eigenvalues of Φ_+ and Φ_- are

$$W_\pm = \tfrac{1}{2}(W_{a'b} + W_{ab'}) \pm \frac{W_{a'b} - W_{ab'}}{\cos 2\alpha} = \tfrac{1}{2}(W_{a'b} + W_{ab'}) \pm \frac{U}{\sin 2\alpha} \tag{3.6}$$

Obviously, there are two limiting cases 1 and 2:

1. $2|U| \ll |W_{a'b} - W_{ab'}|, \quad x \sim 0 \text{ or } \frac{\pi}{2}$

With $\alpha \sim 0$ we have

$$\bar{\Phi}_+ \sim \bar{\Phi}_{a'b} = \varphi_{a'}\varphi_b, \quad W_+ \sim W_{a'b} \tag{3.7}$$

$$\bar{\Phi}_- \sim -\bar{\Phi}_{ab'} = -\varphi_a\varphi_{b'}, \quad W_- \sim W_{ab'} \tag{3.8}$$

This is the non-resonance case where the excitation is essentially localized either in the one or in the other molecule and the energies are those of the corresponding configurations. With $\alpha \sim \pi/2$ the situation is similar, but the sites of the excitation are interchanged.

2. $|U| \gg |W_{a'b} - W_{ab'}|, \quad \alpha \sim \frac{\pi}{4}$

$$\bar{\Phi}_+ \sim \bar{\Phi}_S = \frac{1}{\sqrt{2}}(\varphi_{a'}\varphi_b + \varphi_a\varphi_{b'}), \quad W_+ \sim \frac{1}{2}(W_{a'b} + W_{ab'}) + U \tag{3.9}$$

$$\bar{\Phi}_- \sim \bar{\Phi}_A = \frac{1}{\sqrt{2}}(\varphi_{a'}\varphi_b - \varphi_a\varphi_{b'}), \quad W_- \sim \frac{1}{2}(W_{a'b} + W_{ab'}) - U \tag{3.10}$$

This is the resonance case, where the wave functions are the symmetric and antisymmetric combinations of the locally excited configurations and where the excitation is distributed equally over both molecules. The energies of both states differ by an amount of 2 U, this energy difference is the so-called exciton splitting.

The transition charge densities which enter into the resonance energy U as defined in (2.9) can be expanded into point multipole series, leading to a multipole-multipole-expansion for U. Generally, their first term is a dipole-dipole-term representing the interaction between the transition dipole moments $\vec{m}_a$ and $\vec{m}_b$ of both molecules, the squares of which are proportional to the oscillator strenghts of the transitions between the ground- and excited states of the isolated molecules.

If these transitions are allowed, and the intermolecular

distance R_{ab} is not too small, higher multipole contributions may be neglected and the resonance integral approximated by

$$U \sim \frac{1}{n^2 R_{ab}^3}\left[(\vec{m}_a \vec{m}_b) - \frac{3}{R_{ab}^2}(\vec{m}_a \vec{R}_{ab})(\vec{m}_b \vec{R}_{ab})\right] \qquad (3.11)$$

Here n is the refractive index of the surrounding medium, the square of which replaces the dielectric constant for fast polarizations. For a sandwich type dimer, with the transition moments parallel to each other and at right angles to the distance vector $\vec{R}_{ab}$, U is positive and, according to (3.10), the symmetric state that of higher energy. The opposite holds for a head-to-tail orientation with both transition moments parallel to each other and to the distance vector.

The transition moments $\vec{M}_+$ and $\vec{M}_-$ of the dimer itself, which determine the optical transitions between its ground- and excited states, are in the general case according to (2.2), (3.2) and (3.3), weighted vector sums of the molecular transition moments $\vec{m}_a$ and $\vec{m}_b$. In the resonance case of the symmetric dimer, with $\vec{m}_a$ and $\vec{m}_b$ equal and mutually parallel, the transition to the antisymmetric state is forbidden. This is the lower one in the sandwich type dimer but the higher one in the head-to-tail dimer. Therefore, these two kinds of dimers have quite different spectral properties. Intermediate orientations have also been studied quantitatively[8].

For the discussion of excitation transfer, the time dependent Schrödinger equation

$$i\hbar \frac{\partial \Xi(q,t)}{\partial t} = \mathcal{H}\,\Xi(q,t) \qquad (3.12)$$

has to be used, where $\hbar$ is Planck's constant divided by 2π. The stationary states of the dimer are then described by

$$\Xi_I = \Phi_I\, e^{-\frac{i}{\hbar} W_I t}$$

and a general non-stationary state by

$$\Xi(t) = c_+ \bar{\Phi}_+ e^{-\frac{i}{\hbar} W_+ t} + c_- \bar{\Phi}_- e^{-\frac{i}{\hbar} W_- t} \qquad (3.13)$$

with constant coefficients c_+ and c_-. For $W_+ \neq W_-$ this represents a back and forth oscillation of the excitation between both molecules. If we assume the molecule a alone to be excited at t = 0, we have $c_+ = \cos\alpha$ and $c_- = \sin\alpha$, as can readily be seen from (3.2) and (3.3).

A straight-forward calculation then leads to

$$\Xi(t) = e^{-\frac{i}{\hbar}\bar{W}t}\left[\left(\cos\frac{Ut}{\hbar\sin 2\alpha} - i\cos 2\alpha \cdot \sin\frac{Ut}{\hbar\sin 2\alpha}\right)\varphi_a'\varphi_b - i\sin 2\alpha \cdot \sin\frac{Ut}{\hbar\sin 2\alpha}\,\varphi_a\varphi_b'\right] \qquad (3.14)$$

Here, $\bar{W} = \frac{1}{2}(W_+ + W_-)$ is the average energy of both stationary states.

From (3.14) we get for the expectation value $\varrho_{ab'}$ of $\varphi_a\,\varphi_b'$

$$\varrho_{ab'}(t) = \sin^2 2\alpha \cdot \sin^2\frac{Ut}{\hbar\sin 2\alpha} \qquad (3.15)$$

For sufficiently short times this becomes

$$\varrho_{ab'}(t) \sim \frac{U^2 t^2}{\hbar^2} \qquad (3.16)$$

which is independent of α and holds thus under resonance and under non-resonance conditions. But the maximum value of $\varrho_{ab'}$ is

$$\varrho_{ab'}^{max} = \sin^2 2\alpha = \frac{tg^2 2\alpha}{1 + tg^2 2\alpha} = \frac{4U^2}{(W_{a'b} - W_{ab'})^2 + 4U^2} \qquad (3.17)$$

so that ϱ_{ab} becomes large only under near-resonance conditions $\alpha \sim \pi/4$, It obtains its first maximum at the time

$$t^{max} = \frac{\pi\hbar}{2|U|}\sin 2\alpha = \frac{h}{4|U|}\sin 2\alpha$$

If we define the transfer rate $n_{ab'}$ as the maximum expectation value of $\varrho_{ab'}$ divided by this time, we get

$$n_{a\to b} = \frac{4|U|}{h}\,|\sin 2\alpha| \tag{3.18}$$

Under resonance conditions $\alpha = \pi/4$ this becomes

$$n^{res}_{a\to b} = \frac{4|U|}{h} \tag{3.19}$$

which is generally regarded as the transfer rate for resonance. In principle, a similar result might have been obtained by application of the uncertainty relation. For later applications we may keep in mind that the resonance transfer rate is equal to the exciton splitting between W_+ and W_- in (3.10) divided by $h/2$. But one should note that our present definition of the transfer rate is rather arbitrary, due to the quadratic increase of the expectation value ϱ_{ab} and to the back and forth transfer later on. Also, it would be difficult to perform any experiment by which such a transfer rate might be measured.

4. Polymers. As a second example we consider the singly excited states of a long linear polymer, consisting of N molecules, alike, and in equivalent positions. The polymer may have either translational or screw-translational symmetry such as a helix.

The N wave functions (2.6) can then be constructed as the linear combinations

$$\Phi_K = \frac{1}{\sqrt{N}} \sum_{l=1}^{N} e^{ikl}\, \varphi_l' \prod_{n\neq l} \varphi_n \tag{4.1}$$

The index k determines the phase difference between the excitation at adjacent molecules. Its N different values can be chosen so that the Φ_K are mutually orthogonal and also the nondiagonal elements $\langle \Phi_j^* | \mathcal{H} | \Phi_K \rangle$ of the Hamilton operator disappear. Because of the periodicity in (4.1) the indices k can be restricted to the interval

$$-\pi < k \leq \pi$$

For $N \to \infty$, k becomes a continuously variable parameter within these boundaries. If, for simplicity, interactions between non-adjacent molecules are neglected, the energy values are

$$W_i = W_g + h' - h^c + 2(V' - V) + 2U \cos k \qquad (4.2)$$

The interaction matrix elements V, V' and U are the same as defined in (2.4), (2.8) and (2.9) with the indices dropped. The first terms on the right side of (4.2) represent the static contributions to the energy resulting from the excitation of one molecule and from its Coulombic interactions with its neighbors. The last term represents its resonance interaction which depends essentially on k and so on the phase difference of excitation between adjacent molecules. The energy values from (4.2) are distributed within a band of the width 4 U, the so-called exciton band of the system. The expression (4.2) is equivalent to the corresponding one (3.6) for the dimer with $\alpha = \pi/4$. The double amount of the splitting results from the presence of two nearest neighbors for every molecule in the polymer instead of one in the dimer.

The extreme energy values of (4.2) are those for $k = 0$ and $k = \pm \pi$. The nature of these extrema depends on the sign of U, which in the dipole-dipole-approximation is analogous to the expression given in (3.11) for the dimer. Here too this sign depends on the orientation of the molecular transition moments $\vec{m}_1$ towards each other and towards the translation vector between adjacent molecules. For the two extreme cases of orientation, the band structures are depicted in Fig. 1a,b. The considerance of the interaction between more distant molecules would lead to deviations from the simple cos k-dependence of the energy assumed here.

The symmetry of the system imposes severe restrictions on the optical transitions between the ground state and the excited states. One may easily verify that only M_0, the transition

dipole moment for the state k = 0, has a component along the polymer or, in case of a helix, parallel to the screw axis. Furthermore, if this screw axis is r-fold, so that the translational unit cell consists of r molecules, only M_k with $k = \pm \frac{2\pi}{r}$ has a transverse component. (One should keep in mind that k is based here on the screw-translational of our model. For integer r it can be replaced by k' = rk, the wave 'vector' based on translational symmetry. Our exciton band is then split into r subbands which are, however, connected to each other. Both allowed transitions are k' = 0 - transitions as required for translational symmetry.) In the case r = 2 which has been discussed by McRae and Kasha[9], this is $k = \pi$ so that only transitions to the top and to the bottom of the exciton band are dipole-allowed. The same is true for the 3-dimensional analogue of this case, the molecular crystal with two molecules in equivalent positions in the elementary cell. A more complicated case, that of the double-stranded helix of polypeptides has been treated by Rhodes[10].

Our present model allows further, within certain limits, to understand the spectra of the Scheibe-Jelley-polymers mentioned in I. Their characteristic feature is a sharp band with longitudinal polarization which certainly results from the transition to the k = 0 - state. The transverse absorption is, however, broad and seems to extend over the whole band. This might be explained by a pseudo-helical structure with a certain amount of angular disorder as has been supposed earlier[11]. Or, it might result from the coupling with intramolecular vibrations as suggested by McRae[12].

In the stationary exciton states $\bar{\Phi}_\kappa$, the excitation is equally distributed over all components of the polymer. Here, too, the alteration of a non-stationary distribution can be described by the corresponding time-dependent wave functions. Upon

introduction of the appropriate time factors, multiplication with an arbitrary function c(k) and subsequent integration over k one gets from (4.1)

$$\Xi(t) = \sum_{\ell=1}^{N} \varphi_\ell' \prod_{n \neq \ell} \varphi_n \int c(k)\, e^{i(k\ell - \frac{Wt}{\hbar})}\, dk$$

For a wave packet with k-values centered closely at an average value k_o we can eliminate the strong time dependence under the integral by expanding W(k) and writing

$$\Xi(t) = \sum_{\ell=1}^{N} \varphi_\ell' \prod_{n \neq \ell} \varphi_n\, e^{i(k\ell - \frac{W(k_o)}{\hbar}t)} \int c(k)\, e^{i(\ell - \frac{1}{\hbar}\frac{\partial W}{\partial k}|_{k_o} t)(k-k_o)}\, dk$$

The integral represents now an amplitude factor which, due to the property of our c(k), has a steep maximum at

$$\ell^{max} = \frac{t}{\hbar}\frac{\partial W}{\partial k}\Big|_{k_o} = -\frac{2}{\hbar} U t \sin k_o$$

This corresponds to a linear migration of our wave packet with the time-independent group velocity

$$u_g = \frac{d}{t}\ell^{max} = \frac{2d|U|}{\hbar}\,|\sin k_o| \qquad (4.3)$$

where d is the distance between adjacent molecules. With (4.2) and (4.3), the energy in the region $k \sim 0$ can be expressed as

$$W(k) \sim W(0) - \frac{\hbar^2}{2d^2U} u_g^2 = W(0) + \frac{\mu}{2} u_g^2$$

$$\mu = -\frac{\hbar^2}{2d^2U}$$

μ may therefore be interpreted as the 'mass' of the exciton and can be positive or negative, depending on the sign of U. According to (4.3), the exciton transfer rate between adjacent molecules in the polymer is

$$n_{\ell \to \ell+1} = \frac{2|U|}{\hbar}\,|\sin k_o| \qquad (4.4)$$

This depends essentially on k and is extremely small for $k \sim 0$ or $k \sim \pi$, that is for excitons produced by allowed optical transitions in a polymer with p = 1 or 2. But this does not mean that excitation produced in such a way would not migrate essentially. Any excitation transfer experiment will require some kind of a trap within the lattice. The presence of such a trap within the region of a widely delocalized exciton severely disturbs the quasistationary wave function, and the exciton will be soaked in without much regard to its k-value.

