

## QuantumMechanical Resonance between Identical Molecules

Herbert Jehle

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## Quantum-Mechanical Resonance between Identical Molecules

HERBERT JEHL

*University of Nebraska, Lincoln, Nebraska*

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The process of synopsis of chromosomes in meiosis and the process of self-duplication of genes in mitosis reveal the existence of a highly specific attraction between pairs of large molecules provided they are identical and rigid. We shall investigate the quantum-mechanical behavior of a pair of molecules which interact with each other by means of vibrating electric dipole moments which are thermally excited. Because of resonance between equal frequency modes or commensurable modes of vibration, each one of the molecules shows a statistical preference for certain phase relations between these modes (using the language of the correspondence principle) A pair of molecules interacts strongly if it is an identical pair because of these phase preferences

### INTRODUCTION

SEVERAL investigators have examined the characteristic properties of the interaction forces which are at work in synopsis of chromosomes and in auto-synthesis of genes. It became clear that these specific interaction forces cannot be accounted for by ordinary chemical bond formation. This does not mean, however, that they do not fit into the scheme of intermolecular forces which quantum mechanics is able to explain.

A statement of the biological problem is given in Sections I and II. In Section III we discuss the types of interaction between a pair of thermally excited vibrators. In the remaining sections the interaction by means of vibrating electric dipole moments will be investigated in view of an explanation of a specific attraction between identical large molecules. Classical statistical mechanics cannot account for the specificity in question (Section IV). Also quantum statistics of a pair of simple vibrators does not show an attraction which would be particularly strong if the vibrators are identical (Section V). On the other hand, two large molecules will show a strong attraction toward each other if both have the same commensurabilities in between many of their modes, and they therefore show the same phase preferences between the vibrations of their commensurable modes.

We proceed first to give a qualitative argument in terms of the correspondence principle (Sections VI and VII). Then, in order to check this argument and in order to outline a straightforward quantum-mechanical treatment of the problem, we calculate the quantum-mechanical partition function for a simplified model. After noting what corresponds to classical phase preferences in quantum-mechanical language (Section VIII), we give a short review of quantum-mechanical resonance between commensurable modes in a molecule (Section IX).

The simplified model consists of a pair of molecules, each having but two modes between which there is some coupling (parameter  $\lambda$ ). In Section X some of the eigenfunctions, and first- and second-order energy level perturbations are given. The attraction is calculated by means of the partition function. It is of the same type

as dispersion forces.<sup>1</sup> An extension of the calculation for large molecules (Section XI) shows an attraction which increases very strongly with the coupling parameter  $\lambda$  and with the number of commensurable modes, in analogy to the effect of phase preferences discussed in Section VII.

In order to illustrate the kind of specificity of this strong attraction, we detune the model in various ways (Section XII) and find that the strong attraction depends upon the presence of the same kind of phase preferences in both molecules of the pair. Such corresponding phase preferences evidently prevail if the two molecules are identical.

### I. SPECIFICITY PROBLEMS IN BIOLOGY

In a number of biological phenomena we encounter highly specific interactions between molecules. We have to distinguish between two entirely different phenomena. On the one hand two like or unlike atoms or molecules may combine with each other rather than with another atom or compound available in the surrounding medium, just because of chemical affinity. On the other hand there are several very general types of specific interactions which, for various reasons, cannot be accounted for by chemical bond formation. These we would like to investigate here.

We shall discuss specific interactions as they occur in the process of synopsis of homologous chromosomes (in meiosis) and in the very remarkable process of self-duplication of chromosomes (in mitosis), the specificity of the processes depending on a pair of large molecules being identical, or almost identical. These phenomena are so general that they demand some explanation which will not be dependent upon detailed assumptions about the model by which we hope to explain them.

*Synopsis* is a stage of meiosis (reduction division leading to the formation of gametes). Before the diploid cell can divide into two haploid cells, the 48 chromosomes (in man) of the diploid cell have to conjugate into 24 pairs of homologous chromosomes so that in the subsequent reduction 24 different chromosomes keep company. Here is a phenomenon in which homologous,

<sup>1</sup> F London, Proc. Faraday Soc. (1937).

that is, almost identical gene complexes of two chromosomes line up with each other because of their identity. This is most beautifully evidenced in inverted synapsis. Compared with self-duplication, synapsis is much more a macrophenomenon, involving much larger molecules and larger distances, and it is not quite so highly specific as self-duplication.

The phenomenon of *self-duplication* of the genes is one stage in the reproduction process of chromosomes during mitosis (ordinary somatic cell division). Self-duplication occurs before the double chromosome splits by longitudinal division into two daughter chromosomes. A chromosome is a long fibre-like structure containing a row of genes or gene complexes. Each gene is made up of many large "constituent molecules" linked together by chemical bonds. (We leave it open whether in the following a "constituent molecule" is to be understood as a protein, a nucleic acid, a nucleoprotein molecule, or rather only part of all these, e.g., a peptide ring.) A duplicated chromosome consists of two such fibrous structures which lie parallel close to each other. Their distance, however, is of a larger order of magnitude than the usual distance between chemically bound atoms.

The current view about self-duplication is as follows. The building up of a duplicate by the original gene is understood as a gradual collection of molecules which are readily available from the surrounding medium, and which happen to be identical with the constituent molecules of the original gene. It is a selective attraction of the proper molecules into the neighborhood of the constituent molecules in the original gene. Thereafter, the constituent molecules of the daughter gene have a chance to join together by chemical bond-formation and so provide for the synthesis of a complete daughter gene. If one can show a specific attraction to exist between identical large molecules, one has taken the main hurdle.

We started with the description of synapsis as it involves only the specific interaction (auto-attraction) of almost identical macromolecules, whereas self-duplication (autosynthesis) involves not only the phenomenon of auto-attraction and of bond formation in the daughter genes, but also the assumption that the constituent molecules are readily available in the surrounding medium.<sup>2</sup> The problem of synthesis of the "readily available" constituent molecules (together with many other molecules which are not used in building the genes) is likely to be a much simpler problem, as these molecules are simpler and of a much smaller variety, e.g., such as peptides. In this note we shall, for brevity, use the word "constituent molecules" (or sometimes just "molecules") for both the big macromolecules involved in synapsis (the rigid genes or gene-complexes of which a chromosome thread is made) and

the much smaller molecules which are being attracted in the process of self-duplication of a gene.

## II. BASIC FACTS BEARING UPON SELF-DUPPLICATION

Let us try to explain the specificity involved in the above described phenomena, looking at chromosomes and their constituent genes and smaller parts as unsophisticated molecules, and see how far we are able to go before we consider them as servomechanisms.

What is particularly characteristic about these phenomena? As H. J. Muller has pointed out, synapsis and even more so self-duplication are very general processes of unbelievable versatility. These processes work for all kinds of genes to the extent that even mutations become accurately inheritable through self-duplication. Furthermore, there is the enormous accuracy which makes exact self-duplication usually not fail in the sequence of many chromosome generations through which identical replicas of a gene are transmitted.

What would happen if there were an occasional mistake in self-duplication, meaning a production and (in the case of sex cells) a handing down of a defective set of chromosomes to the next generation? The result would be similar to that when a gene changes by itself (lethal or non-lethal change). We have thus two different types of mutations. We understand the latter mutations (in particular their mutation rates in their dependence on temperature and on radiation) to behave like a monomolecular reaction of the individual gene by itself;<sup>3</sup> the mistakes in self-duplication on the other hand behave differently. Therefore we have some means of discriminating between the two types' share in the total mutation rate. Experimental work is now going on to determine the relative number of mistakes in self-duplication compared with the monomolecular gene mutations.

The versatility and accuracy of the self-duplication process make it hopeless to look for explanations which involve chain reactions<sup>4</sup> because they present the difficulty that a different reaction would have to be invoked for every different gene.

Also in other respects this specificity does not fit into the pattern of ordinary chemical bond formation. It does not seem very promising to consider self-duplication as a surface phenomenon in which exact replica formation of a gene is explained on the hypothesis that the gene is a surface structure and that the shape of the new molecules' surface is to fit exactly that of the original molecule. Steric effects are not sufficient to explain the accuracy of self-duplication. Furthermore, it is artificial to assume that self-duplicating genes are an almost monatomic layer. This they

<sup>2</sup> H. J. Muller, *Sci. Monthly* 44, 212 (1937).

<sup>3</sup> N. W. Timofeeff-Ressovsky and M. Delbrück, *Goettinger Nachrichten, (Biologie)*, p. 189, (1935).

<sup>4</sup> M. Delbrück, *Cold Spring Harbor Symposium* 9, 1941.

would have to be if steric effects were to account for the formation of exact replicas.

The distance between a pair of molecules which shows specific interaction is usually very large compared with the range of chemical bonds. In the case of self-duplication of a gene this interaction force must at least act over a range equal to the distance between corresponding constituent molecules of a gene and its self-duplicated daughter gene, a distance of the order of the diameter of a gene. In synapsis it will even have to act over a range equal to the distance between the center lines of the two chromosome threads, a distance large compared with interatomic distances. Specific interaction of corresponding genes during synapsis, particularly in the case of inverted synapsis, is the most interesting evidence for a fairly long-range specific interaction in the cell.

### III. COUPLED THERMAL VIBRATIONS OF A PAIR OF IDENTICAL MOLECULES

Let us follow up some suggestions brought up by H. J. Muller.<sup>5</sup> We shall investigate how the interaction between a pair of large molecules is influenced by the circumstance that at least part of their vibrational modes are identical for the two molecules. By identical we understand that the vibrational spectrum, the preferred phase-relationships between commensurable modes, and the relative orientations of the vibrational modes of one of the molecules are the same as those of the other molecule.

It is reasonable to investigate thermal vibrations as the cause of specificity because of the fact that the genes in whose interaction we are interested are molecules which perform well-defined vibrations, as they have a very definite structure. X-ray investigations of some proteins by Bernal and others have shown such enormous numbers of Fourier components that even without knowing their structure we know that every atom is located at a well-defined place. This well-defined structure and the rigidity of the molecules exist as long as they are not denatured or dehydrated. (Rigidity is also often inferred from entropy changes with denaturation, or from behavior of viscosity.) Protein molecules are extraordinary in this respect.<sup>6</sup>

A different kind of argument can be advanced for the fixed structure of the genes. Organic molecules in the cell are usually forming and breaking bonds at a considerable rate. If a long chain molecule breaks into two, there may be several possibilities of the two broken ends joining other different molecules, rather than healing with each other again. The healing process is unlikely because of the small probability of the broken ends returning into each other's spheres of influence. On the contrary, if a molecule has a well-defined structure with

little or no possibility of performing internal rotations about single bonds, any bond will have a high probability of healing up again after it was broken. This circumstance will bring about a high stability for such a molecule. Conversely, a gene must owe its notorious stability, besides other factors, to its rigidly defined molecular structure (necessary condition for stability).

We shall assume that the smaller constituent molecules of which a gene is built up (e.g. peptide rings) are rigid also.

Each molecule of a pair of constituent molecules is assumed to vibrate as an independent unit. The interaction of the internal vibrational modes of these molecules with the surrounding medium or with the adjacent constituent molecules are both assumed to be small. The interaction of the surrounding medium with the pair of molecules amounts to a weak coupling of the Brownian motion of the temperature bath provided by the medium with the thermal vibrations of the two molecules.

The range of frequencies and amplitudes of mechanical vibrations are discussed in the appendix. We know the vibrational spectrum to be as high as  $3000\text{ cm}^{-1}$  or  $300\text{ cm}^{-1}$ . From there on, of course, we have many lower frequencies just as a solid has in Debye's theory of specific heat. Remembering that  $kT/hc \sim 200\text{ cm}^{-1}$  we have level spacings of vibrational modes both  $>$  and  $< kT$ . The vibrational amplitudes range in the order of  $10^{-9}\text{ cm}$ .

We come now to the problem: what forces provide for the interaction between the vibrations of one molecule and those of another, i.e., what are the coupling forces between a pair of vibrators? We have to consider the following properties of various forces when deciding which ones are responsible:

(1) Their range.

As a cause for the coupling it excludes exponentially decreasing forces such as direct chemical bonds between the pair.

(2) Their relaxation time.

Forces which involve an adjustment towards a statistical equilibrium distribution cannot follow the frequencies of a vibrating molecule. So the Debye-Hückel forces and the orientation effect contributions to Van der Waals forces (Keesom) take too much time to provide for vibrational coupling.

(3) The effect of the medium between the pair of molecules on the coupling force.

The coupling of the vibrations of the two molecules with the mechanical vibrations of the medium is small. Otherwise it would be difficult to understand why the experiments show that a molecule's vibrational spectrum is so little dependent on it being in solution or not. If this were not the case, it would also not be explainable why two molecules are supposed to be able to recognize each other with high accuracy on account of their having an identically same frequency spectrum. We there-

<sup>5</sup> Proc. Roy. Soc. B134, 1 (1947). Cold Spring Harbor Symposium 9, 290 (1941). The Am. Naturalist 56, (1922).

<sup>6</sup> I. Langmuir, Proc. Phys. Soc. 51, 592 (1939). J. D. Bernal and I. Fankuchen, J. Gen. Physiol. 25, 111.

fore do not expect hypersonic vibrations transmitted through the medium to be responsible for the coupling. A further difficulty would come up if the interaction were provided by vibrations of the medium. The Brownian movement in the medium would cause much noise to be superimposed on interaction forces and actually jam them, because the interaction energy is small compared with the vibrational energy of the thermally excited pair of molecules, and very small compared with the energy of the noise.

Let us therefore consider electric dipole-dipole interactions between the pair; the mechanical vibrations of each of the two molecules will evidently be accompanied by vibrations of their charge distributions. For simplicity we take just the electric dipole moment of the vibrational modes in considering their interaction, though actually quadrupole and higher moments are important too. Every kind of vibrational mode will usually have some electric dipole moment associated with it. As the highest frequencies have an electromagnetic wave-length between (1/300) cm and (1/3000) cm, we usually need not take into account retardation effects. We shall not consider the Debye induction effect because it is not specific.

So far we have discussed the vibrating electric charge distribution (of the electronic shells and of the nuclei) which accompanies the mechanical vibrations of the nuclei. But perhaps this may not be the most important source of vibrating charge distributions. It may be that vibrations of the hydrogen bridges or extended electronic oscillators<sup>7</sup> or even ordinary electronic transitions provide the essential contribution to the molecules' electric dipole vibrations. For the following sections, however, it is of but secondary importance which of these phenomena provide the source for the electric vibrations.

If we want to explain specific interaction, we have to see how the interaction of an identical pair differs from that of an almost identical pair and of a non-identical pair of molecules. We want to find out how the interaction depends on the coupling between the dipole pairs, i.e. on the distance  $R$  between the molecules. We want to investigate first a pair of simple vibrators and afterwards a pair of molecules represented by two orchestras of vibrators. The word "orchestra" does not mean that we represent a molecule by a set of independent vibrators, but that we think of the coupling between the modes of a molecule. This is a generalization essential for the understanding of specificities. Finally, we want to study the dependence of the effect on  $h/T$ .

#### IV. CLASSICAL LIMIT (ABSENCE OF SPECIFIC EFFECTS)

In the following we like to use the work "specific attraction" as denoting an attraction which depends on identical vibrational behavior of the pair of molecules.

<sup>7</sup> F London, AAAS Publication No 21, 141 (1943).

Consider a pair of linear harmonic vibrators, e.g. two negatively charged mass points vibrating about two positively charged centers a distance  $R$  apart. The vibration goes along the line connecting the centers, with displacements,  $z_I, z_{II}$ .  $I, II$  stand for molecules  $I$  and  $II$ . Their Hamiltonian is

$$\mathcal{T} + \mathcal{V} = \frac{1}{2}(m_I^{-1}\dot{p}_{zI}^2 + m_{II}^{-1}\dot{p}_{zII}^2) + \frac{1}{2}(k_I z_I^2 + k_{II} z_{II}^2) - 2e^2 R^{-3} z_I z_{II}. \quad (4.1)$$

Therefore the partition function

$$Z = \int \int \exp(-\mathcal{T}/kT) dp_{zI} dp_{zII} \times \int \int \exp(-\mathcal{V}/kT) dz_I dz_{II} \quad (4.2)$$

will contain the masses  $m_I, m_{II}$  only through the first double integral, i.e. as factors in  $Z$ . Thus the attractive force  $-kT \partial \log Z / \partial R$  is independent of the masses, i.e., independent of whether the frequencies of the pair are identical or not.

#### V. QUANTUM-MECHANICAL RESONANCE OF A PAIR OF SIMPLE VIBRATORS

Let us first study what would happen if only one of the vibrational modes of each molecule were excitable. We represent them by coordinates  $q_I, q_{II}$ ; normal coordinates can be defined for small  $q$  if we can neglect anharmonic terms. In the one dimensional case we define  $q_I = m_I^{-1/2} z_I$  and we use the abbreviation  $\kappa_I = m_I^{-1} k_I$ . The  $x, y$  axes shall be perpendicular to the line connecting the two molecules. Then the molecules' orientation with respect to the axes may be described by stating that the components of the electric dipole moments which accompany the two linear mechanical vibrations  $q_I, q_{II}$  are

$$\mu_{xI} q_I, \mu_{yI} q_I, \mu_{zI} q_I, \mu_{xII} q_{II}, \mu_{yII} q_{II}, \mu_{zII} q_{II}. \quad (5.1)$$

We consider first the interaction for a given fixed orientation; the ratios of the  $\mu$ 's are regarded as parameters which describe orientation effects to be discussed later.