A more reasonable expression for the transfer rate should be obtained by averaging over the k-values. This leads to

$$\overline{n_{\ell \to \ell+1}} = \frac{2|U|}{\hbar} \overline{|\sin k_0|} = \frac{2|U|}{\hbar} \frac{2}{\pi} = \frac{8|U|}{h} \qquad (4.5)$$

which is just twice the value (3.19) calculated for the dimer.

Another way to discuss excitation transfer is to assume that the exciton at $t = 0$ is completely localized at one single molecule. Later on it will spread out over surrounding molecules. According to calculations by Merrifield[13] and also by Magee and Funabashi[14] the mean square distance from the origin increases in proportion to the time as follows:

$$\sqrt{\overline{\ell^2}}/t = \frac{\sqrt{2}|U|}{\hbar} = \frac{\sqrt{8}\pi|U|}{h}$$

Numerically, this is not much different from our result (4.5).

III. STRONG AND WEAK COUPLING

5. Potential energy surfaces. In our foregoing discussion we have considered the electrons of the system at fixed nuclear positions. We have so disregarded not only nuclear vibrations but also the differences in the equilibrium positions accompanying electronic excitation. This may be justified in cases of strong resonance interaction where the interaction energy exceeds that of the vibrational quanta involved and where also the time for excitation transfer is so fast that nuclear rearrangement cannot take place. Our results from chapter II can be valid, therefore, in the strong coupling limit only.

For the treatment of cases of weaker interaction, and even for an understanding of their limitation against strong coupling cases, the variation of nuclear coordinates has to be considered. As a first step, we confine our interest to the variation of the electronic wave functions and their energies with the intramolecular coordinates which will be summarized by Q. That is, we consider the potential energy surfaces for the nuclear vibrations but still do not discuss these vibrations in detail. Likewise, intermolecular motions shall not be discussed, so that we can retain our previous assumption of rigid separations and orientations of the individual molecules toward each other.

The original treatments of this problem have been given by Simpson and Peterson[15] and by McClure[16]. The more general aspects have been discussed later by Wittkowsky and Moffitt[17] in an admirably elegant way. Our present discussion will use similar ideas but proceed along a somewhat different line.

For a single molecule, we take the following expressions for

the electronic wave functions and energies of ground- and excited state:

$$\varphi(q,Q), \qquad W = W_0 + \frac{\varkappa}{2}(Q-Q_0)^2 \tag{5.1}$$

$$\varphi'(q,Q), \qquad W' = W_0' + \frac{\varkappa}{2}(Q-Q_0')^2 \tag{5.2}$$

As before, the prime shall indicate electronic excitation. Explicitely, we restrict ourselves to one nuclear coordinate Q for each molecule. At the moment, this is no restriction of generality since the alteration in equilibrium position with excitation can be represented by one coordinate alone, as long as it has not to be a normal coordinate of vibration.

We suppose further that the wave functions depend smoothly on this coordinate and that their energy values are quadratic functions of the distances from the respective equilibrium positions Q_0 and Q_0' for both states. It has been for simplicity only that we have taken the same force constant for the nuclear vibrations of both states. This seems justified because in actual molecules the alteration in equilibrium position is more important than that of the vibrational frequency. However, we shall relax this additional assumption later if necessary.

According to (5.1), (5.2) vertical excitation - in the sense of the Franck-Condon-principle - leads to an excited state energy of

$$W' = W_0' + \frac{\varkappa}{2}(Q_0' - Q_0)^2$$

With W_0' as the minimum energy of the same state, we can take

$$\Delta W = \frac{\varkappa}{2}(Q_0' - Q_0)^2 \tag{5.3}$$

as a rough measure for the total width of the vibronic band system in the monomer. For short, we shall call this later the electronic band width.

Our following treatment of composite systems will be exclusively restricted to dimers. We shall try, however, to generalize some of the results to polymer systems as far as this seems possible.

For a dimer, consisting of two molecules of the same kind, the ground-state wave function is again

$$\Phi_G = \psi_a \psi_b \tag{5.4}$$

but depends now not only on the electronic but also on the nuclear coordinates Q_a and Q_b. The corresponding energy as a function of these is

$$W_G = 2w_o + V + \frac{\kappa}{2}\left[(Q_a - Q_o)^2 + (Q_b - Q_o)^2\right] \tag{5.5}$$

where w_o is again the monomer ground-state energy and V the interaction of both molecules in that state. If a possible Q-dependence of V is neglected, the equilibrium configuration is at $Q_a = Q_b = Q_o$ and the corresponding energy

$$W_G^{min} = 2w_o + V \tag{5.6}$$

In the absence of resonance interaction the excited states would be simply the locally excited ones

$$\Phi_{a'b} = \psi_a' \psi_b, \qquad \Phi_{ab'} \sim \psi_a \psi_b' \tag{5.7}$$

with their energies

$$W_{a'b} = w_e + w_o' + V' + \frac{\kappa}{2}\left[(Q_a - Q_o')^2 + (Q_b - Q_o)^2\right]$$
$$W_{ab'} = w_o + w_e' + V' + \frac{\kappa}{2}\left[(Q_a - Q_o)^2 + (Q_b - Q_o')^2\right] \tag{5.8}$$

In case of $Q_o' \neq Q_o$ these energies are different for all nuclear configurations with $Q_a \neq Q_b$. For the treatment of resonance interaction we must, therefore, refer to the general case of unsymmetrical dimers in 3. Here too, we write for the wave functions

$$\bar{\Phi}_+ = \cos\alpha\ \Psi_a'\Psi_b + \sin\alpha\ \Psi_a\Psi_b' \qquad (3.2)$$

$$\bar{\Phi}_- = \sin\alpha\ \Psi_a'\Psi_b - \cos\alpha\ \Psi_a\Psi_b' \qquad (3.3)$$

In the first place, these functions depend on the nuclear configuration by way of the parameter α which according to (3.4) and (5.8) is now determined by

$$\operatorname{tg} 2\alpha = \frac{2U}{|W_{a'b} - W_{ab'}|} = \frac{2U}{\kappa(Q_a - Q_b)(Q_0 - Q_0')} \qquad (5.9)$$

The energy values, as calculated from (3.6) become now for $U > 0$ (sandwich-type dimer):

$$W_\pm = W_c + W_c' + V' + \frac{\kappa}{4}\left[(Q_0 - Q_0')^2 + (Q_a + Q_b - Q_c - Q_c')^2 + (Q_a - Q_b)^2\right] \pm \frac{1}{2}\sqrt{\kappa^2(Q_a - Q_b)^2(Q_0' - Q_0)^2 + 4U^2} \qquad (5.10)$$

For $U < 0$ the signs must be interchanged.

From (5.10) the following equilibrium configurations and their energies are calculated:

$\bar{\Phi}_+$: Minimum at $Q_a = Q_b = \frac{1}{2}(Q_c + Q_0')$

with the energy $W_+^{min} = W_c + W_c' + V' + \frac{\kappa}{4}(Q_0' - Q_0)^2 + U \qquad (5.11)$

for all values of U.

$\bar{\Phi}_-$: Minimum at $Q_a = Q_b = \frac{1}{2}(Q_0 + Q_0')$

with the energy $W_-^{min} = W_c + W_c' + V' + \frac{\kappa}{2}(Q_0' - Q_0)^2 - U \qquad (5.12)$

for $2|U| \geq \kappa(Q_0' - Q_0)^2 \qquad (5.13)$

but <u>two</u> minima at

$$Q_a = \frac{1}{2}(Q_0' - Q_0) \pm \frac{1}{2}\sqrt{(Q_0' - Q_0)^2 - \frac{4U^2}{\kappa^2(Q_0' - Q_0)^2}} \qquad (5.14)$$

$$Q_b = \frac{1}{2}(Q_0' - Q_0) \mp \frac{1}{2}\sqrt{(Q_0' - Q_0)^2 - \frac{4U^2}{\kappa^2(Q_0' - Q_0)^2}}$$

with the same energy

$$W_-^{min} = W_0 + W_0' + V' - \frac{U^2}{\varkappa (Q_0' - Q_0)^2} \qquad (5.15)$$

for $$2|U| \leq \varkappa (Q_0' - Q_0)^2 \qquad (5.16)$$

In Fig.2 potential energy surfaces with Q_a and Q_b as variables are represented as calculated from (5.10) for W_- in two typical cases. Fig.2a corresponds to the inequality (5.13). This is obviously a strong coupling case. Both molecules have the same equilibrium position which is half way in between those of the ground- and excited monomer states. Fig.2b corresponds to the inequality (5.16) and is a weak coupling case. Here the potential energy surface shows two minima which are close to the equilibrium configurations of the two locally excited states (5.7).

The most essential parts of the potential energy surfaces of the excited states are those within the plane

$$Q_a + Q_b = Q_0 + Q_0'$$

where all extrema are located. The intersections with this plane of both surfaces are, therefore, represented in Fig.3 with the same values as in Fig.2a,b. In addition, the borderline case

$$2|U| = \varkappa (Q_0' - Q_0)^2 \qquad (5.17)$$

is also represented there (designated p = 1).

It follows from (5.9) that in the strong coupling case A, for configurations not too far from those of the minima at $Q_a = Q_b = \frac{1}{2}(Q_0 + Q_0')$, α is close to $\pi/4$. The wave functions φ_+ and φ_- are then, according to (3.2) and (3.3), nearly the symmetric and antisymmetric combinations of $\bar{\Phi}_{a'b}$ and $\bar{\Phi}_{ab'}$. Thus the excitation is essentially <u>delocalized</u>. The energy

difference between the two states W_+ and W_- in (5.10) is, then, much more than the monomer electronic band width w defined in (5.3). The splitting should, therefore, lead to an essentially different spectrum. This is in accord with our empirical criterium for the strong coupling case in chapter I.

For the weak coupling case, (5.14) predicts equilibrium positions for Φ_- which in the limit are at $Q_a \sim Q_o'$, $Q_b \sim Q_o$ and vice versa. For configurations within this range, (5.9) gives $\alpha \sim 0$ (or $\sim \pi/2$) which according to (3.2) and (3.3) means $\bar{\Phi}_+ \sim \bar{\Phi}_{a'b}$, $\bar{\Phi}_- \sim \bar{\Phi}_{ab'}$, that is <u>essential localization</u>. As the potential energy surface is then nearly the same as for non-interacting molecules, the general appearance of the spectrum is the same as that of the monomer. This too is in accord with our previous empirical classification.

From our consideration of potential energy surfaces, the inequalities (5.13) and (5.16) seem to provide a natural limitation between strong and weak coupling. Together with our expression for the electronic band width (5.3) this can be formulated as follows:

$$|U| \gtrsim \frac{\kappa}{2}(Q_o' - Q_o)^2 \sim \Delta w \qquad (5.18)$$

In this form the criterium is similar to that one derived originally by Simpson and Peterson[15] from quite different considerations. Their criterium would be obtained by introduction of the factor 2 into the left side of (5.18), but in regard of the $\gtrsim$-sign and of our crude definition of the electronic band width this difference does not seem to be important. It is quite interesting that this criterium can be obtained from a consideration of potential energy surfaces alone, without taking the vibrational part of the wave functions into account explicitely.

It should be mentioned, however, that the Simpson-Peterson-criterium cannot be applied without some restrictions, as has been emphasized recently by McRae and Siebrand[18]. This results from the fact that the criterium, as derived here, considers the qualitative behavior of the potential energy surfaces only but neglects their quantitative properties. Actually, it is not so much the existence of two minima in the lower potential energy surface but their depth in relation to the vibrationel energy which decides between strong and weak coupling behavior. Under Simpson-Peterson weak coupling conditions (5.16), but with a sufficiently small difference between the equilibrium configurations Q_o and Q'_o of both states, the minima are close to each other and so shallow that even the lowest vibrational state will extend over both of them and not feel much of the small hump in between. This can be visualized from Figs. 2 and 3 if one consideres that there the nuclear coordinates are represented in units of $Q'_o - Q_o$ and the energies in units of $\frac{\nu}{2}(Q'_o - Q_o)^2$.

6. Inclusion of nuclear vibrations. Before we proceed further, we should investigate how far our potential energy surfaces can be used for the description of the vibronic states of our system. The complete Schrödinger equation, including nuclear vibrations, has the form

$$[\mathcal{H}^{(q)} + \mathcal{T}^{(Q)} - E]\,\Psi(q,Q) = 0 \qquad (6.1)$$

Here, $\mathcal{H}^{(q)}$ is the electronic part of the Hamilton operator which we have considered alone up to now. $\mathcal{T}^{(Q)}$ is an additional operator representing the kinetic energy of the nuclei. The superscripts in parenthesis are used to indicate that these operators contain differential procedures acting on the respective coordinates. $\Psi(q,Q)$ is the complete vibronic wave function of the system and E the total energy.

The usual procedure in solving (6.1) is that of the Born-Oppenheimer approximation[19] which is called often the adiabatic approximation. The vibronic wave function is written as a product

$$\bar{\Psi}(q,Q) = \bar{\Phi}(q,Q)\,X(Q) \qquad (6.2)$$

Here, $\bar{\Phi}(q,Q)$ is the electronic wave function for the nuclei at rest, that is, the solution of the electronic part of the Schrödinger equation which we had considered in 5:

$$[\mathcal{H}^{(q)} - W(Q)]\,\bar{\Phi}(q,Q) = 0 \qquad (6.3)$$

X(Q) is a solution of the Schrödinger equation for nuclear motion alone under the potential W(Q) appearing in (6.3):

$$[T^{(Q)} + W(Q) - E]\,X(Q) = 0 \qquad (6.4)$$

By multiplication of (6.3) with X(Q) and of (6.4) with $\bar{\Phi}(q,Q)$ we get by subsequent addition

$$[\mathcal{H}^{(q)} + T^{(Q)} - E]\,\bar{\Psi}(q,Q) =$$

$$= [T^{(Q)}\,\bar{\Phi}(q,Q) - \bar{\Phi}(q,Q)\,T^{(Q)}]\,X(Q) \qquad (6.5)$$

This is a good approximation to the exact Schrödinger equation (6.1), if the term on the right side is small. This requires that the electronic wave function depends only smoothly on the nuclear coordinates Q within the range of the vibrational function X(Q). It can be shown that this holds if the electronic state in question is well separated energetically from other states for the nuclear configurations in question.

We have already supposed that the monomer wave functions are smooth functions of the Q so that for these functions the Born-Oppenheimer separation is justified. We shall see, that the same holds also for the dimer states in the extreme cases of strong or of weak coupling either for a restricted range of

nuclear vibrations at least.

For strong coupling the parameter α is close to $\pi/4$ in that region and varies little over a wide range of nuclear configurations. Therefore, $\underline{\tilde{\phi}}_+$ and $\underline{\tilde{\phi}}_-$ will vary smoothly, as the monomer functions, with a change in the internal nuclear coordinates Q. For weak coupling α is close to 0 or $\pi/2$ and it remains so, at least in the neighborhood of each of the minima of W_-. Although α and $\underline{\tilde{\phi}}_-$ will vary quite abruptly in the region of $Q_a = Q_b$, this is unimportant for vibronic functions which are confined mainly to the regions of the minima.

The situation is different, however, in the intermediate range under conditions like those represented in Fig.3 (for $\gamma = 1$). Here, α still varies considerably near $Q_a = Q_b$, and the vibrational functions are large in that region. Our treatment based on the electronic wave functions (3.2) and (3.3) should therefore be restricted to the nearly extreme coupling cases.

At first we shall investigate the width of the electronic band for one of the individual transitions of the dimer. For this purpose, in Fig.2 the potential energy surfaces of the ground state are represented also. From a comparison of Fig.2a and 2b it is evident that the distance between the equilibrium configurations of ground and excited state is less in the strong coupling case. For extremely weak coupling this difference is, of course, the same as in the monomer but for the strong coupling case less by a factor of $1/\sqrt{2}$. Therefore, the width of the individual electronic band should be essentially reduced and this should further contribute to the difference in appearence of monomer and strongly coupled dimer spectra.

This can be established more quantitatively from (5.10). For the strong coupling limit, vertical excitation ($Q_a = Q_b = Q_o$) leads to

$$W_{\pm}^{\text{vertical}} = W_0 + W_0' + V' + \frac{k}{2}(Q_0' - Q_0)^2 \pm U$$

Since the energy minima from (5.11) and (5.12) are

$$W_{\pm}^{\min} = W_0 + W_0' + V' + \frac{k}{4}(Q_0' - Q_0)^2 \pm U$$

one gets for the Franck-Condon widths of the dimer by comparison with (5.3)

$$W_{\pm} = \frac{k}{4}(Q_0' - Q_0)^2 = \frac{1}{2} E_M$$

The widths of the individual electronic band in the strongly coupled dimer should, therefore, be only one half of that of the monomer.

Some indications for this reduction in band width can be found in the spectra of a pyridocyanine dye, as by McRae[12]. Further experimental evidence for dimers is somewhat meager, probably because of the overlap between the two electronic transitions and also because of the interference with the spectra of higher association stages.

However, the extrapolation of this result to polymers with large N leads to an understanding of the drastic reduction of vibrational broadening in the k = 0 - exciton band of the Scheibe-Jelley-polymers. Obviously, this results from the distribution of the difference between ground- and excited state equilibrium position over a large number of molecules.

7. Detailed consideration of vibronic states. We shall now proceed in formulating the vibronic wave functions for the dimer in its two extreme coupling cases, where the Born-

Oppenheimer separation is possible. We write the wave function then in a general way as

$$\Psi_{k,vw}(q,Q) = \Phi_k(q_a, q_b, Q_a, Q_b)\,\chi_{vw}(Q_a, Q_b) \qquad (7.1)$$

where k denotes one of the electronic states, while v and w are vibrational quantum numbers. Our restriction to one single intramolecular coordinate for each molecule becomes now essential, because we have to regard it as a normal coordinate. This is not too serious since at least in the more symmetric molecules one vibration is predominantly involved in an electronic transition. Furthermore we regard the vibronic levels of (7.1) as infinitely sharp. This might seem obvious here, but our later considerations in chapter IV will show that this is an essential assumption which is not always justified.

For the ground state k = G we can simply use the electronic wave function (5.4) and combine it with the vibronic functions $\chi(Q_a)$ and $\chi(Q_b)$ of the individual molecules in their ground-state centered at Q_o. Thus we get

$$\Psi_{G,vw} = \varphi_a \varphi_b \chi_v(Q_a)\chi_w(Q_b) \qquad (7.2)$$

The electronic wave functions φ_a and φ_b contain not only the electronic but also the nuclear coordinates. This latter dependence is not strong and may be neglected, but it would seem reasonable to take the functions at the ground state equilibrium position $Q_a = Q_b = Q_o$. Because the nuclear potential has been supposed to be harmonic, the χ_v are Hermite-functions of their respective coordinates, and the energy values belonging to (7.2), including zero point energy, are

$$E_s = 2W_o + V + (v + w + 1)\hbar\nu_o \qquad (7.3)$$

In our harmonic approximation, these vibronic states are $(v + w + 1)$-fold degenerate. For the excited states the two

coupling cases need separate treatments. In the strong coupling limit we get with the electronic wave functions for $\alpha = \pi/4$ together with the appropriate vibrational functions

$$\Psi_{\pm,vw} = \frac{1}{\sqrt{2}}\left[\varphi'_a \varphi_b \pm \varphi_a \varphi'_b\right] \chi_v^{(\prime)}(Q_a)\chi_w^{(\prime)}(Q_b) \qquad (7.4)$$

The prime in parenthesis is used here to indicate that the respective vibrational functions are centered at the 'half excited' equilibrium configuration $Q_a = Q_b = \frac{1}{2}(Q_o + Q'_o)$ found in 5 for the excited states. The electronic wave functions too should be specified for these values of the nuclear coordinates. Wave functions of this type, which are constructed from electronic and vibrational functions for the system as a whole, have been called E-V-functions by McRae[12]. The energy values belonging to (7.4) are

$$E_{\pm,vw} = W_o + W'_o + V \pm \mathcal{U} + (v + w + 1)\hbar\nu_o \qquad (7.5)$$

As in the ground state, there is a (v + w + 1)-fold degeneracy for harmonic vibrations. This degeneracy would not even be removed if the force constants for the ground and excited state of the monomer would have been taken different in (5.1) and (5.2). One may verify from an expansion of the potential energy surfaces (5.10) near the equlibrium configuration $Q_a = Q_b = \frac{1}{2}(Q_o + Q'_o)$ that the force constants and therefore also the frequencies are in fact those of the monomer. This can also be visualized from an inspection of Fig.2a.

Under decreasing coupling, the vibrational functions remain centered at the same equilibrium configuration. However, the force constants change, as can be verified from (5.10) and is evident from Figs.2 and 3. More specifically, the force constant for the antisymmetric vibration $\int Q_a = -\delta Q_b$ increases for the higher one of the two states, whereas it decreases

for the lower one (Φ_+ and Φ_- respectively, if $U > 0$ is assumed). On the other hand, the force constant of the symmetric vibration stays the same. This removes the vibrational degeneracy and leads to a first order splitting of the energy values in (7.5). This corresponds to a mixing between wave functions (7.4) with the same vibrational quantum number sum v + w. In next order, the Q-dependence of the parameter α in the electronic wave functions becomes essential so that even a more general product formulation than (7.4) of the vibronic wave functions becomes invalid. If these functions are to be retained, heavy mixing among them must be considered under which only the total symmetry of the vibronic states (not the electronic or the vibrational ones alone) is retained. Starting from his E-V-coupling limit (our strong coupling one), McRae[12] has used a perturbational method for such less strong coupling cases.

In the weak coupling limit, the higher one of the excited states (Φ_+ for $U > 0$) has not much interest because its equilibrium configuration is far from that of the ground state. The potential energy surface of the lower excited state Φ_- has two minima of equal energy at the two configurations

$$Q_1 = Q_0', \; Q_2 = Q_0 \qquad \text{and} \qquad Q_1 = Q_0, \; Q_2 = Q_0'$$

If these minima are deep enough, the lowest vibrational states will be confined mainly to their regions. Since in this case the force constants are those of the free molecule, we can again use products of monomer vibrational functions. But the inherent degeneracy of the double minimum potential should be resolved by taking suitable linear combinations such as

$$\chi_{vw,\pm} = \frac{1}{\sqrt{2}}\left[\chi_v'(Q_1)\chi_w(Q_2) \pm \chi_w(Q_1)\chi_v'(Q_2)\right] \qquad (7.6)$$

The primed monomer vibrational function denotes one of the excited stateswhich is centered at Q_0'.

For $v + w > 0$, we would have another degeneracy resulting from our former assumption of equal frequencies in ground- and excited state. Here we shall lift this degeneracy by making the more realistic assumption of a certain difference between the frequency ν_0' of the excited monomer and the frequency ν_0 of the unexcited one. We shall call this further the <u>non-degenerate</u> weak coupling case.

For the construction of vibronic wave functions the vibronic part (7.6) has to be multiplied by the electronic part Φ_-. As we have already stated in 6, the parameter α is essentially constant within each of the two equilibrium regions but has there different values, close to 0 at the one and close to $\pi/2$ at the other. According to our general expression (3.3) for Φ_-, this function has now a somewhat peculiar character, being $\varphi_a' \varphi_b$ near one minimum and $\varphi_a \varphi_b'$ near the other. Thus we can write for sufficiently low vibronic states

$$\Psi_{v w,\pm} = \frac{1}{\sqrt{2}}\left[\varphi_a' \varphi_b \chi_v'(Q_a)\chi_w(Q_b) \pm \varphi_a \varphi_b' \chi_w(Q_a)\chi_v'(Q_b)\right] \quad (7.7)$$

The corresponding energies are conveniently calculated as the diagonal elements of the complete Hamiltonian:

$$E_{v w,\pm} = \langle \Psi_{v w,\pm} | \mathcal{H} | \Psi_{v w,\pm} \rangle = N_- + N_-' + V' + (v+\tfrac{1}{2})\hbar\nu_-' + (w+\tfrac{1}{2})\hbar\nu_0 \pm U S_{vw}^2 \quad (7.8)$$

Here U is the same electronic resonance integral (2.9) as before. It is, however multiplied with the square of the vibrational overlap integral

$$S_{vw} = \langle \chi_v' | \chi_w \rangle \quad (7.9)$$

This is different from 0 for $v \neq w$, because both vibrational functions belong to different centers. The S_{vw} observe the completeness relation

$$\sum_v S_{vw}^2 = \sum_w S_{vw}^2 = 1 \qquad (7.10)$$

Therefore, the splitting in (7.8) is not only small because of the small value of U in the weak coupling case, but it is further reduced by the factor S_{vw}^2 which is less than unity.

Our wave functions (7.7) and the corresponding energies (7.8) are sufficient, if this splitting is small compared with the energy differences between the vibronic levels with different quantum numbers of v and w. Since, generally, the states with the same quantum number sum v + w will be close to each other, this condition can be specified as

$$|U| S_{vw}^2 \ll \hbar |\nu_v - \nu_v'| \qquad (7.11)$$

If $|U|$ is larger but still close to the weak coupling limit, as defined in (5.16), it is reasonable to return to our previous assumption of $\nu_v' = \nu_v$. We shall call this the <u>degenerate</u> weak coupling subcase.