The Hamiltonian is

$$H = \frac{1}{2}(\dot{q}_I^2 + \dot{q}_{II}^2) + \frac{1}{2}(\kappa_I q_I^2 + \kappa_{II} q_{II}^2) + \text{anharmonic terms} + R^{-3}[\mu_{xI}\mu_{xII} + \mu_{yI}\mu_{yII} - 2\mu_{zI}\mu_{zII}]q_I q_{II}. \quad (5.2)$$

The equations of motion yield, in the harmonic limit, a secular equation for the frequencies  $\omega_+$  and  $\omega_-$  of the inphase and the antiphase vibrations,

$$\omega_{\pm}^4 - \omega_{\pm}^2(\kappa_I + \kappa_{II}) + \kappa_I \kappa_{II} - R^{-6}[\mu\mu]^2 = 0. \quad (5.3)$$

The well-known solution of this equation is

$$\omega_{\pm}^2 = \omega^2(1 \pm \epsilon), \quad \omega_{\pm} = \omega(1 \pm \frac{1}{2}\epsilon - \frac{1}{8}\epsilon^2 \pm \frac{1}{16}\epsilon^3 - (5/128)\epsilon^4) \quad (5.4)$$

where

$$\omega^2 = \frac{1}{2}(\kappa_I^2 + \kappa_{II}^2) \quad (5.5)$$

$$\epsilon = \{(\kappa_I^2 - \kappa_{II}^2)^2 + 4R^{-6}[\mu\mu]^2\}^{\frac{1}{2}}(\kappa_I^2 + \kappa_{II}^2)^{-1}. \quad (5.6)$$

$\epsilon$  is small compared with unity; the signature of the square root is to be equal to the signature of  $[\mu\mu]$  of Eq. (5.2).

$$\begin{aligned} \frac{1}{2}(\omega_+ + \omega_-) &\sim \omega(1 - \frac{1}{8}\epsilon^2 - (5/128)\epsilon^4), \\ \frac{1}{2}(\omega_+ - \omega_-) &\sim \omega(\frac{1}{2}\epsilon + \frac{1}{16}\epsilon^3). \end{aligned} \quad (5.7)$$

For identical or almost identical vibrators we have

$$|2R^{-3}[\mu\mu]| \gg |\kappa_I^2 - \kappa_{II}^2| \quad (5.8)$$

$$\begin{aligned} \epsilon^2 &\sim 4R^{-6}[\mu\mu]^2(\kappa_I^2 + \kappa_{II}^2)^{-2} \\ \omega_{\pm}^2 &\sim \frac{1}{2}(\kappa_I^2 + \kappa_{II}^2) \pm R^{-3}[\mu\mu] \end{aligned} \quad (5.9)$$

For dissimilar vibrators we have

$$|2R^{-3}[\mu\mu]| \ll |\kappa_I^2 - \kappa_{II}^2| \quad (5.10)$$

$$\left. \begin{aligned} \epsilon^2 &\sim \{1 + 4R^{-6}[\mu\mu]^2(\kappa_I^2 - \kappa_{II}^2)^{-2}\} \\ &\quad \times (\kappa_I^2 - \kappa_{II}^2)^2(\kappa_I^2 + \kappa_{II}^2)^{-2}. \end{aligned} \right\} \quad (5.11)$$

If we let  $\kappa_I$  be larger than  $\kappa_{II}$  we can write

$$\omega_{\pm}^2 \sim \frac{1}{2}(\kappa_I^2 + \kappa_{II}^2) \pm \frac{1}{2}(\kappa_I^2 - \kappa_{II}^2) \pm R^{-3}[\mu\mu]\{R^{-3}[\mu\mu](\kappa_I^2 - \kappa_{II}^2)^{-1}\},$$

with the understanding that the upper and lower signs, respectively, on the right-hand side correspond to  $\omega_+$  and  $\omega_-$ , respectively, if  $[\mu\mu]$  is positive, and to  $\omega_-$  and  $\omega_+$ , respectively, if  $[\mu\mu]$  is negative. We find (5.9) and (5.11) plotted in Herzberg.<sup>8</sup> Note that even far away from exact resonance, i.e.  $\kappa_I - \kappa_{II} \sim |R^{-3}[\mu\mu](\kappa_I^2 + \kappa_{II}^2)^{-\frac{1}{2}}|$ , the resonance effect  $\omega_- - \kappa_I = \kappa_{II} - \omega_+$  still is of the order of  $|R^{-3}[\mu\mu](\kappa_I^2 + \kappa_{II}^2)^{-\frac{1}{2}}|$ . The quantum states of these harmonic vibrators are

$$E_{n_+n_-} = \hbar\{(n_+ + \frac{1}{2})\omega_+ + (n_- + \frac{1}{2})\omega_-\}. \quad (5.12)$$

We see from Fig. 1 immediately<sup>9</sup> that (for  $[\mu\mu] < 0$ )  $n_+$  predominates over  $n_-$  among thermally accessible quantum states, i.e. we get attraction.

Let us discuss the eigenfunctions in the case of identical pairs of vibrators, see Section VIII. Dots represent  $\psi$  functions which are symmetric functions of  $q_I$  and  $q_{II}$ , circles represent antisymmetric functions. Instead of this representation of  $\psi$  as a product of inphase  $\psi$  and antiphase  $\psi$ , i.e.

$$\psi_{n_+n_-} = \psi_{n_+}(q_+)\psi_{n_-}(q_-), \quad q_{\pm} = q_I \pm q_{II} \quad (5.13)$$

we could have used, in this case of close resonance, a "resonance" representation whose zero-order eigenfunction is

$$\psi_{nm}^{(0)} = 2^{-\frac{1}{2}}(\psi_n(q_I)\psi_m(q_{II}) \pm \psi_m(q_I)\psi_n(q_{II})). \quad (5.14)$$

<sup>8</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 216; L. Pauling, *Chemical Bonds* (Cornell University Press, Ithaca, New York, 1940), p. 18, or H. Jehle, *Proc. Nat. Ac. Sci.* **36**, 242 (1950).

<sup>9</sup> See W. Heisenberg, *Zeits. f. Physik* **38**, 415 (1926).

The partition function  $Z$  for the pair of harmonic vibrators gives

$$\log Z = -\{\frac{1}{2}\hbar\omega_+/kT + \log(1 - \exp(-\hbar\omega_+/kT)) + \frac{1}{2}\hbar\omega_-/kT + \log(1 - \exp(-\hbar\omega_-/kT))\}. \quad (5.15)$$

In the classical limit  $\hbar\omega/kT \ll 1$

$$\begin{aligned} \log Z &\rightarrow -\log\hbar\omega_+/kT - \log\hbar\omega_-/kT \\ &= -\log\{(1 - \epsilon^2)^{\frac{1}{2}}(\hbar\omega/kT)^2\} \end{aligned} \quad (5.16)$$

$$\partial \log Z / \partial R \rightarrow \frac{1}{2}(1 - \epsilon^2)^{-1} \partial \epsilon^2 / \partial R. \quad (5.17)$$

In the other limit  $\hbar\omega/kT \gg 1$

$$\begin{aligned} \log Z &\rightarrow -\frac{1}{2}\hbar\omega_+/kT - \frac{1}{2}\hbar\omega_-/kT \\ &\quad + \exp(-\hbar\omega_+/kT) + \exp(-\hbar\omega_-/kT) \\ &= -(1 - \frac{1}{8}\epsilon^2 - (5/128)\epsilon^4)(\hbar\omega/kT) \\ &\quad + (2 + \frac{1}{4}\epsilon^2(\hbar\omega/kT) + \frac{1}{4}\epsilon^2(\hbar\omega/kT)^2) \\ &\quad \times \exp(-\hbar\omega/kT) \end{aligned} \quad (5.18)$$

$$\begin{aligned} \partial \log Z / \partial R &\rightarrow \{\frac{1}{8}(1 + \frac{5}{8}\epsilon^2)(\hbar\omega/kT) \\ &\quad + (\frac{1}{4}(\hbar\omega/kT) + \frac{1}{4}(\hbar\omega/kT)^2) \\ &\quad \times \exp(-\hbar\omega/kT)\} \partial \epsilon^2 / \partial R. \end{aligned} \quad (5.19)$$

The attractive force between the pair of vibrators which is proportional to  $\partial \log Z / \partial R$  is non-specific in both limits because  $\partial \epsilon^2 / \partial R$  does not depend on  $(\kappa_I^2 - \kappa_{II}^2)$  (i.e. on the coincidence of  $\kappa_I$  and  $\kappa_{II}$ ); the factors  $(1 - \epsilon^2)^{-1}$  and  $(1 + \frac{5}{8}\epsilon^2)$  are both of the order of magnitude one. In the classical limit we have proved this already in Section IV. In the other limit we have actually the case of London's dispersion forces before us.

## VI. A MOLECULE CONSIDERED AS A SET OF COUPLED VIBRATORS (CORRESPONDENCE TREATMENT)

In a large molecule we may have many repetitions of the same radicals or atoms which, if they were non-interacting ("unperturbed"), would perform similar vibrations with identical or almost identical frequencies. Actually they interact because of their vibrating electric dipole-dipole coupling and because they all are attached to the main body of the molecule.

In a large molecule we also have many radicals or atoms which perform commensurable vibrations. Anharmonic terms in the potential energy of the restoring forces bring about coupling between "modes" with commensurable or almost commensurable frequencies. In the case of a molecule with anharmonicities we can talk about vibrational modes only in the approximation of infinitely small vibrational amplitudes. Let  $q_1$  and  $q_2$  denote two "normal coordinates." The word "modes" then implies that there are no bilinear terms  $q_1q_2$  in the Hamiltonian, but among cubic and higher terms there are perturbing coupling terms between the modes  $q_1$  and  $q_2$ . These coupling terms may be very strong since  $q_1$  and  $q_2$  are modes of a single molecule.

If the unperturbed modes  $q_1$  and  $q_2$  have the same or almost the same frequency, or if they have commensurable or almost commensurable frequencies, then the eigenfunctions of the coupled system correspond to different phase relations between the phases of the

unperturbed "modes." In the simplest case this would imply inphase and antiphase relations if we express the coupled system in terms of the zero-order wave functions of the uncoupled modes, see the analysis of an analogous case in Section VIII. The energy difference of these different eigenfunctions, due to coupling, is strongest in this case of resonance. It is advantageous to carry through at least the qualitative considerations in terms of the corresponding Bohr quantum theory. Speaking in terms of the correspondence principle, we get, because of the Boltzmann factor  $\exp(-E/kT)$ , a statistical preference for certain phase relations which we may call "inphase," whatever the commensurability ratio may be.