For v = w = 0, (7.7) and (7.8) are valid in this case too, since there is no further vibronic level with the same quantum number sum. For higher vibronic levels, the zero order wave functions are linear combinations of the wave functions (7.7) with the same $v + w = \bar{v}$. The function for the one quantum levels $\bar{v} = \bar{1}$ may be given here as an example

$$\Psi_{\bar{1},\pm,\pm} = \frac{1}{2}\left[\varphi_a' \varphi_b \left(\chi_1'(Q_a)\chi_0(Q_b) \pm \chi_0'(Q_a)\chi_1(Q_b)\right)\right.$$
$$\left. \pm \varphi_a \varphi_b' \left(\chi_1(Q_a)\chi_0(Q_b) \pm \chi_0(Q_a)\chi_1'(Q_b)\right)\right] \qquad (7.12)$$

The signs in the round brackets are here assumed to be interchanged together, but independently from the signs outside, so that the total number of states is 4. Their energies can be calculated as those in (7.8).

$$E_{\bar{1},\pm,\pm} = \nu_0 + \nu_0' + V' + \ldots\nu_0 \pm U(S_{00}S_{11} \pm S_{01}^2) \qquad (7.13)$$

Wave functions and energy levels for some higher vibronic states have been given by Siebrand[20].

For $\nu_0' = \nu_0$, that is for the degenerate case, and for harmonic vibrations the S_{vw} are functions of one single parameter

$$\gamma = \frac{\chi(Q_0' - Q_0)^2}{\ldots\nu_0} = \frac{\ldots W}{h\nu_0} \qquad (7.14)$$

γ can so be regarded as the width of the monomer electronic band, measured in units of vibrational quanta. A general expression for the S_{vw} is [21]

$$S_{vw} = \sqrt{v!\,w!} \sum_r \frac{(-1)^{v-r}\,\gamma^{v+w-r}}{(v-r)!\,(w-r)!\,r!}\, e^{-\frac{\gamma}{2}}$$

$$\text{with} \quad 0 \le r \le \begin{matrix} v+1 \\ w+1 \end{matrix} \qquad (7.15)$$

The first few members are

$$S_{00} = e^{-\frac{\gamma}{2}}, \quad S_{01} = \sqrt{\gamma}\, e^{-\frac{\gamma}{2}}, \quad S_{11} = (1-\gamma)\, e^{-\frac{\gamma}{2}}$$

Further members of this series have been published, together with their graphical representations[20].

Appropriate values of γ might be estimated from spectra because the intensities of allowed $v \leftarrow 0$-vibronic bands should be proportional to S_{0v}^2. For instance, the intensity ratio of the first two vibronic bands in the 3650 Å-transition of anthracene suggests $\gamma \sim 1$. As this might be typical for weak coupling cases,

the reduction of band splitting by the occurrence of the vibronic overlap integrals in (7.8) and (7.13) is not so drastic as one might suspect.

With stronger deviations from the weak coupling limit the mixing of vibronic states extends to those of different total vibrational quantum numbers $\bar{v}$, as far as they have the same symmetry. First order wave functions, and energies correct to the second order, have been obtained by McRae[21] with a pertubation treatment, starting from his m-m-coupling case which corresponds to our degenerate weak coupling case. Earlier, the same author[12] has treated intermediate coupling cases by another approximation, based on the application of zero order pertubation theory to the accidental degeneracies which occur in that region between wave functions of the type (7.7). For the same purpose, Siebrand[20], in his treatment of a quite analogous polaron problem, has preferred a variation method based on the use of strong and weak coupling limit wave functions together. Energy diagrams have been obtained by both authors for that intermediate region. Further perturbational treatments, starting from both limits, have been given by Fulton and Gouterman[22].

It might be possible also to start with the exact vibrational wave functions for the single- or double-minimum potential (5.10) However in this case the term on the right side of (6.5) resulting from the incomplete separation of the variables by the Born-Oppenheimer procedure, would deserve special considerations. Up to now, this possibility has not yet been explored.

Our present results can easily be formulated in terms of excitation transfer. It is now obvious that the transfer rate

$$n_{a\to b} = \frac{4|U|}{\hbar} \qquad (3.19)$$

calculated earlier for a dimer of alike molecules will be valid in the strong coupling case only. The transfer occurs, in this case, with fixed nuclear configuration, corresponding to the average between ground- and excited state.

As we have found for the symmetric dimer in 3, the transfer rate is equal to the resonance splitting divided by 2/h. This should be valid also in the weak coupling case, if there is essential interaction only between one pair of equivalent levels. Thus we get from (7.8) for non-degenerate weak coupling

$$n_{a\to b}^{v\,w} = \frac{4|U|}{h} S_{v\,w}^{2} \qquad (7.16)$$

This is the transfer rate between an excited molecule with the vibrational quantum number v and an unexcited one with the quantum number w. As may be seen from an inspection of the corresponding wave functions (7.7), this transfer is accompanied by an exchange of the vibrational quanta so that the excited molecule stays in the same vibrational level. Likewise, the average values of the nuclear coordinates change according to the temporary excitation of the one or the other molecule. As is evident from (7.16) the transfer rate depends on the vibrational quantum numbers of both molecules.

Schematically, this kind of transfer is represented in Fig.4a, where the molecule a returns from its original vibronic level v of the excited state to the ground state level w, while the molecule b undergoes the inverse process. One may call this a pair of coupled transitions within these molecules.

In the degenerate weak coupling case the situation is somewhat different. As one may conclude from the inspection of wave functions like (7.12) the transfer of electronic excitation may or may not be connected with an exchange of the vibrational quanta. However, here too the alteration of nuclear coordinates

is connected with the transfer.

Fig.4b represents an example for transfer under these conditions. From an original pair of levels v and w of the excited molecule and the unexcited one, several pairs of coupled transitions may now occur. These are

$$v \to v + n \quad \text{for a, together with}$$

$$w \to w - n \quad \text{for b, with the condition that}$$

$$-v \leq n \leq w$$

This gives a total number of v + w + 1 pairs of coupled transitions. For v = w = 0, the transfer rate is that of (7.16). Vibronically excited states would deserve an individual treatment because of the different participation of vibrational quanta, but it is evident that then the transfer rate for degenerate weak coupling transfer exceeds that of (7.16).

Although in this chapter we have restricted ourselves to the consideration of dimers only, it is tempting to extrapolate these results to polymers. From (4.4) together with (7.16) we may expect for non-degenerate weak coupling a transfer rate between adjacent molecules of

$$W^{v,w}_{a\to b} = \frac{2|U|\,S^2_{vn}}{\hbar}\,|\sin k_0| \qquad (7.17)$$

where k_0 describes the phase of the exciton state. For v = w = 0, this would apply as well in the degenerate subcase. It corresponds to the migration of an exciton in which the temporatily excited molecule alone has the excited state equilibrium configuration but all other molecules that of the ground state. One may describe this as a <u>lattice distortion</u> which is strictly connected with the exciton.

Higher approximations for exciton migration under stronger coupling have been obtained by McRae[12,21] and by Merrifield[23]. The lattice distortion extends then, together with the excitation, over an increasing number of molecules until it finally, in the strong coupling case, disappears because it is distributed among an infinite number of molecules.

IV. VERY WEAK COUPLING

8. Preliminary considerations. In chapter III we have considered the effects of vibrational structure of our system but have disregarded a possible structure of the vibronic levels themselves. More specifically, we have based our treatment on the assumption of infinitely sharp vibronic levels. To this one cannot object, in actual cases, as long as the vibronic splitting resulting from coupling exceeds the finite width of the indidual vibronic band. One must expect, however, that for very weak interaction even two coinciding vibronic levels are not completely at resonance with each other, but certain regions of them only. In that case, the theory developed for weak coupling can no more be valid, but instead we have another, well defined, coupling case. It is this case, which we shall call the very weak coupling case. This definition is in accord with our experimental one given in chapter I, because all eventual splitting effects would be masked by the finite vibronic band width.

Solution spectra of organic compounds have usually fairly broad vibronic bands. Quite often, the width of these is not much less than the vibrational spacing, and even at liquid nitrogen temperature band widths of 100 cm^{-1} or more, to be compared with spacing of 1000 cm^{-1} or less, are the rule rather than an exception. It is under special conditions only that sharper bands are observed, such as for aromatic hydrocarbons in adequate crystalline hydrocarbon solvents at liquid nitrogen temperature or below[24]. But these so called 'line spectra' still have widths of the order of 10 cm^{-1}, and even at liquid helium temperature 3 cm^{-1} seems to be a lower limit[25].

Certainly, this finite band width, which is several orders of magnitude larger then that calculated from the life times of the excited electronic states themselves, may have different causes. Different local environments of the molecules might be a possible cause in solid solution spectra. It is out of the question that this would seriously hamper the transfer in cases, where the coupling energy is less than the differences of the vibronic levels between different molecules.

Another cause might be more important, at least in liquid systems at higher temperature. The intramolecular vibrations of different molecules are certainly coupled to some extent with each other and with the multitude of intermolecular lattice vibrations. As a result of this, each supposedly intramolecular normal vibration is, in fact, a bunch of normal vibrations of the system. The frequency spectrum of this extends over a certain range which can be regarded as the vibronic band width. In our previous model, part of this might have been considered by allowing a mechanical coupling between the vibrations of the separate molecules as well as a change of their mutual distance and orientation.

Alternatively, we can still regard the vibrations as essentially intramolecular but then we must take into account vibrational energy exchange. We can ascribe this to a kind of collisional process between the molecule and its neighbors. Such processes are responsible for the comparatively fast establishment of thermal equilibrium between the vibrational degrees of freedom of an excited molecule and its surroundings. The time required for this has been estimated to about 10^{-12} sec or even shorter.[26] From thermal conductivity data, 10^{-12} sec would seem reasonable under room temperature conditions,

corresponding to a band width of 30 cm^{-1}.*

If the coupling is so weak that the transfer has not been accomplished during the collisional lifetime of such a vibronic level, the transfer will necessarily be afflicted by such collisions. We shall illustrate this by a rough calculation.

Let us consider again an initial state in which the excited molecule a occupies the vibrational level v, and the unexcited molecule b occupies the level w. Under our conditions of very weak coupling the transfer can solely occur with the exchange of the vibrational quanta v and w between both molecules as it has been depicted in Fig.4a. The increasing expectation value for the final state of the system which may be designated here as $\varrho_{aw,b'v}$ can be calculated from (3.16) if we replace there the electronic interaction energy U by the vibronic interaction energy, which according to (7.8) is $U\,S^2_{vw}$ or for short:

$$U S_{vw}^2 = u_{vw} \tag{8.1}$$

Thus we get

$$\varrho_{aw,b'v} \sim \frac{u_{vw}^2 t^2}{\hbar^2}$$

as long as this stays small and as long as no collision occurs. If the first collision occurs at $t = \tau$, $\varrho_{aw,b'v}$ will have increased by an amount of

$$\Delta \varrho_{aw,b'v} \sim \frac{u_{vw}^2 \tau^2}{\hbar^2}$$

Since such a collision destroys all phase relations between

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* Thermal conductivities of non-metallic substances are of the order of 10^{-3} $cm^2 \cdot sec^{-1}$. For equilibrium within molecular distances ($3 \cdot 10^{-8}$ cm) this leads to the time given here.

the wave functions, the increase during the further collision time periods will be the same, so that we get

$$\varrho_{av,b'w}(t) \sim \frac{t}{\tau}\,\Delta\varrho_{av,b'w} \sim \frac{u_{vw}^2\,\tau}{\hbar^2}\,t \qquad (8.2)$$

In contradistinction from the strong and the weak coupling case, the transfer is now linear in time, and the rate can be unambigously calculated as

$$n_{a\to b'}^{vw} \sim \frac{\varrho_{av,b'w}}{t} = \frac{u_{vw}^2\,\tau}{\hbar^2}$$

If we express the collision time interval by the corresponding band width $\Delta\varepsilon = h/\tau$, we get finally

$$n_{a\to b}^{vw} \sim \frac{2\pi\,u_{vw}^2}{\hbar\,\Delta\varepsilon} = \frac{4\pi^2\,u_{vw}^2}{h\,\Delta\varepsilon} \qquad (8.3)$$

The linear increase of the expectation value of the final state, and the square dependence of the interaction energy are the characteristic features of our present very weak coupling case. The comparison with (7.16) shows that for the same but small interaction the transfer rate is less than that for so-called weak coupling. The transition from weak to very weak coupling occurs unavoidably if the transfer calculated from (7.16) would last longer than the collisional time τ. This places the approximate limit between these two cases at

$$|u_{vw}| \sim \frac{\hbar}{4\tau} = \frac{\Delta\varepsilon}{4} \qquad (8.4)$$

A reciprocal argument, based on (8.3) would place it at

$$|u_{vw}| \sim \frac{\Delta\varepsilon}{3\pi}$$

which is not much different from (8.4).

Several misconceptions seem to exist - even in the more recent literature - about the nature of this very weak coupling case.

It has been considered based on a different model[4] (the interaction-of-continua-model as opposed to the exciton-model). Actually it is just one typical case of excitation transfer based on the same interaction matrix as for weak coupling. This leaves the system no choice between two different mechanisms. In the contrary, the system has to arrange its transfer in accordance with the prevailing conditions. If due to large distances or other reasons the [illegible] matrix element is less than the vibronic band width, we have the conditions of the very weak coupling case.

Furthermore, there is the belief that very weak coupling formalism would apply only to excitation transfer between different molecules[27]. It is the purpose of our present considerations to show that this is not true. It is only true that very weak coupling allows for such transfer too provided the necessary requirements, which will be investigated later, are met.

In order to make our further treatment as general as possible we shall formulate it for continuous vibronic levels. However, this includes discrete level systems as well, and we shall see that even the strong and the weak coupling cases are covered.

9. Detailed Theory. We suppose again that a molecule a is excited and another molecule b unexcited at the beginning. Both molecules may be of the same kind or different. Their total vibronic energies shall be named E'_a and E_b respectively. We shall follow then the developement with time of all situations in which molecule b is excited instead of a and where the vibronic energies are, then, E_a and E'_b respectively.

By use of molecular vibronic wave functions $\bar{\Psi}(q,Q,E)$ with the corresponding energies as additional parameters, such processes can be described as

$$\psi_a'(E_a')\psi_b(E_b) \longrightarrow \psi_a(E_a)\psi_b'(E_b')$$

or shorter by use of dimer vibronic wave functions as

$$\bar{\Psi}_{a'b}(E_a', E_b) \longrightarrow \bar{\Psi}_{ab'}(E_a, E_b')$$

It is convenient here to normalize the molecular wave functions belonging to the original state $\bar{\Psi}_{a'b} = \psi_a'\psi_b$ and those belonging to the final state $\bar{\Psi}_{ab'} = \psi_a\psi_b'$ differently [28,29]. Retaining for the former ones the usual normalization:

$$\langle \psi_a' | \psi_a' \rangle = \langle \psi_b | \psi_b \rangle = 1$$

we define the normalization of the latter ones as follows:

$$\langle \psi_a | \psi_a \rangle = \frac{dv_a}{dE}, \quad \langle \psi_b' | \psi_b' \rangle = \frac{dv_b'}{dE}$$

Here $\langle\ |\ \rangle$ denotes the product of the functions in brackets integrated over the corresponding coordinates q and Q, while v_a and v_b' are quantum numbers of intramolecular vibration. As before, only real wave functions are considered.

With these definitions the orthonormalization relations for wave functions with different energy values E and $\bar{E}$ are

$$\langle \psi(E) | \psi(\bar{E}) \rangle = \delta(E-\bar{E}) = \frac{dv}{dE}\delta(v-\bar{v})$$

with $\psi = \psi_a'$ or ψ_b. Here v and $\bar{v}$ are the vibrational quantum numbers belonging to the energies E and $\bar{E}$. $\delta(x)$ is the Dirac δ-function, which has the property $a\delta(ax) = \delta(x)$. Furthermore, the expectation value of any operator Op is

$$\overline{exp}(Op) = \langle \psi | Op | \psi \rangle \frac{dE}{dv}$$

so that $\langle \psi | Op | \psi \rangle$ now represents the <u>density</u> of this expectation value on the energy scale. The expectation value itself for

any final state energy interval is obtained by integration over this interval. The properties of the final state system wave function $\Psi_{ab'}$ follow from those of its factors ψ_a and ψ'_b. These wave functions are, of course, also functions of their respective electronic and nuclear coordinates q and Q.

The corresponding time dependent wave function is then

$$\Xi(t) = c_0(t)\,\Psi_{a'b}(E'_a, E_b)\, e^{-\frac{i}{\hbar}(E'_a+E_b)t} + \iint c(E_a, E'_b, t)\,\Psi_{ab'}(E_a, E'_b)\, e^{-\frac{i}{\hbar}(E_a+E'_b)t}\, dE_a\, dE'_b \tag{9.1}$$

The time dependence of the slowly varying coefficients $c(E_a, E'_b, t)$ follows from the time dependent Schrödinger equation which we write here

$$i\hbar \frac{\partial \Xi}{\partial t} = (\mathcal{H}_0 + \mathcal{V})\,\Xi \tag{9.2}$$

$\mathcal{H}_0$ is the unperturbed Hamilton operator, of which $\Psi_{a'b}(E'_a, E_b)$ and $\Psi_{ab'}(E_a, E'_b)$ are eigenfunctions with their respective energies as eigenvalues. $\mathcal{V}$ represents the interaction between these, which is supposed to be resonance interaction only, while the Coulombic interaction is thought to be already included in $\mathcal{H}_0$. By insertion of (9.1) into (9.2) together with the initial conditions $c_0(0) = 1$, $c(E_a, E'_b, 0) = 0$ one obtains

$$\frac{\partial c_0}{\partial t}\Psi_{a'b}(E'_a, E_b)\, e^{-\frac{i}{\hbar}(E'_a+E_b)t} + \iint \frac{\partial c(E_a, E'_b)}{\partial t}\Psi_{ab'}(E_a, E'_b)\, e^{-\frac{i}{\hbar}(E_a+E'_b)t}\, dE_a\, dE'_b = \frac{-i}{\hbar}\mathcal{V}\,\Psi_{a'b}(E'_a, E_b)\, e^{-\frac{i}{\hbar}(E'_a+E_b)t} \tag{9.3}$$

This and the following results are valid as long as the final states are not essentially populated and the depletion of the original state can be neglected.

Multiplication with $\Psi_{ab'}(\bar{E}_a,\bar{E}_b')$, where the bar denotes a pair of other values of E_a and E_b', and subsequent integration over the q,Q-apace leads under consideration of the orthonormalization relations between the unparturbed wave functions

$$\langle \Psi_{a'b}(E_a',E_b)|\Psi_{ab'}(\bar{E}_a,\bar{E}_b')\rangle = 0 \qquad (9.4)$$

and $$\langle \Psi_{ab'}(E_a,E_b')|\Psi_{ab'}(\bar{E}_a,\bar{E}_b')\rangle = \delta(E_a-\bar{E}_a)\,\delta(E_b'-\bar{E}_b') \qquad (9.5)$$

to $$\frac{\partial c(E_a,E_b,t)}{\partial t} = -\frac{i}{\hbar}\langle \Psi_{a'b}(E_a',E_b)|V|\Psi_{ab'}(E_a,E_b')\,e^{-\frac{i}{\hbar}\Delta E t} \qquad (9.6)$$

where $$\Delta E = E_a' - E_a - E_b + E_b' \qquad (9.7)$$

is the energy difference between the initial and the final state. In the following we shall use the short hand notation

$$\langle \Psi_{a'b}(E_a',E_b)|V|\Psi_{ab'}(E_a,E_b')\rangle = u(E_a,E_b') \qquad (9.8)$$

where the dependence on the initial energies E_a' and E_b is dropped because these are considered to be constant. With our normalization for the final state $u(E_a,E_b')$ is the density of the interaction matrix element in the E_a-E_b'-plane. The integration of (9.6) with the initial condition $c(E_a,E_b',0) = 0$ leads to

$$c(E_a,E_b',t) = -\frac{i}{\hbar}\,u(E_a,E_b')\int_0^t e^{-\frac{i}{\hbar}\Delta E t}\,dt = u(E_a,E_b')\,\frac{e^{-\frac{i}{\hbar}\Delta E t}-1}{\Delta E} \qquad (9.9)$$

The expectation value for the state $\varrho_{ab'}(E_a,E_b',t)$ becomes then

$$|c(E_a,E_b',t)|^2 = \frac{4u^2(E_a,E_b')}{(\Delta E)^2}\sin^2\frac{\Delta E t}{2\hbar} \qquad (9.10)$$

By integration over the final state energies E_a and E_b' we obtain finally the probability $\varrho_{ab'}$ that molecule b is excited, independent of the final vibronic energies of both:

$$\varrho_{ab'}(t) = \iint |c(E_a, E_b', t)|^2 \, dE_a \, dE_b'$$

$$= 4 \iint \frac{U^2(E_a, E_b') \sin^2 \frac{\Delta E t}{2\hbar}}{(\Delta E)^2} \, dE_a \, dE_b' \qquad (9.11)$$

This expression is valid as long as $\varrho_{ab'} \ll 1$. For sufficiently short times, such that

$$\frac{\Delta E t}{2\hbar} \ll 1 \qquad (9.12)$$

for the energy differences considered, we can approximate the sine by its argument and obtain

$$\varrho_{ab'}(t) \sim \frac{t^2}{\hbar^2} \iint U^2(E_a, E_b') \, dE_a \, dE_b' \qquad (9.13)$$

If the condition (9.12) is satisfied for all energy values within the total ranges Δw and $\Delta w'$ of the electronic transitions, the integration in (9.13) can be performed over these ranges. In regard of our normalization, we obtain then

$$\varrho_{ab'}(t) \sim \frac{U^2 t^2}{\hbar^2} \qquad (9.14)$$

where U^2 is the square of the total electronic interaction-matrixelement as defined in (2.9). (9.14) is identical with our earlier result (3.16) for the strong coupling case, which, therefore, is covered also by our present treatment. If we require that essential transfer occurs under these conditions so that $\varrho_{ab'}(t)$ approaches unity (disregarding here the depletion of the initial state and a possible back transfer), we have $|U| \sim \hbar/t$ for times within the limits of (9.12), which are

$$t \ll \frac{2\hbar}{\Delta E} \sim \frac{2\hbar}{\Delta W}$$

This leads to

$$2|U| \gg \Delta W \qquad (9.15)$$

as an approximate condition for strong coupling transfer, which is in fact the original Simpson-Peterson criterium for this case.

In case of molecules with well defined vibronic levels (9.13) can be used for even longer time intervals, if the integration is restricted to those regions $\Delta\varepsilon_v$ and $\Delta\varepsilon_w$ of E_a and E'_b which correspond to the vibrational levels v and w, respectively, of the original state of the system. The integration then leads to

$$\varrho_{aw,b'v}(t) \sim \frac{u_{vw}^2 t^2}{\hbar^2} \qquad (9.16)$$

where u_{vw} as before is the vibronic matrix element of resonance interaction. We have neglected here further contributions to $\varrho_{aw,b'v}$ from other bands within the integration range in (9.11) since these contributions are small because of the denominator ΔE^2 under the integral. Obviously, (9.16) describes the transfer under non-degenerate weak coupling conditions. For the degenerate subcase we have merely to perform the summation over the degenerate final levels v + n and w + n, with $-v \leq n \leq w$ as in 7:

$$\varrho_{a,v+n;\,b',w-n}(t) \sim \frac{\sum_n u_{v+n,w-n}^2}{\hbar^2} t^2 \qquad (9.17)$$

Our approximation (9.13) becomes invalid here too if the condition (9,12) is no more satisfied for energy values within the same pair of vibronic levels. By the same reasoning as applied to the strong coupling case we get now

$$2|u_{vw}| >> \Delta\varepsilon \qquad (9.18)$$

as a <u>lower limit</u> for the weak coupling case, where $\Delta\varepsilon$ is the vibronic band width. This is not much different from the limit (8.4) found earlier by our preliminary considerations.

If the interaction matrix element becomes smaller than allowed by (9.18) we enter the region of very weak coupling.

For this (9.11) is still valid, but $\sin \frac{\Delta E t}{2\hbar}$ can no more be replaced by its argument for the long times required, even within small energy ranges. Instead of this, we must now take the limiting value of the integral in (9.11) for large t

$$\varrho_{ab'}(t) = 4 \lim_{t\to\infty} \iint \frac{u^2(E_a, E_b') \sin^2 \frac{\Delta E t}{2\hbar}}{(\Delta E)^2} dE_a\, dE_b'$$

$$= \frac{\pi t}{\hbar^2} \iint u^2(E_a, E_b') \lim_{t\to\infty} \frac{\sin^2 \frac{\Delta E t}{2\hbar}}{\pi \left(\frac{\Delta E}{2\hbar}\right)^2 t} dE_a\, dE_b'$$

By use of the δ-function we can write this*

$$\varrho_{ab'}(t) = \frac{\pi t}{\hbar^2} \iint u^2(E_a, E_b') \delta\left(\frac{\Delta E}{2\hbar}\right) dE_a\, dE_b'$$

$$= \frac{2\pi t}{\hbar} \iint u^2(E_a, E_b') \delta(\Delta E)\, dE_a\, dE_b' \qquad (9.19)$$

Here, the increase of $\varrho_{ab'}(t)$ is <u>linear</u> with time, as it should be in the very weak coupling case. In order to carry out the integration, we transform to new energy variables, namely to ΔE as defined in (9.7) and

$$E = \frac{1}{2}(E_a' - E_a + E_b' - E_b) \qquad (9.20)$$

Since the transformation determinant is unity, we get

$$\varrho_{ab'}(t) = \frac{2\pi t}{\hbar} \iint u^2(E, \Delta E) \delta(\Delta E)\, dE\, d(\Delta E) = \frac{2\pi t}{\hbar} \int u^2(E, 0)\, dE \qquad (9.21)$$

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* One of the representations of the δ-function is $\delta(x) = \lim_{t\to\infty} \frac{\sin^2 tx}{\pi t x^2}$.