The establishment of preferred phase relations will be particularly strong if we have a great number  $n$  of commensurable modes in one molecule. Such a molecule will, in the course of the period of lowest mode (most of the time), perform a fairly well-defined motion. The large molecule can therefore be cautiously replaced by a single macroscopic "representative vibrator" vibrating, say, with the frequency of the lowest mode and with a very large representative amplitude. We have to keep in mind only that this molecule's number of quantum states, or phase space volume which it occupies while performing vibrations of a given representative amplitude, increases very strongly with a small rise of this amplitude. This is because the number of neighboring states all belonging to the same representative amplitude goes up enormously with increasing amplitudes.

Let us point to a well-known analogous phenomenon which, strictly speaking, belongs to the domain of self-excited rather than free vibrations. If you sing a clear tone before a microphone, the acoustic system of the singer plus the microphone causes oscillations with various overtones. These have phase relationships established among themselves. This becomes evident from inspection by means of an oscilloscope connected to the microphone. Just these phase relationships permit a distinct pattern to be seen on the screen during many sweeps of the oscilloscope. The strong coupling between the various "modes" of one molecule brings about such phase related motion also in the thermally excited vibrations of a molecule.

In order to simplify this qualitative description we may momentarily make a crude assumption which certainly will not satisfy the actual case. We assume that instead of phase preferences we have true phase locking in between the modes of a large molecule.

## VII. THE PAIR OF MOLECULES

Such a molecule behaves somewhat like a large amplitude vibrator when interacting with another identical molecule. This it does for the following reason. If the lowest modes of the pair of molecules are inphase, then because of the phase locking between the various modes of each one of the molecules, all other modes are pairwise inphase too, and they all add up to a strong dipole-

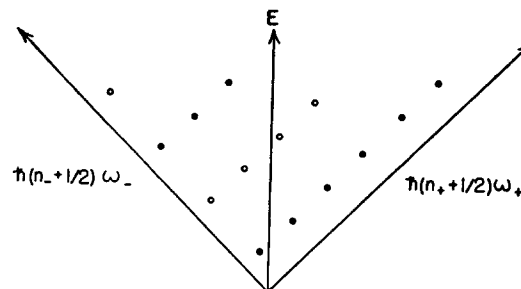


FIG. 1. Energy states for negative  $[\mu\mu]$ , e.g. parallel aligned dipoles vibrating in the  $Z$  direction.

dipole interaction energy between the pair of molecules. Other phase relations between the pair of lowest modes, of course, do not give this strong interaction energy. The phase relations between the pair of molecules  $I, II$  correspond to eigenfunctions which are symmetric or antisymmetric with respect to  $I, II$ . Though under the influence of Brownian motion there is always intercombination between symmetric and antisymmetric states and thus between different phase relations of molecules  $I$  and  $II$ , we have a strong statistical preference for the energetically lower inphase vibrations, inphase in the case of  $z$  components in dipole-dipole coupling. The situation may be represented by a diagram similar to Fig. 1, representing the thermally accessible quantum states with the modification that higher statistical weights will have to be attributed to higher quantum states. More precisely, a state  $n_+ = 3, n_- = 1$  which indicates a strong excitation of the inphase mode and a weak excitation of the other mode will, in this picture, have the same statistical weight as a state  $n_+ = 1, n_- = 3$ ; the statistical weights will very strongly increase with higher quantum numbers of this representative pair of large amplitude vibrators. Thermal accessibility on the other hand, can be represented by a horizontal line  $E = \text{constant}$ , limiting the region of accessible states. Consequently, the thermal excitation of the inphase mode will be overwhelming compared with that of the antiphase mode, i.e. the number of thermally excited states in which  $n_+$  dominates over  $n_-$  is much larger than that in which  $n_- > n_+$ . The net effect of the contribution of all quantum states amounts to a decrease of the free energy, which means that it amounts to an attraction.

If we consider phase preferences instead of strict phase locking inside the molecules, we will get a similar effect but of a smaller order. In the classical limit  $\hbar/T \rightarrow 0$ , resonance effects and specific attraction disappear. In order for this effect to arise, quite an orchestra of modes of one of the molecules has to correspond to that of the other, i.e. the two molecules have to show the same vibrational commensurabilities in between their modes. This is likely to happen only if the two molecules are structurally identical.<sup>10</sup> A slight difference

<sup>10</sup> I. Langmuir once suggested that a cumulative effect of many small interaction energies be responsible for specificity.



in between the two molecules usually will cause differences in their mode orientations and frequencies, and phase relations between their modes so as to nullify the effect.

A condition which has to be satisfied concerns the relative orientation of the two molecules. Consider two identical molecules in the same mutual orientation as, for example, two identical closed books lying one on top of the other with each book's front cover facing upwards, but with the bindings facing opposite directions (cf. Fig. 2). Let the  $z$  axis in this illustration be vertical, i.e. in the direction connecting the centers of the two molecules. If each of the molecules vibrates *en bloc* with established phase relationships and if the pair of molecules vibrates in synchronism, we have a form of motion in which the  $z_I, z_{II}$  components of vibration all vibrate e.g. inphase and therefore all  $x_I, x_{II}$  components of vibration and all  $y_I, y_{II}$  components vibrate in antiphase. So all three components contribute an attractive perturbation potential through  $[\mu\mu]$  cf. Eq. (5.2).

The peculiar kind of mutual orientation mentioned is caused by the same anharmonic resonance effect as the attraction itself: The pair has lower energy if orientated in that way. Brownian motion will bring about an orientation of lowest energy.

#### VIII. CORRESPONDENCE BETWEEN THE QUANTUM-MECHANICAL DESCRIPTION AND THE OLD QUANTUM THEORETICAL DESCRIPTION

Let us recall some simple correspondence arguments. Consider the simple one-dimensional problem of a pair of identical linear harmonic vibrators  $I$  and  $II$ , a distance  $R$  apart, and vibrating along the axis connecting them. The effect of a perturbing interaction energy  $-2z_I z_{II} e^2 R^{-3}$  causes resonance between the pair. The classical and old quantum theoretical description states that the classical frequency suffers a shift up or down depending on the classical phase relations between the two vibrations (inphase or antiphase). We can introduce an inphase and an antiphase mode which will stay normal in the perturbed system.

From the unperturbed individual eigenfunctions

$$\psi_n(z_I, t) \quad \text{and} \quad \psi_m(z_{II}, t),$$

the wave mechanical description of this resonance phenomenon builds a symmetric and an antisymmetric wave function.

$$\psi_{nm}^{(0)} = 2^{-\frac{1}{2}}(\psi_n(z_I, t)\psi_m(z_{II}, t) \pm \psi_m(z_I, t)\psi_n(z_{II}, t)). \quad (8.1)$$

The first-order term of the perturbation of the energy can be written

$$\begin{aligned} & -2e^2 R^{-3} \iint \psi_{nm}^{(0)*} z_I z_{II} \psi_{nm}^{(0)} dz_I dz_{II} \\ & = \mp 2e^2 R^{-3} \int \psi_n^*(z_I, t) z_I \psi_m(z_I, t) dz_I \\ & \quad \times \int \psi_m^*(z_{II}, t) z_{II} \psi_n(z_{II}, t) dz_{II} \\ & \quad + \text{conj. complex.} \quad (8.2) \end{aligned}$$

The upper sign refers to the synchronous inphase vibration of  $\langle n|z_I|m \rangle$  with  $\langle m|z_{II}|n \rangle$  in the correspondence description, the lower sign to the antiphase. (The product of the two integrals is time independent.) Instead of this resonance description we could have used  $\psi_{n+n_-} = \psi_{n_+}(z_+) \psi_{n_-}(z_-)$  where  $z_{\pm} = z_I \pm z_{II}$ ; even or odd values of  $n_-$  represent symmetric or antisymmetric wave functions, respectively.

From this well-known relation between classical and wave mechanical description it follows that arguments in correspondence language, based on classical phase relations or phase-preferences, have their quantum-mechanical counterpart in arguments about stationary states of the pair, made up from symmetric or antisymmetric combinations of resonating quantum states. (The perturbation integral of a stationary state of the pair reveals resonating transitions of the systems  $I$  and  $II$ .) To get the statistical effect of phase-preferences we have, in the classical picture, inphase domains occupying a larger phase-space volume than antiphase domains of the same energy. In quantum statistics the effect of phase-preferences is completely registered in the level shifts of the *stationary* states of the pair, brought about by the above calculated perturbation energy.

*Transitions* between different stationary states of the pair give a non-vanishing  $z_I + z_{II}$  if a symmetric state combines with a symmetric neighbor state or if an antisymmetric one combines with an antisymmetric neighbor. They give a non-vanishing  $z_I - z_{II}$  if a symmetric state combines with an antisymmetric neighbor state. For a pair of large molecules imbedded in a liquid medium, the Brownian motion in the medium causes both kinds of transitions.

Analogous considerations hold for pairs of modes in a single molecule where the interaction between the "modes" originates in anharmonic terms.