Compare E.Madelung, Die mathematischen Hilfsmittel des Physikers, 6. Aufl. 1957, Springer Verlag Berlin, Göttingen, Heidelberg, pag.18

This integration requires that u^2 (E, ΔE) is not essentially different from u^2 (E,0) within a range of at least $|\Delta E| \sim 2\hbar/t$. Here, we are interested only in times longer than those required for weak coupling transfer. According to (7.16) these are times $t > \frac{\hbar}{4 u_{vw}}$, so that nearly constant values of u^2 (E, ΔE) within $|\Delta E| < |u_{vw}|$ are sufficient. Since for very weak coupling the inverted inequality (9.18) holds, we have

$$|\Delta E| << |u_{vw}| << \frac{\Delta\varepsilon}{2}$$

Near constancy of u^2 (E,ΔE) is then required within the region of the vibronic band widths only. This can be supposed, however, because otherwise these bands would not appear simple, but would show further structure. A better approximation than (9.21) in the region near the weak coupling limit should be possible by a more accurate integration of (9.11) than by way of the δ-function, but this is outside of our present intentions.

According to (9.7) $E \sim 0$ states simply the conservation of unperturbed energy, which is more strictly observed in our present very weak coupling case than in the other cases with stronger interaction. The quantity E as defined in (9.20) is then exactly the amount of energy transferred between both molecules.

From (9.21) the transfer rate can be unambiguously calculated as

$$n^{vw}_{a\to b} = \frac{2\pi}{\hbar}\int u^2(E,v)\,dE \qquad (9.22)$$

The remaining integration here requires a knowledge of u^2 (E,0) as a function of E. If we assume each of the vibronic levels v and w to have the same precisely defined width $\Delta\varepsilon$, the function $u^2(E_a, E_b')$ will be constant within that region so that we have

$$u^2(E_a, E_b') = \frac{u^2_{vw}}{(\Delta\varepsilon)^2}$$

The integration in (9.22) extends over a linear interval of E which is of the order of $\Delta\varepsilon$. We get therefore

$$\eta^{\nu\omega}_{a\to b} = \frac{2\pi\sigma\, u^2_{\nu\omega}}{\hbar\,\Delta\varepsilon}$$

with a numerical factor σ not far from unity. Under our present assumption, σ depends on the location of the original energy values E'_a, E_b within their band, so that we must take the average. A straightforward calculation under these assumption gives $\sigma = 3/4$ and therefore

$$\overline{\eta^{\nu\omega}_{a\to b}} = \frac{3\pi\, u^2_{\nu\omega}}{2\hbar\,\Delta\varepsilon} \qquad (9.23)$$

We should not give too much attention to the numerical factor here and to the deviation from its value in (8.3) or in other expressions for the weak coupling transfer rate published earlier.[3] The value of that factor depends largely on our assumption of a sharply defined band width. A Gaussian distribution leads to a similar but somewhat different result, the definition of the vibronic band width is, however, somewhat arbitrary here.

Our present considerations allow for the broadening of the vibronic levels. Therefore, we can go one step further and assume thermal equilibrium to be established not only for the primarily unexcited molecule b but also for the primarily excited one a. With a vibrational relaxation time τ - the time between two collisions, that lead to other vibronic levels of the same electronic state - the broadening is $\Delta\varepsilon \sim \hbar/\tau$ and insertion into (9.23) gives

$$\tau\ \overline{\eta^{\nu\omega}_{a\to b}} \sim \frac{3\pi^2\, u^2_{\nu\omega}}{(\Delta\varepsilon)^2} \qquad (9.24)$$

Within the very weak coupling range (but by no way within the weak coupling one!) this can be less than unity so that thermal equilibrium can be obtained before excitation transfer

occurs. By introduction of Boltzmann-factors g'_v for the originally excited molecule and g_v for the unexcited one we get then a total transfer rate of

$$n_{a\to b} = \sum_v \sum_w g'_v g_w n^{vw}_{a\to b} = \frac{3\pi}{2\hbar\Delta\varepsilon} \sum_v \sum_w g'_v g_w u^2_{vw} \qquad (9.25)$$

This refers to excitation transfer under our very weak coupling conditions for any pair of alike molecules with well defined vibronic levels in thermal equilibrium. In this case we have still more reason to regard the excitation as temporarily localized at one single molecule. Since now no phase relations exist any more between the wave functions of both molecules, the depletion of the original state as well as an eventual back reaction can be treated by the formulation of a suitable first order differential equation for the expectation values $\varrho_{a'b}$ and $\varrho_{ab'}$. A transfer to other molecules could be treated in a similar way as a statistical hopping or diffusional process, without any consideration of the wave-like properties of the excitation.

We shall now consider in detail molecules with <u>continuous spectra</u>, that is those which show no or only weakly developed vibronic structure. Continuous spectra result if the individual vibronic levels of one or of both states merge together. This may be due to extreme life-time broadening as in the case of dissociation continua, where the nuclear motion may even no more be vibrational at all. It may also [b2] due to the crowding of vibrational levels in larger molecules. This is the general cause for the continuous or quasi-continuous appearance of the spectra which is so often met in solution spectroscopy of polyatomic molecules.

With the distribution of the total vibronic resonance interaction among many vibronic levels, the matrix elements u_{vw}

become necessarily small. This leads not only to a reduction of the weak coupling transfer rate (7.16) but also to a shift of the boundary (9.18) between weak and very weak coupling.

Let us suppose that there are z vibronic bands with comparable values of their Franck-Condon-integrals S_{vw} and of the same width $\Delta\varepsilon$. The spectrum will be continuous if the sum of the energy ranges covered by these bands exceeds the total electronic band width Δw, that is, if

$$z\,\Delta\varepsilon > \Delta W \tag{9.26}$$

We shall suppose that this is true for the ground- and excited states of both molecules a and b. Now, the total resonance interaction is

$$|U| = \sqrt{\sum_{vw} u_{vw}^2} \sim z\,|\bar{u}_{vw}| \tag{9.27}$$

if $\bar{u}_{vw}$ is the average vibronic matrix element. By insertion of (9.26) and (9.27) into (9.18) we get

$$2|U| >> z\,\Delta\varepsilon > \Delta W \tag{9.28}$$

as the lower limit for weak coupling. Comparison with (9.15) shows, however, that this is also the limit for strong coupling. With other words, if U is large enough to allow for weak instead of very weak coupling, it is already so large that the coupling is strong. Thus we arrive at the important result that <u>for systems with continuous vibronic levels no weak coupling case exists</u> any more. It is not surprising that the experimental criterium for weak coupling (compare chapter I) fails for continuous spectra.

Even for systems which show vibronic structure, but where this structure is not well pronounced insofar as the vibronic band widths are not much less than the band separations, the upper and lower limits from (9.15) and (9.18) are so close together that the weak coupling case is not much more than

an intermediate one between the two others. This is so for all solution systems and many crystalline ones, with the exception, perhaps, at very low temperature. It is only the widespread use of the present terminology which may justify us to call this intermediate case that of weak coupling.

If, for vibronic continua, the range of the weak coupling case is reduced to zero, then that of the very weak coupling case must extend further. The reason for this is not difficult to see. We have found that the integration of (9.11) by use of the δ-function requires that u^2 (E, ΔE) does not vary essentially in the region around $\Delta E = 0$. For molecules with well separated vibronic levels, this is only within the widths of these. But for continuous spectra, this region extends over an essential part of the electronic band widths. This results from the fact that the spectral intensity distribution of an absorption- or emission transition is determined by the same vibrational o erlap integrals which also determine the variation of $u(E_a, E_b')$ and of its square.

More quantitatively, this may be stated as follows. By integration of (9.22), but now over the total electronic band width Δw, we get

$$n_{a \to b} = \frac{2\pi\sigma' U^2}{\hbar \Delta W}$$

with a numerical factor σ' not far from unity. The use of the δ-function in going from (9.11) to (9.22) requires that for a time t corresponding to the reciprocal of the rate, and for an energy interval ΔE of the order Δw

$$\frac{\Delta E t}{2\hbar} >>$$

This leads to the condition

$$2\sqrt{\pi}\,|U| << \Delta W$$

which, in fact, is close to the strong coupling limit (9.15).

Near this limit, the 'very weak coupling' transfer may become quite fast. One must then be careful in using Boltzmann-distributions in a way analogous to that in (9.25), because the transfer time might be less than the thermal relaxation time τ.

Although our general considerations in this chapter are not restricted to molecules of the same kind, we have been concerned mainly with excitation transfer between those. The possible extension to dissimilar molecules needs, therefore, some further considerations. In the strong coupling case, collective excitation or excitation transfer will certainly occur if the differences between the electronic energies do not exceed the resonance interaction energy U. Such cases might be treated by use of (3.18) in chapter II.

In the weak or the very weak coupling case, excitation transfer between molecules with well separated vibronic levels would require some more or less accidental coincidence between these. But for molecules with continuous or quasi-continuous levels, some overlap of these regions will be sufficient. The detailed nature of this overlap will be discussed below within the aspects of the very weak coupling case which, as we have seen, is the only one in question here.

10. Quantitative formulations. Our further procedure shall be mainly concerned with very weak coupling transfer under prevailing dipole-dipole-interaction. It is under these conditions only that the transfer rates can be expressed by the spectral data of the molecules involved.

For the calculation of the transfer rate by use of (9.22), we have to specify the matrix element u(E,0) further. If we

return to the original energy parameters by (9.7) and (9.20), this becomes in the complete notation of (9.8)

$$u(E,0) = u(E_a', E_b; E_a, E_b') = u(E_a', E_b; E_a - E, E_b + E) \qquad (10.1)$$

The final state energies have been expressed here by the original state energies and the transfer energy E. For simplicity, we take Born-Oppenheimer vibronic functions

$$\bar{\Psi}_{a'b}(E_a, E_b) = \varphi_a' \varphi_b \chi_a'(E_a') \chi_b(E_b)$$

$$\bar{\Psi}_{ab'}(E_a, E_b') = \varphi_a \varphi_b' \chi_a(E_a - E) \chi_b'(E_b + E) \qquad (10.2)$$

where χ_ℓ and χ_ℓ' are the vibrational wave functions of the excited and of the unexcited molecule ℓ, respectively, characterized by their vibronic state energies. Their normalization is already determined by our normalization procedure for the vibronic wave functions. The square of the matrix element u (E,0) in (10.1) becomes then under neglection of vibrational terms, that is for electronically allowed interaction,

$$u^2(E,0) = \langle \varphi_a' \varphi_b | V | \varphi_a \varphi_b' \rangle^2 S_a^2(E_a', E_a' - E) S_b^2(E_b, E_b + E)$$

$$= U^2 S_a^2(E_a', E_a' - E) S_b^2(E_b, E_b + E) \qquad (10.3)$$

Here, U is the electronic interaction matrix element as defined in (2.9), and

$$S(E_1, E_2) = \langle \chi'(E_1) | \chi(E_2) \rangle$$

a vibrational overlap integral analogous to (7.9). Under restriction to dipole-dipole-interaction we can use (3.11) to obtain:

$$u^2 = \frac{\varkappa^2 m_a^2 m_b^2}{n^4 R_{ab}^6} \qquad (10.4)$$

where $\varkappa$ is a numerical factor containing the directional dependence of the interaction energy and where m_a, m_b are the electronic transition dipole moments of both molecules. If we finally insert (10.3) and (10.4) into (9.22) and replace there the transfer energy E by the transfer frequency $\nu = E/h = E/2\pi\hbar$ and change the normalization of our vibrational functions as well to a frequency scale, we arrive at

$$n_{a\to b}(E_a', E_b) = \frac{\varkappa^2}{n^4\hbar^2 R_{ab}^6} \int m_a^2 S_a^2(E_a', E_a'-h\nu)\, m_b^2 S_b^2(E_b+h\nu)\, d\nu \qquad (10.5)$$

This is the transfer rate for molecules with the initial states E_a' and E_b. From this we can get the total transfer rate for thermal equilibrium by the introduction of suitable Boltzmann factors and subsequent integration over all energies E_a' and E_b. These Boltzmann factors are here continuous functions g'(E) for the excited molecule and g(E) for the unexcited one, which are normalized on an energy scale. Thus we get

$$n_{a\to b} = \frac{\varkappa^2}{n^4\hbar^2 R_{ab}^6} \int \left[m_a^2 \int g'(E_a') S_a^2(E_a', E_a'-h\nu)\, dE_a'\right]\left[m_b^2 \int g(E_b) S_b^2(E_b, E_b+h\nu)\, dE_b\right] d\nu \qquad (10.6)$$

The expressions within the squared brackets under the integral are closely related to the spectroscopic transition probabilities between ground and excited states within the molecules a and b. Each of them consists of the square of an electronic transition moment and a Franck-Condon factor, averaged over the Boltzmann-distribution of the original state. More specifically, the first bracket is proportional to the spectral density of the emission spectrum of molecule a for thermal equilibrium in its excited state. This is the regular fluorescence spectrum. In a similar way, the second bracket is

proportional to the spectral density of the absorption spectrum of molecule b. Therefore, the integral in (10.6) is proportional to the overlap integral of the fluorescence spectrum of a with the absorption spectrum of b.