#### IX. QUANTUM-MECHANICAL RESONANCE BETWEEN COMMENSURABLE MODES

Placzek<sup>11</sup> presented the detailed theory of resonance between two commensurable vibrations in one molecule, anharmonic terms providing the coupling. He considered the case in which there are just two non-degenerate "modes" in the molecule and  $2\kappa_1 \sim \kappa_2$ . Using the abbreviations

$$\kappa_2 + 2\kappa_1 = 4\kappa, \quad \kappa_2 - 2\kappa_1 = 4\delta \quad (9.1)$$

one starts with a Hamiltonian which contains the essential interaction term

$$\begin{aligned} H = & \frac{1}{2}[\dot{q}_1^2 + \dot{q}_2^2 + \kappa_1^2 q_1^2 + \kappa_2^2 q_2^2] + a_{112} q_1^2 q_2 \\ & \sim \frac{1}{2}[\dot{q}_1^2 + \dot{q}_2^2 + 4\kappa^2(q_2^2 + \frac{1}{4}q_1^2)] \\ & \quad + 4\kappa\delta(q_2^2 - \frac{1}{4}q_1^2) + a_{112} q_1^2 q_2. \quad (9.2) \end{aligned}$$

<sup>11</sup> G. Placzek, *Handbuch der Radiologie*, edited by Marx, second edition, vol VI, p 319, Akad. Verlag Leipzig. Cf. also E. Fermi, *Zeits. f. Physik* **71**, 250, (1931), and D. M. Dennison, *Phys. Rev.* **41**, 304 (1932).



The terms in the square bracket are independent of  $\delta$ . One considers them as describing the unperturbed system whose levels (2, 0) and (0, 1) coincide exactly. The first-order perturbation theory with the remaining two terms furnishes the two energy levels (energies with reference to the ground level)

$$2\hbar\{\kappa \pm (\delta^2 + 2p^2)^{1/2}\}, \quad p = \frac{1}{2}\kappa^{-1/2}a_{112}\hbar^{1/2}, \quad (9.3)$$

and the two eigenfunctions

$$\begin{aligned} & (2\xi)^{-1/2}\{(\xi + |\delta|)^{1/2}\psi_{01} \pm (\xi - |\delta|)^{1/2}\psi_{20}\} \\ \text{and} & (2\xi)^{-1/2}\{(\xi - |\delta|)^{1/2}\psi_{01} \mp (\xi + |\delta|)^{1/2}\psi_{20}\} \end{aligned} \quad (9.4)$$

where  $\xi = (\delta^2 + 2p^2)^{1/2}$  and the upper and lower signs have to be taken according to whether  $p$  and  $\delta$  have equal signature or not, respectively. For  $\delta^2 \ll p^2$  the two energy levels become

$$2\hbar\{\kappa \pm 2^{1/2}p(1 + \delta^2/4p^2)\}, \quad (9.5)$$

and for  $\delta^2 \gg p^2$  they become

$$2\hbar\{\kappa \pm \delta(1 + p^2/\delta^2)\}, \quad (9.6)$$

which equals

$$\hbar(\kappa_2 + 2p^2/\delta) \quad (9.6a)$$

and

$$\hbar(2\kappa_1 - 2p^2/\delta). \quad (9.6b)$$

Cf. the similar situation, Sections V and X. It is clear that anharmonicity, i.e.,  $p$  causes a repulsion between the two levels (9.3) and therefore in thermal equilibrium it causes a predominance of one eigenfunction over the other, in analogy to the phase preferences discussed above.

## X. QUANTUM-MECHANICAL CALCULATION OF THE INTERACTION BETWEEN AN IDENTICAL MOLECULE PAIR

We mentioned in Section VI that, in a complicated molecule, we may have many radicals or atoms which, if vibrating each one by itself, unperturbed by the others, would show the same or almost same frequencies. They actually resonate with each other by virtue of some coupling  $\lambda q_{1I}q_{2I}$ , or some more complicated  $\lambda$  terms, cf. (11.1). We shall occasionally call  $q_{1I}$ ,  $q_{2I}$  pseudomodes because  $\lambda q_{1I}q_{2I}$  could be transformed away by a principal axes transformation. We shall, however, describe our system in terms of these coordinates  $q_{1I}$ ,  $q_{2I}$  etc. of the unperturbed systems as we want to investigate the effect of the interaction parameters  $\lambda$  and  $\mu$  (10.2), (11.1) on the attraction between the molecule pair.

Furthermore we have resonance between commensurable vibrations, causing level shifts (between e.g. symmetric and antisymmetric combinations of reso-

nating function  $\psi_{01}$  and  $\psi_{20}$ ). These level shifts are the stronger, the stronger the anharmonic coupling coefficient, the closer the commensurability, and the larger the number of resonating modes (cf. Section XI). Instead of following through the fairly complicated elaboration of Section IX for a pair of complicated molecules, let us make the rough assumption that the essential features of this situation can again be represented by an interaction  $\lambda q_{1I}q_{2I}$  and  $\lambda q_{1II}q_{2II}$  of two harmonic pseudomodes of exactly equal frequency, inside each of the identical molecules  $I$  and  $II$ . Indeed, the effects discussed above in terms of the correspondence principle, do not much depend on the kind of coupling which is assumed to exist between the modes of each one of the molecules.  $\lambda q_{1I}q_{2I}$ , just like  $\lambda q_{1I}^2q_{2I}$ , has the effect of pushing two resonating levels in molecule  $I$  apart.

$q_{1I}$  and  $q_{2I}$  may be parallel oriented, and we assume  $\lambda$  to be negative which of course might not be the case. As we look for a quantum effect, and as we want the calculations to be as simple as possible we assume that, apart from the ground level 0, practically only the next two bunches of levels 1 and 2 are thermally excited. We calculate the ground level and the bunches 1 and 2 up to second-order perturbation which means that we have to take into account the influence of the levels up to the 4th bunch. The unperturbed energies of the ground level 0 and of the bunches 1 and 2 have the values

$$E_0^{(0)} = 4 \cdot \frac{1}{2}\hbar\kappa = 2\hbar\kappa, \quad E_1^{(0)} = 3\hbar\kappa, \quad E_2^{(0)} = 4\hbar\kappa. \quad (10.1)$$

In order to calculate the electric dipole-dipole interaction of a pair of molecules, we assume a perturbation function

$$H_1 = \lambda(q_{1I}q_{2I} + q_{1II}q_{2II}) + \mu(q_{1I}q_{1II} + q_{1I}q_{2II} + q_{2I}q_{1II} + q_{2I}q_{2II}) \quad (10.2)$$

where  $\mu$  is some expression of the type

$$R^{-3}[(\mu_{zI}\mu_{zII} + \mu_{yI}\mu_{yII} - 2\mu_{zI}\mu_{zII})]. \quad (10.3)$$

$H_1$  is symmetric with respect to permutations (12) and with respect to ( $II$ ). As unperturbed wave functions we may take the set (10.4)

$$\begin{aligned} \psi_{00} &= \psi_0(q_{1I})\psi_0(q_{2I})\psi_0(q_{1II})\psi_0(q_{2II}) \equiv (0000) \\ &= \text{sym. (12), sym. (II)} \end{aligned}$$

for the ground state,

$$\begin{aligned} \psi_{10} &= \frac{1}{2}\{(0100) + (1000) + (0001) + (0010)\} \\ &= \text{sym. (12), sym. (II)} \end{aligned}$$

$$\begin{aligned} \psi_{11} &= \frac{1}{2}\{(0100) + (1000) - (0001) - (0010)\} \\ &= \text{sym. (12), antis. (II)} \end{aligned}$$

$$\begin{aligned} \psi_{12} &= \frac{1}{2}\{(0100) - (1000) + (0001) - (0010)\} \\ &= \text{antis. (12), sym. (II)} \end{aligned}$$

$$\begin{aligned} \psi_{13} &= \frac{1}{2}\{(0100) - (1000) - (0001) + (0010)\} \\ &= \text{antis. (12), antis. (II)} \end{aligned}$$

for the first bunch,

$$\begin{aligned}
\psi_{20} &= \frac{1}{4} \{ (0200) + (2000) + (0002) + (0020) \} \\
&\quad + 2^{-\frac{1}{2}} \{ (1100) + (0011) \} \\
&\quad + 2^{-\frac{1}{2}} \{ (0101) + (0110) + (1001) + (1010) \} \\
\psi_{21} &= \frac{1}{4} \{ (0200) + (2000) + (0002) + (0020) \} \\
&\quad + 2^{-\frac{1}{2}} \{ (1100) + (0011) \} \\
&\quad - 2^{-\frac{1}{2}} \{ (0101) + (0110) + (1001) + (1010) \} \\
\psi_{22} &= 2^{-\frac{1}{2}} \{ (0200) + (2000) + (0002) + (0020) \} \\
&\quad - \frac{1}{2} \{ (1100) + (0011) \} \\
\psi_{23} &= \frac{1}{2} \{ (0101) - (0110) - (1001) + (1010) \} \\
&\quad \text{all sym. (12), sym. (II)}, \\
\psi_{24} &= 2^{-\frac{1}{2}} \{ (0200) + (2000) - (0002) - (0020) \} \\
&\quad + \frac{1}{2} \{ (1100) - (0011) \} \\
\psi_{25} &= -2^{-\frac{1}{2}} \{ (0200) + (2000) - (0002) - (0020) \} \\
&\quad + \frac{1}{2} \{ (1100) - (0011) \} \\
&\quad \text{both sym. (12), antis. (II)}, \\
\psi_{26} &= 2^{-\frac{1}{2}} \{ (0200) - (2000) + (0002) - (0020) \} \\
&\quad + \frac{1}{2} \{ (0101) - (1010) \} \\
\psi_{27} &= -2^{-\frac{1}{2}} \{ (0200) - (2000) + (0002) - (0020) \} \\
&\quad + \frac{1}{2} \{ (0101) - (1010) \} \\
&\quad \text{both antis. (12), sym. (II)}, \\
\psi_{28} &= 2^{-\frac{1}{2}} \{ (0200) - (2000) - (0002) + (0020) \} \\
&\quad + \frac{1}{2} \{ (0110) - (1001) \} \\
\psi_{29} &= -2^{-\frac{1}{2}} \{ (0200) - (2000) - (0002) + (0020) \} \\
&\quad + \frac{1}{2} \{ (0110) - (1001) \} \\
&\quad \text{both antis. (12), antis. (II)},
\end{aligned}$$

for the second bunch.