The transition rate (10.6) can be calculated quantitatively from spectral data if one uses the following relations which can easily be derived from Einstein's well known expressions for induced absorption and for spontaneous emission

$$\varepsilon(\nu) = \frac{4\pi^2 N' m^2 \nu}{3(\ln 10) n \hbar c} \int g(E) S^2(E, E+h\nu)\, dE \qquad (10.7)$$

$$f(\nu) = \frac{2^5 \pi^3 n \tau_e m^2 \nu^3}{3 \hbar c^3} \int g'(E') S^2(E', E'-h\nu)\, dE \qquad (10.8)$$

Here $\varepsilon(\nu)$ is the molar decadic extinction coefficient and $f(\nu)$ the fluorescence quantum spectrum, normalized to unity on a frequency scale. N' is the number of molecules per millimole, c the velocity of light and τ_e the natural fluorescence life time, that is in the absence of radiationless processes. Insertion of (10.7) and (10.8) into (10.6) gives finally

$$n_{a\to b} = \frac{9\pi^2 (\ln 10) c^4}{128 \pi^5 n^4 N' \tau_{e,a}} \frac{1}{R_{ab}^6} \int f_a(\nu)\, \varepsilon_b(\nu)\, \frac{d\nu}{\nu^4} \qquad (10.9)$$

This is essentially the same result as has been obtained in earlier calculations[28,29]. Apart from the factor ν^{-4}, the integral here represents the overlap of the fluorescence spectrum of the initially excited molecule a with the absorption spectra of the finally excited molecule b. An appreciable overlap of these spectra is a necessary condition for excitation transfer under very weak coupling. It permits transfer between molecules of the same or of different kind provided that in the second case the excited state of the acceptor molecule is somewhat

less then that of the donor. It is remarkably that this expression does not contain Planck's constant. Actually, it can also be derived on an essentially classical basis.* If the spectra are represented on a wave number scale $\tilde{\nu}$ and the fluorescence spectrum is normalized in that way, (10.9) reads

$$\eta_{a\to b} = \frac{9\varkappa^2 \ln 10}{128\pi^5 n^4 N' \tau_{e,a}} \frac{1}{R_{ab}^6} \int f_a(\tilde{\nu}) \varepsilon_b(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \qquad (10.10)$$

The numerical factor $\varkappa$ can be calculated from (3.11) for any mutual orientation of both molecules. For sufficiently fast Brownian rotation of both molecules, the average $\varkappa^2 = 2/3$ may be used. An average for random but fixed orientations has been calculated by Maksimov and Rozman[30].

Several further simplifying approximations are possible here, such as replacing $\tilde{\nu}$ by an average value and taking it out of the integral or by using the mirror symmetry in order to replace the fluorescence spectrum by the inverted absorption spectrum[30].

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*This has been done in the monograph: Fluoreszenz organischer Verbindungen, Vandenhoek und Ruprecht, Göttingen, 1961. In part of the edition, (10.9) has incorrectly been printed with π^6 instead of π^5, and this error has been transfered to some other articles.

V. CONCLUSIONS

In our foregoing treatment delocalized excitation and excitation transfer have been discussed in terms of stationary and of non stationary wave functions. We have arrived at the result that the apparently different cases of strong, weak and of very weak coupling are intimately related to each other and might, in principle, be described by one single theory. Their different characteristics result merely from a difference in magnitude of the interaction energy, in relation to the electronic band width and to the individual vibronic band width.

The conditions for very weak coupling, in our present revised notation, seem to be met much more often, than has been recognized in the recent literature. Actually, for this case to be present, the interaction energy has not even to be small on an absolute scale, as has been found in our discussion of molecules with continuous spectra.

Excitation transfer between triplet states, that is $T_1 \rightarrow S_0$ in one molecule together with $T_1 \leftarrow S_0$ in the other, is spin forbidden, and the interaction energy is small even for molecules in close contact with each other. A value of 8 cm^{-1} has been found by Nieman and Robinson[31] for this energy in case of the benzene crystal. At liquid helium temperature this may be sufficient for weak coupling but no more at essentially higher temperatures where the vibronic band widths exceed that amount considerably. Then, stepwise transfer of excitation instead of exciton propagation should be expected, and the individual transfer rates should be treated by very weak coupling theory, in Dexter's modification for forbidden transitions[29].

Even if the conditions for strong or for weak coupling apply, so that electronic or vibronic excitons do exist, their migration is still modified by the thermal redistribution of energy between different vibronic levels. In exciton theory this is considered by the inclusion of exciton-phonon-scattering. This allows linear migration of excitons in a lattice over restricted distances only, but leads then to diffensive motion. Model calculations under such conditions have been performed by Goad[32]. As Katshura[33] has shown, frozen lattice irregularities lead to a similar behavior. In both cases the root-mean-square displacement of the excitation becomes finally proportional to $\sqrt{t}$, as in diffusion or in a random walk process. With the same individual transfer rate this may result in much smaller rates for trapping by impurities, especially in one-dimensional systems where a random walk includes repeated visits of the same place.

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CAPTIONS TO FIGURES

Fig.1 Energy of the exciton state of the polymer as function of k.
a: $U > 0$
b: $U < 0$

Fig.2a Potential energy surface of a dimer under strong coupling.

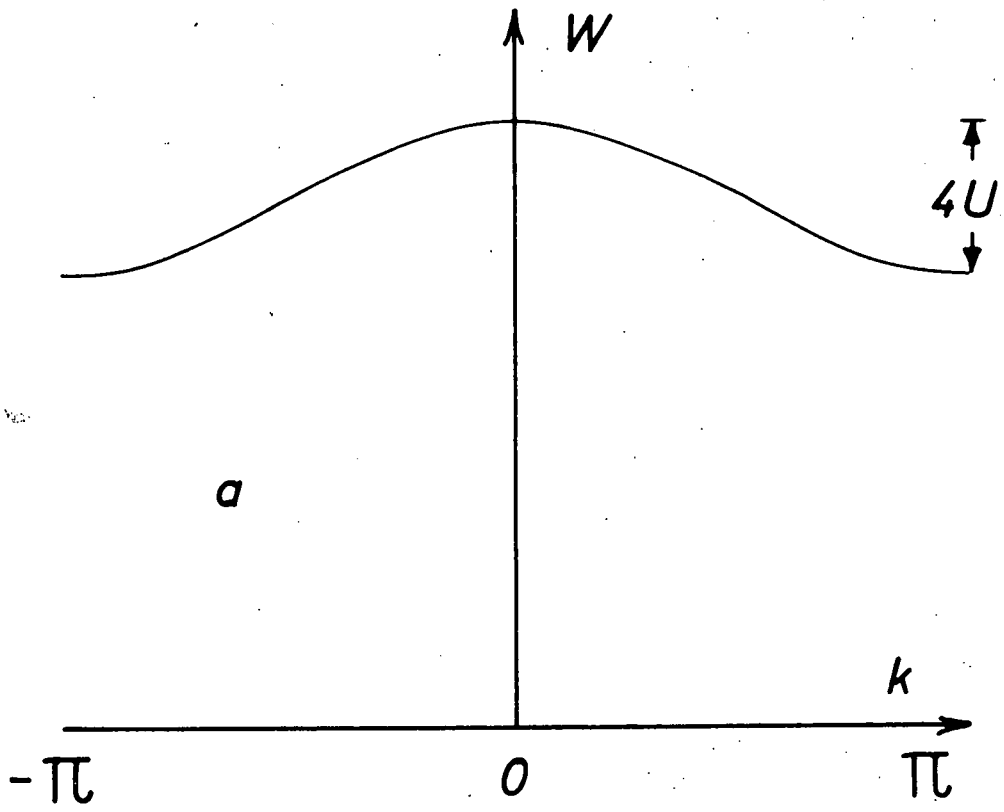
$$(p = \frac{2\,|U|}{\varkappa (Q_o' - Q_o)^2} = 3)$$

Q_a, Q_b: nuclear coordinates
Q_o, Q_o': equilibrium configurations of monomer ground- and excited states
------ ground state
——— lower excited state

Fig.2b Potential energy surface of a dimer under weak coupling.
$(p = 0.1)$

Fig.3 Potential energies in the configuratitional plane $Q_a + Q_b = Q_o + Q_o'$.
$p = 0.1$ (weak coupling)
$p = 1$ (borderline case)
$p = 3$ (strong coupling)
Distance in units of $(Q_o' - Q_o)$
$\bar{z}$: energy in units of $\frac{\varkappa}{2}(Q_o' - Q_o)^2$

Fig.4 Coupled transitions in weak coupling transfer.
a. non-degenerate subcase
b. degenerate subcase