As we use the higher levels only for the purpose of calculating second-order perturbations of the ground level and the first and second bunches, we simply choose the wave functions

(3000), (0300), (0030), (0003), (2100), (1200), (0021), (0012), (2010), (2001), (1020), (0120), (0210), (0201), (1002), (0102), (1110), (1101), (1011), (0111) 3rd

$$\begin{aligned}
E_{00}^{(1)} &= 0, \\
E_{10}^{(1)} &= (\lambda + 2\mu)\hbar/2\kappa, & E_{11}^{(1)} &= (\lambda - 2\mu)\hbar/2\kappa, & E_{12}^{(1)} &= E_{13}^{(1)} = -\lambda\hbar/2\kappa, \\
E_{20}^{(1)} &= 2(\lambda + 2\mu)\hbar/2\kappa, & E_{21}^{(1)} &= 2(\lambda - 2\mu)\hbar/2\kappa, & E_{24}^{(1)} &= 2\lambda\hbar/2\kappa, \\
E_{22}^{(1)} &= E_{23}^{(1)} = E_{25}^{(1)} = -2\lambda\hbar/2\kappa, & E_{26}^{(1)} &= E_{28}^{(1)} = 2\mu\hbar/2\kappa, & E_{27}^{(1)} &= E_{29}^{(1)} = -2\mu\hbar/2\kappa.
\end{aligned} \quad (10.6)$$

In order to carry through the second-order perturbations for this degenerate system, we use Van Vleck's method<sup>12</sup> which becomes particularly simple in the present case. For the ground level we get

$$\begin{aligned}
E_0^{(2)} &= \sum_{j''} \langle 00 | H_1 | 2j'' \rangle \langle 2j'' | H_1 | 00 \rangle / (E_0^{(0)} - E_2^{(0)}) \\
&= -\hbar\kappa(\frac{1}{4}\lambda^2 + \frac{1}{2}\mu^2) / \kappa^4. \quad (10.7)
\end{aligned}$$

For the first bunch of levels the second-order perturbations yield a matrix

$$\begin{aligned}
\langle 1j | G_2 | 1j' \rangle \\
= 0 - \sum_{j''} \langle 1j | H_1 | 3j'' \rangle \langle 3j'' | H_1 | 1j' \rangle / 2\hbar\kappa, \quad (10.8)
\end{aligned}$$

in Kemble's notation. This matrix, however, is already diagonal, the second-order perturbations of the energy

<sup>12</sup> E. C. Kemble, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), pp. 388-396.

for the third bunch. And we choose

(4000), (0400), (0040), (0004), (3100), (1300), (0031), (0013), (3010), (3001), (1030), (0130), (0310), (0301), (1003), (0103), (2020), (2002), (0220), (0202), (2200), (0022), (2110), (2101), (1021), (0121), (1210), (1201), (1012), (0112), (2011), (0211), (1120), (1102), (1111)

for the fourth bunch.

The only non-vanishing off-diagonal elements of the hermitian  $H_1$  which connect the ground level or the first or the second bunch of levels among each other or with any other bunch are the following.

Elements connecting the ground level with other levels:

$$\begin{aligned}
\langle 00 | H_1 | 20 \rangle &= 2^{-\frac{1}{2}}(\lambda + 2\mu)\hbar/2\kappa \\
\langle 00 | H_1 | 21 \rangle &= 2^{-\frac{1}{2}}(\lambda - 2\mu)\hbar/2\kappa \\
\langle 00 | H_1 | 22 \rangle &= -\lambda\hbar/2\kappa.
\end{aligned} \quad (10.5)$$

The 4 states of the first bunch are on speaking terms only with 16 out of the 20 states of the third bunch, there are 64 non-vanishing matrix elements. These are all the elements which connect the first bunch with some other. The 10 states of the second bunch are on speaking terms with 31 out of the 35 states of the fourth bunch, there are 257 non-vanishing matrix elements. Furthermore, 3 states of the second bunch speak to the ground level, cf. (10.5). These are all the elements which connect the second bunch with some other.

With the choice (10.4) of eigenfunctions,  $H_1$  is a diagonal matrix inside the first bunch and it is a diagonal matrix inside the second bunch. Therefore the first order perturbation theory is already carried through, we have only to list these diagonal elements of  $H_1$ , they are

levels are these diagonal elements

$$\begin{aligned}
E_{10}^{(2)} &= -\hbar\kappa(\frac{3}{8}\lambda^2 + \frac{1}{2}\lambda\mu + \mu^2) / \kappa^4, \\
E_{11}^{(2)} &= -\hbar\kappa(\frac{3}{8}\lambda^2 - \frac{1}{2}\lambda\mu + \mu^2) / \kappa^4, \\
E_{12}^{(2)} &= E_{13}^{(2)} = -\hbar\kappa(\frac{3}{8}\lambda^2 + \frac{1}{2}\mu^2) / \kappa^4.
\end{aligned} \quad (10.9)$$

Similarly, for the second bunch, the matrix

$$\begin{aligned}
\langle 2j | G_2 | 2j' \rangle &= 0 - \sum_{j''} \langle 2j | H_1 | 4j'' \rangle \langle 4j'' | H_1 | 2j' \rangle / 2\hbar\kappa \\
&\quad + \langle 2j | H_1 | 00 \rangle \langle 00 | H_1 | 2j' \rangle / 2\hbar\kappa \quad (10.10)
\end{aligned}$$

is diagonal. The calculations give

$$\begin{aligned}
E_{20}^{(2)} &= -\hbar\kappa(\frac{1}{2}\lambda^2 + \lambda\mu + \frac{3}{2}\mu^2) / \kappa^4 \\
E_{21}^{(2)} &= -\hbar\kappa(\frac{1}{2}\lambda^2 - \lambda\mu + \frac{3}{2}\mu^2) / \kappa^4 \\
E_{24}^{(2)} &= -\hbar\kappa(\frac{1}{2}\lambda^2 + \frac{3}{2}\mu^2) / \kappa^4 \\
E_{22}^{(2)} &= E_{23}^{(2)} = E_{25}^{(2)} = -\hbar\kappa(\frac{1}{2}\lambda^2 + \frac{1}{2}\mu^2) / \kappa^4 \\
E_{26}^{(2)} &= E_{28}^{(2)} = -\hbar\kappa(\frac{1}{2}\lambda^2 + \frac{1}{2}\lambda\mu + \mu^2) / \kappa^4 \\
E_{27}^{(2)} &= E_{29}^{(2)} = -\hbar\kappa(\frac{1}{2}\lambda^2 - \frac{1}{2}\lambda\mu + \mu^2) / \kappa^4.
\end{aligned} \quad (10.11)$$

We form the partition function  $Z$  by means of (10.1), (10.6), (10.7), (10.9), (10.11). We finally arrive to the

following expression for the attractive force

$$\begin{aligned}
 -kT \frac{\partial \log Z}{\partial R} &= -kT \frac{d\mu}{dR} Z^{-1} \frac{\partial Z}{\partial \mu} = -kT \frac{d}{dR} \left( \frac{\mu}{\kappa^2} \right) \frac{\hbar \kappa}{kT} \\
 &\times \left[ 1 + \exp \left\{ - \left( 1 + \frac{1}{2} \frac{\lambda}{\kappa^2} - \frac{1}{8} \frac{\lambda^2}{\kappa^4} \right) \frac{\hbar \kappa}{kT} \right\} \right. \\
 &\cdot \left( 2 + 2 \frac{\hbar \kappa}{kT} - 2 \frac{\lambda}{\kappa^2} \frac{\hbar \kappa}{kT} + \frac{1}{2} \frac{\lambda^2}{\kappa^4} \frac{\hbar \kappa}{kT} \right) \\
 &+ \exp \left\{ - \left( 2 + \frac{\lambda}{\kappa^2} - \frac{1}{4} \frac{\lambda^2}{\kappa^4} \right) \frac{\hbar \kappa}{kT} \right\} \\
 &\cdot \left( 2 + 4 \frac{\hbar \kappa}{kT} - 4 \frac{\lambda}{\kappa^2} \frac{\hbar \kappa}{kT} + \frac{\lambda^2}{\kappa^4} \frac{\hbar \kappa}{kT} \right) \left. \right]. \quad (10.12)
 \end{aligned}$$

In working out this expression we made use of the relation  $\mu \ll \lambda$ , but of course only after the differentiation of  $Z$  with respect to  $\mu$ . This relation means that the coupling between two modes of one molecule is strong compared with the coupling between two modes, one in the one molecule, the other in the other molecule. The formula (10.12) checks with the corresponding one in reference 8, i.e., if we drop the higher order perturbation terms from (10.12).