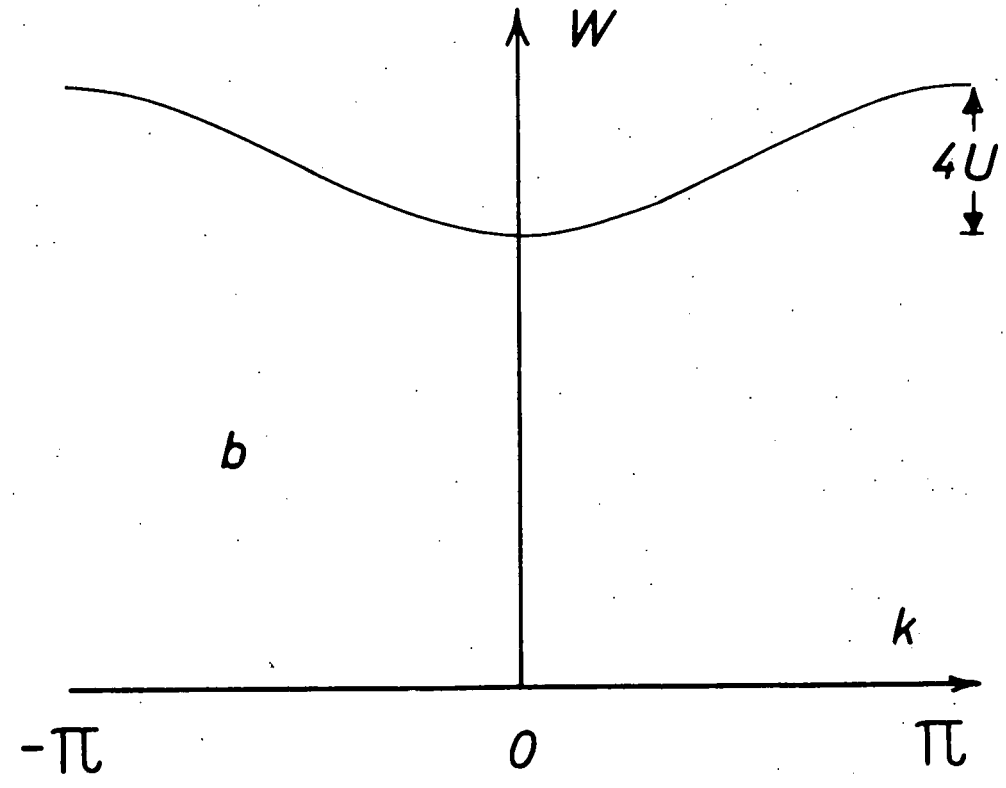


Fig. 1

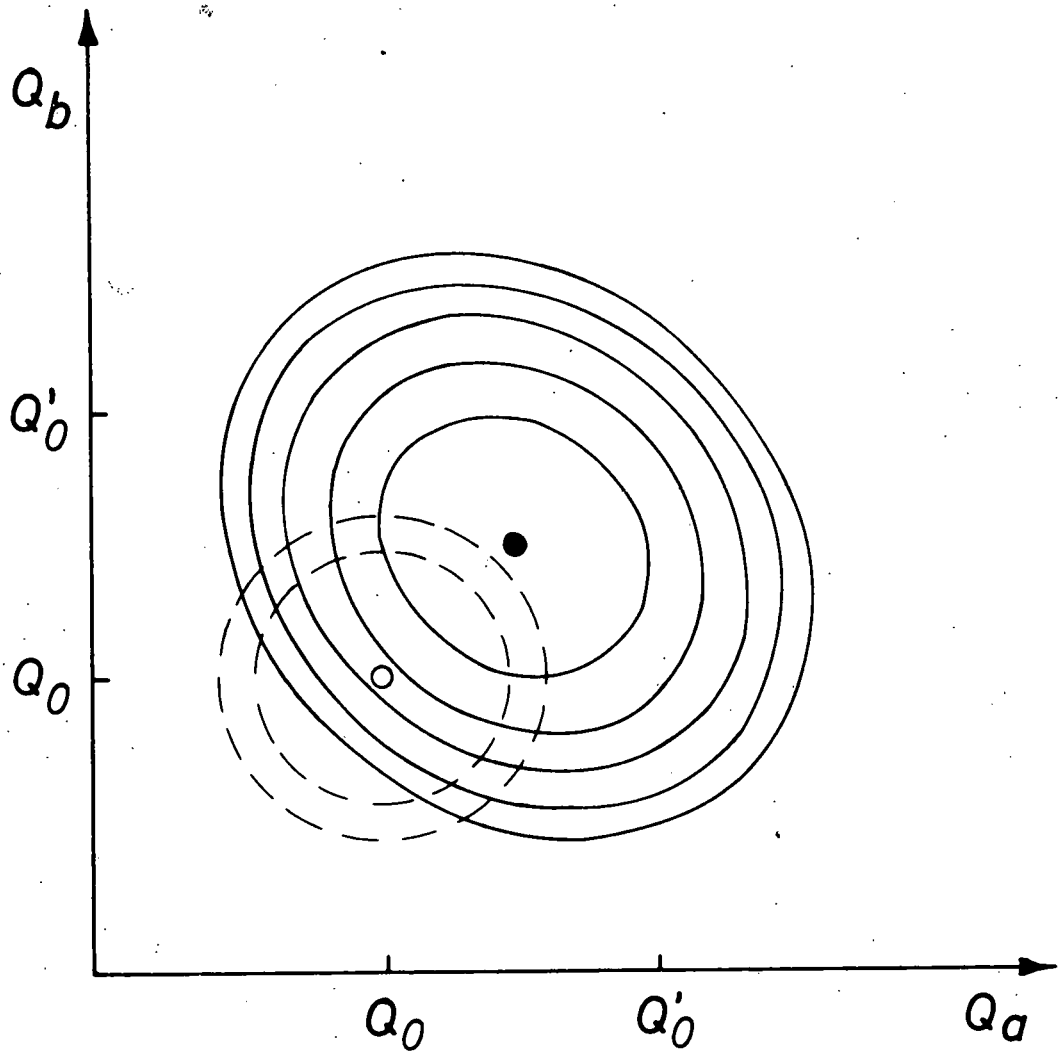


Fig. 2a

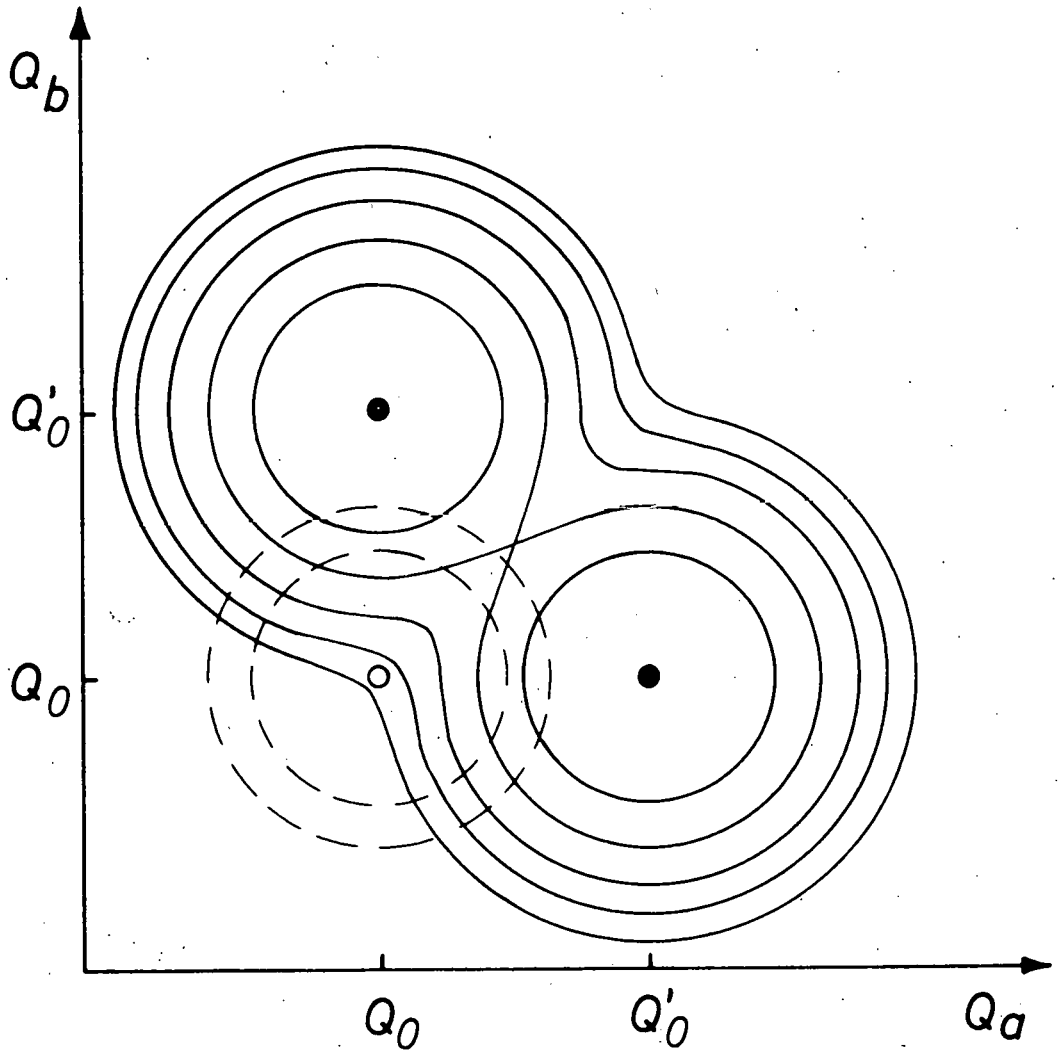


Fig. 2b

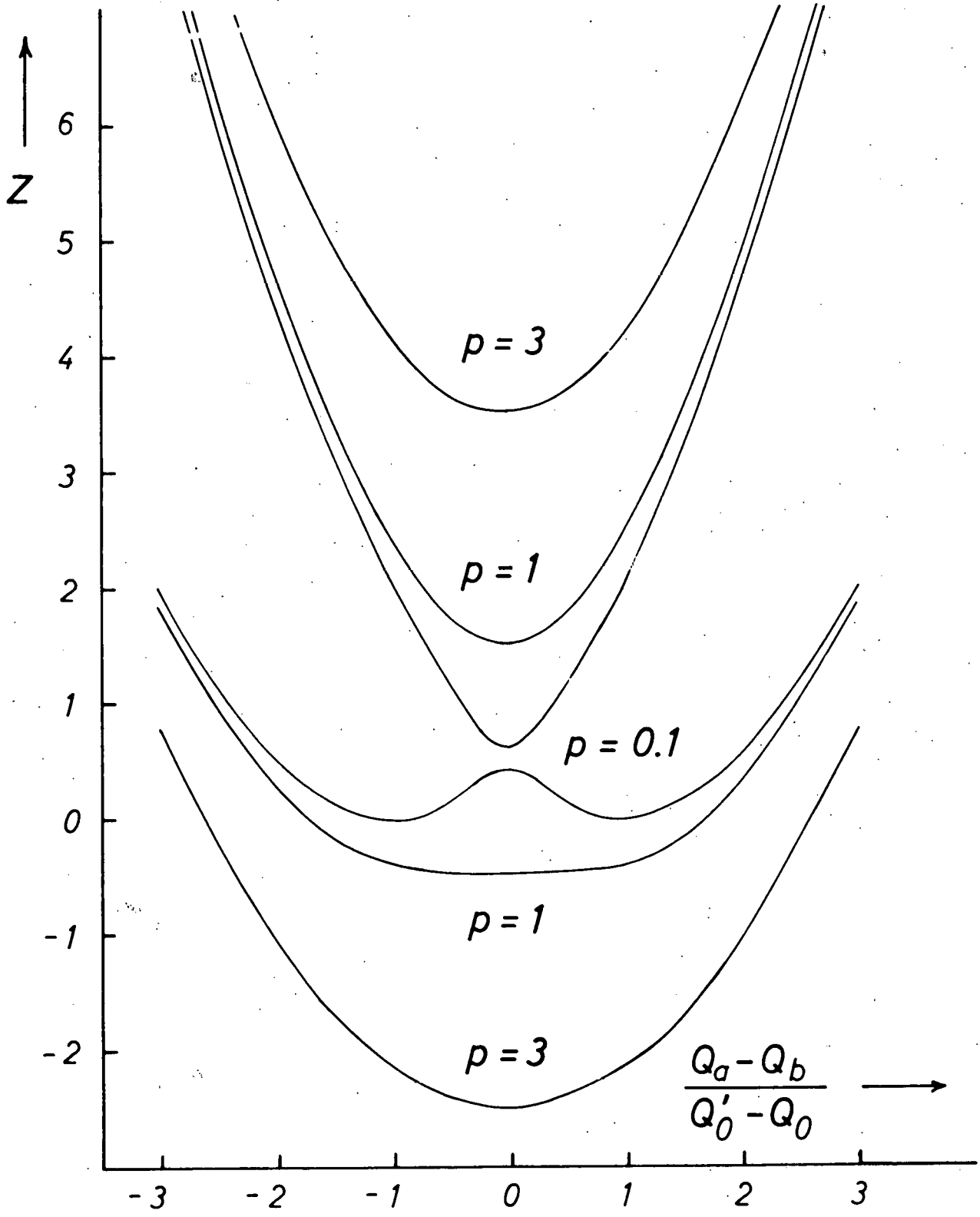


Fig. 3

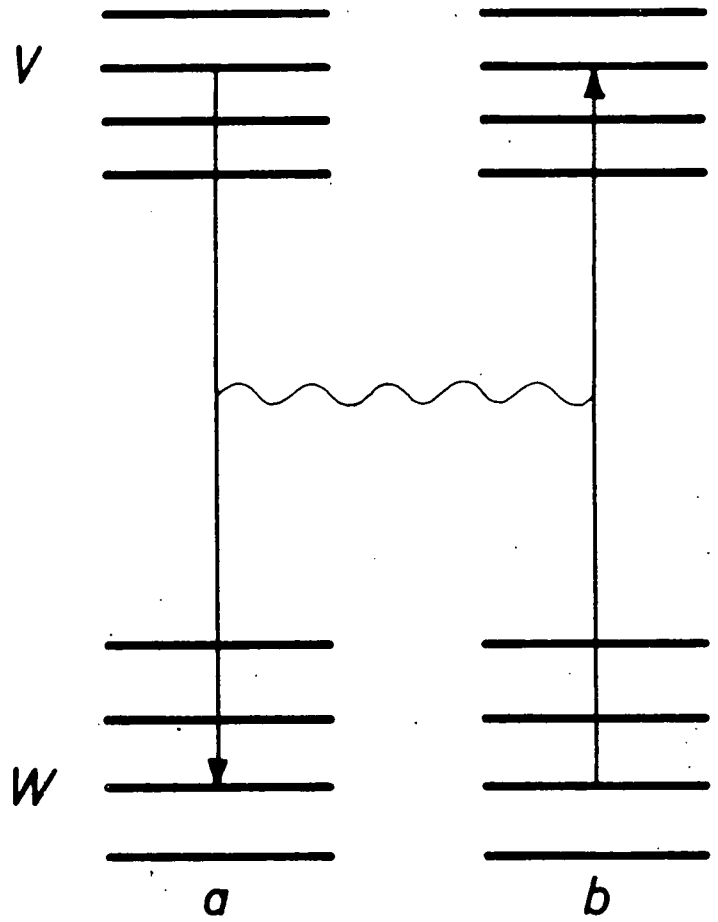


Fig. 4a

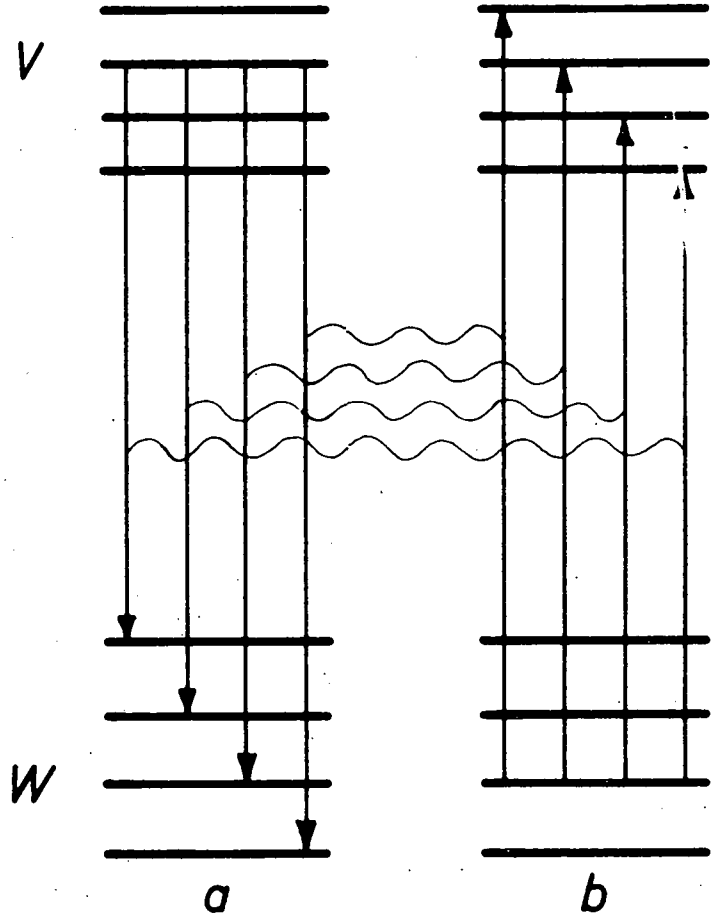


Fig. 4b