We see that the attractive force depends on  $\hbar$ , we have a quantum-mechanical resonance effect. The force of this dipole-dipole interaction depends on  $\mu d\mu/dR$ , i.e., it is proportional to  $R^{-7}$ . The first term 1 in the square bracket represents the ground levels contribution to London's dispersion force. The exponential terms in the square bracket interest us most of all because they register the influence of the excited states toward the attraction. They are therefore the terms in which the effect of phase preferences show up. They contain a factor

$$\exp \left\{ - \frac{1}{2} \frac{\lambda}{\kappa^2} \frac{\hbar \kappa}{kT} \right\}$$

and

$$\exp \left\{ - \frac{\lambda}{\kappa^2} \frac{\hbar \kappa}{kT} \right\}, \quad \text{respectively,} \quad (10.13)$$

which means that for strong coupling between the modes of each one of the molecules (and  $\lambda < 0$ ), we get an exponential multiplicative factor in the expression for the attractive force. Although for molecules with only two modes, this factor has not much influence, for molecules with many ( $n$ ) modes it becomes important, as shown in the following section. (If  $E_{12}^{(1)} = E_{13}^{(1)}$  would have been  $= +\lambda \hbar / 2\kappa$ , i.e. if we would not have had phase preferences, then the expression for  $Z^{-1}$  would have been different, and the result (10.12) would not have given this strong attraction effect.)

This result (10.12) is interesting for some more reasons. We assumed  $\lambda$  to be negative. (Let us note en

passant that the exponential functions are each multiplied by a sum of four positive quantities, the quantities in round parentheses.) The exponential functions in (10.12) have an exponent which is larger than  $-\hbar \kappa / kT$ , larger by an amount determined by  $\lambda / \kappa^2$ . Other exponential functions like  $\exp \{ - [1 - \frac{1}{2} (\lambda / \kappa^2) - \frac{1}{8} (\lambda^2 / \kappa^4)] (\hbar \kappa / kT) \}$  and similar ones referring to the second bunch of levels, cancelled out altogether in the formation of the attractive force. We see therefore that the second order perturbation terms  $+\frac{1}{8} (\lambda^2 / \kappa^4) (\hbar \kappa / kT)$  and  $+\frac{1}{4} (\lambda^2 / \kappa^4) (\hbar \kappa / kT)$  in the exponents of the exponential functions have the same positive signature as the first order terms,  $-\frac{1}{2} (\lambda / \kappa^2) (\hbar \kappa / kT)$  and  $-(\lambda / \kappa^2) (\hbar \kappa / kT)$ . First-order perturbation theory alone will therefore give an effect (10.13) in the same direction as this complete second-order theory. This is important for the calculations done in the following sections by first-order theory only. In order to estimate the order of magnitude of the attraction term, we compare it with the above mentioned London force term. For this purpose we evidently needed to carry through the second-order perturbation theory.

Another observation can be made with (10.12). The second bunch of levels has an influence on the attraction force, an influence similar to that of the first bunch. For complicated molecules the higher bunches become more and more in thermal reach, and difficulties of calculation make but the lowest bunches accessible to even first-order perturbation calculations. So it is good to know in this example that the first-order perturbation of the first bunch already characterizes the over-all effect given by the  $\lambda$  dependence of the square bracket in (10.12).

This is the effect of phase preferences on the attraction. Our arguments in Section VII show that in the case of commensurable rather than equal frequency modes, specific attraction has its cause in corresponding phase preferences in the pair of molecules—and those corresponding phase preferences depend on the identity of the pair.

## XI. LARGE MOLECULES

We should like to see how this attraction effect depends on the number of modes, i.e., on the size of the molecules. Therefore, we shall look at a more complicated model, one which more closely resembles the case of molecules with many commensurable modes. Consider the case of molecules *I* and *II* each having 4 modes of equal frequency, and let us calculate the first order perturbation of the first bunch of levels above the ground level

$$\begin{aligned}
 \psi_{00} &= \psi_0(q_{1I}) \cdots \psi_0(q_{4II}) \\
 &= (0000 \ 0000) \sim ((1234)) \langle\langle I \ II \rangle\rangle
 \end{aligned}$$

by which symbol we mean complete symmetry in 1, 2, 3, 4 and in *I*, *II*.<sup>13</sup>

<sup>13</sup> E. Fues, *Quantenmechanik*, *Handb. d. Expphys. Ergänzungswerk*, Vol. II, p. 167 (1935). F. Hund, *Handb. der Phys.* 24.1, p. 585 (1933).

We assume a perturbation function

$$H_1 = \lambda(q_{1I}q_{2I} + q_{2I}q_{3I} + q_{3I}q_{4I} + q_{4I}q_{1I} + q_{1I}q_{3I} + q_{2I}q_{4I}) + \lambda(q_{1II}q_{2II} + \dots + q_{2II}q_{4II}) + \mu(q_{1I}q_{1II} + q_{1I}q_{2II} + q_{1I}q_{3II} + q_{1I}q_{4II} + \dots + q_{4I}q_{4II}). \quad (11.1)$$

Let us find the eigenfunctions and levels of each of the molecules by themselves, e.g. of molecule *I*. For the levels of bunch 1, in which case all but one mode are in the ground state, we have four orthonormal eigenfunctions:

$$\begin{aligned} \psi_{10}^I &= \frac{1}{2}\{(0100) + (1000) + (0001) + (0010)\} \sim \langle(1234), 2\rangle \\ \psi_{11}^I &= \frac{1}{2}\{(0100) + i(1000) - (0001) - i(0010)\} \sim \langle(134), 2\rangle \\ \psi_{12}^I &= \frac{1}{2}\{(0100) - (1000) + (0001) - (0010)\} \sim \langle(134), 2\rangle \\ \psi_{13}^I &= \frac{1}{2}\{(0100) - i(1000) - (0001) + i(0010)\} \sim \langle(134), 2\rangle. \end{aligned} \quad (11.2)$$

(In the table of Fues these are the only non-vanishing eigenfunctions in the case of four identical modes.) The first order perturbations of the levels of the first bunch are

$$\begin{aligned} \langle 10 | H_1^I | 10 \rangle &= 3\lambda\hbar/2\kappa \\ \langle 11 | H_1^I | 11 \rangle &= \langle 12 | H_1^I | 12 \rangle = \langle 13 | H_1^I | 13 \rangle \\ &= -\lambda\hbar/2\kappa. \end{aligned} \quad (11.3)$$

The off diagonal elements vanish. This shows already that the first symmetrical state is, because of the Boltzmann factor  $\exp(-E/kT)$ , the statistically most preferred one ( $\lambda < 0$ ), which is in accordance with the phase preference argument.

For a pair of molecules, the orthonormal eigenfunctions for the first bunch of levels are

$$\begin{aligned} 2^{-\frac{1}{2}}(\psi_{10}^I\psi_{00}^{II} \pm \psi_{00}^I\psi_{10}^{II}), \\ 2^{-\frac{1}{2}}(\psi_{11}^I\psi_{00}^{II} \pm \psi_{00}^I\psi_{11}^{II}), \\ 2^{-\frac{1}{2}}(\psi_{12}^I\psi_{00}^{II} \pm \psi_{00}^I\psi_{12}^{II}), \\ 2^{-\frac{1}{2}}(\psi_{13}^I\psi_{00}^{II} \pm \psi_{00}^I\psi_{13}^{II}). \end{aligned} \quad (11.4)$$

The diagonal elements of  $H_1$  are

$$(3\lambda + 4\mu)\hbar/2\kappa, \quad (3\lambda - 4\mu)\hbar/2\kappa, \quad (11.5)$$

and six equal elements  $-\lambda\hbar/2\kappa$ . The quantity  $\mu$  again shows up in the level shifts of the phase-preferred first pair of states and therefore has a strong influence on the attractive force.

Finally, let us consider the general case of a pair of identical molecules each having  $n$  modes of identical frequency, and let us calculate the first-order perturbation of the first bunch of levels. We rewrite the above example for  $n=4$ . We may choose as eigenfunctions the eight functions

$$(1000 \ 0000), (0100 \ 0000), \dots, (0000 \ 0001). \quad (11.6)$$

The diagonal elements  $E^{(1)} \equiv \epsilon\hbar/2\kappa$  of the perturbation function  $H_1$  [Eq. (11.1)] are the roots of

$$0 = \begin{vmatrix} -\epsilon & \lambda & \lambda & \lambda & \mu & \mu & \mu & \mu \\ \lambda & -\epsilon & \lambda & \lambda & \mu & \mu & \mu & \mu \\ \lambda & \lambda & -\epsilon & \lambda & \mu & \mu & \mu & \mu \\ \lambda & \lambda & \lambda & -\epsilon & \mu & \mu & \mu & \mu \\ \mu & \mu & \mu & \mu & -\epsilon & \lambda & \lambda & \lambda \\ \mu & \mu & \mu & \mu & \lambda & -\epsilon & \lambda & \lambda \\ \mu & \mu & \mu & \mu & \lambda & \lambda & -\epsilon & \lambda \\ \mu & \mu & \mu & \mu & \lambda & \lambda & \lambda & -\epsilon \end{vmatrix}. \quad (11.7)$$

It is easily seen that the roots are the ones given by (11.5). Indeed, we add the rows 2, 3, 4, 5, 6, 7, 8 to row 1 and realize that the determinant has a factor  $(-\epsilon + 3\lambda + 4\mu)$ . Then we add the rows 2, 3, 4 and subtract rows 5, 6, 7, 8 from row one and see that the determinant has also a factor  $(-\epsilon + 3\lambda - 4\mu)$ . To prove that the remaining six roots  $\epsilon$  are all equal to  $-\lambda$ , we subtract the second column from the first, the third from the second, the fourth from the third, the seventh from the eighth, the sixth from the seventh, and the fifth from the sixth. The resulting determinant has  $(\epsilon + \lambda)^6$  as a factor.

In the general case the first-order perturbations of the energy levels are  $((n-1)\lambda + n\mu)\hbar/2\kappa$ ,  $((n-1)\lambda - n\mu)\hbar/2\kappa$  and there are  $2n-2$  equal levels with perturbation  $-\lambda\hbar/2\kappa$ .

Forgetting second-order perturbation terms and neglecting all but the first excited bunch of levels, we have, analogous to (10.12),

$$\begin{aligned} Z \sim \exp\{-n\hbar\kappa/kT\} \\ + \exp\{-[(n+1) + (\frac{1}{2}(n-1)\lambda + \frac{1}{2}n\mu)/\kappa^2]\hbar\kappa/kT\} \\ + \exp\{-[(n+1) + (\frac{1}{2}(n-1)\lambda - \frac{1}{2}n\mu)/\kappa^2]\hbar\kappa/kT\} \\ + (2n-2) \exp\{-[(n+1) - \frac{1}{2}\lambda/\kappa^2]\hbar\kappa/kT\}. \end{aligned} \quad (11.8)$$

$$\begin{aligned} -kT \frac{d\mu}{dR} Z^{-1} \frac{\partial Z}{\partial \mu} \sim -kT \frac{d}{dR} \left( \frac{\mu}{\kappa^2} \right) \cdot \frac{n^2}{2} \frac{\mu}{\kappa^2} \left( \frac{\hbar\kappa}{kT} \right)^2 \\ \times \exp\left\{ - \left( 1 + \frac{n-1}{2} \frac{\lambda}{\kappa^2} \right) \frac{\hbar\kappa}{kT} \right\}. \end{aligned} \quad (11.9)$$

This shows the influence of  $\lambda$  on the attractive force;  $-(n-1)\lambda/2\kappa^2$  can become large compared with unity.

In a macromolecule with large  $n$  we certainly have to take into account the perturbations of the higher bunches of levels. This is very complicated to do, and the correspondence description is more adequate. In the case of  $n=2$  we can, however, already see the influence of perturbations of the levels of bunch two, cf. Eq. (10.12).

## XII. SPECIFICITY

Let us look at the calculations of Section X in case of a pair of molecules which has been detuned (verstimmt). This should, at least for this particular model, tell us something about the specificity of interaction. To get a deeper insight, however, one has to carry out

these calculations for a pair of molecules which have many anharmonically coupled modes.

We are going to detune the frequency  $\kappa$  of the modes by amounts  $\delta$ . We want to study the behavior of the ground and first bunch of levels in first-order perturbation theory in order to find out the influence of  $\delta$  on the partition function and on the attractive force. We work in the neighborhood of resonance  $\delta=0$ , i.e. small values  $\delta \ll \kappa$  because we are interested in the comparison of an identical pair with a nearly identical pair. (A comparison with large values of  $\delta$  is meaningless as such case would represent an altogether different situation.) Therefore, we may neglect terms  $\delta^2$  compared with terms  $\kappa\delta$ . Our notation is made so that  $\delta \geq 0$ .

When detuning, we shall shift as many frequencies upwards as we shift downwards, by the same amount  $\delta$ , so that the mean value of the frequencies is not changed. (A change of this mean value would cause a change in attraction, but this effect is again not what we are interested in.)

We study four kinds of detuning. In every case we split  $H = H_0 + H_1$  with

$$H_0 = \frac{1}{2}(\dot{q}_{1I}^2 + \dot{q}_{2I}^2 + \dot{q}_{1II}^2 + \dot{q}_{2II}^2) + \frac{1}{2}\kappa^2(q_{1I}^2 + q_{2I}^2 + q_{1II}^2 + q_{2II}^2). \quad (12.1)$$

#### Detuning A

$$H_1 = \kappa\delta(q_{1I}^2 + q_{2I}^2) - \kappa\delta(q_{1II}^2 + q_{2II}^2) + \lambda(\cdot) + \mu(\cdot). \quad (12.2)$$

where the  $\lambda$  and  $\mu$  terms are as in (10.2). For  $\kappa^2\delta^2 \ll \mu^2$  there is no change compared with the calculation in Section X. For  $\kappa^2\delta^2 \gg \mu^2$  the first-order perturbations are  $E_0^{(1)} = 0$ ;  $E_{10}^{(1)}, E_{11}^{(1)} = \{\lambda \mp (2\kappa\delta + \mu^2/\kappa\delta)\}\hbar/2\kappa$ ;

$$E_{12}^{(1)}, E_{13}^{(1)} = \{-\lambda \mp 2\kappa\delta\}\hbar/2\kappa. \quad (12.3)$$

The first bunch of eigenfunctions are of course no longer (10.4). The attractive force becomes

$$-kT \frac{d\mu}{dR} Z^{-1} \frac{\partial Z}{\partial \mu} = -kT \frac{d}{dR} \left( \frac{\mu}{\kappa^2} \right) \cdot \frac{\mu}{\kappa^2} \frac{\hbar\kappa}{kT} \times \left[ 2 \frac{\hbar\kappa}{kT} \exp \left\{ - \left( 1 + \frac{\lambda}{2\kappa^2} \right) \frac{\hbar\kappa}{kT} \right\} \right]. \quad (12.4)$$

(12.4) is identical with (10.12) when the second-order perturbation of the groundlevel is ignored. We conclude that in this particular model the detuning A does not affect the attraction, in analogy to the simple oscillator pair, Eq. (5.19).

#### Detuning B

$$\kappa_{1I} = \kappa + \delta, \quad \kappa_{1II} = \kappa - \delta, \quad \kappa_{2I} = \kappa_{2II} = \kappa \quad (12.5)$$

$$H_1 = \kappa\delta q_{1I}^2 - \kappa\delta q_{1II}^2 + \lambda(\cdot) + \mu(\cdot)$$

For  $\kappa^2\delta^2 \gg \lambda^2$  we get

$$E_0^{(1)} = 0; \quad E_{10}^{(1)}, E_{11}^{(1)} = \pm (2\kappa\delta + \frac{3}{4}\mu^2/\kappa\delta)\hbar/2\kappa; \quad (12.6)$$

$$E_{12}^{(1)}, E_{13}^{(1)} = \pm (\mu^2\kappa\delta/\lambda^2)\hbar/2\kappa$$

and the attractive force

$$-kT \frac{d}{dR} \left( \frac{\mu}{\kappa^2} \right) \cdot \frac{\mu}{\kappa^2} \frac{\hbar\kappa}{kT} \times \left[ \frac{\hbar\kappa}{kT} \left( \frac{3}{2} + \frac{\mu^2\kappa^2\delta^2}{\lambda^4} \right) \exp \left\{ - \frac{\hbar\kappa}{kT} \right\} \right]. \quad (12.7)$$

The term (10.13) which causes the strong attraction between large molecule pairs, has disappeared.

#### Detuning C

$$\kappa_{1I} = \kappa + \delta, \quad \kappa_{2I} = \kappa - \delta, \quad \kappa_{1II} = \kappa_{2II} = \kappa \quad (12.8)$$

$$H_1 = \kappa\delta q_{1I}^2 - \kappa\delta q_{2I}^2 + \lambda(\cdot) + \mu(\cdot)$$

For  $\kappa^2\delta^2 \gg \lambda^2$  we get

$$E_0^{(1)} = 0; \quad E_{10}^{(1)} = (\lambda - 2\lambda\mu^2/\kappa^2\delta^2)\hbar/2\kappa, \quad E_{11}^{(1)} = -\lambda\hbar/2\kappa \quad (12.9)$$

$$E_{12}^{(1)}, E_{13}^{(1)} = \pm (2\kappa\delta + \lambda^2/4\kappa\delta + \mu^2/\kappa\delta)\hbar/2\kappa$$

and the attractive force

$$-kT \frac{d}{dR} \left( \frac{\mu}{\kappa^2} \right) \cdot \frac{\mu}{\kappa^2} \frac{\hbar\kappa}{kT} \times \left[ \left( 2 \frac{\lambda}{\delta^2} \exp \left\{ - \frac{\lambda}{2\kappa^2} \frac{\hbar\kappa}{kT} \right\} + 2 \frac{\hbar\kappa}{kT} \right) \exp \left\{ - \frac{\hbar\kappa}{kT} \right\} \right]. \quad (12.10)$$

Here the term (10.13) has been slashed (the factor of (10.13) in (10.12) is large compared with that in (12.10)). This is a particularly interesting detuning as it shows that if phase preference is established only in molecule II then specific attraction is gone. In other words it shows that (10.12) is not just a cumulative effect of two level lowerings in the two molecules.

#### Detuning D

$$\kappa_{1I} = \kappa_{1II} = \kappa + \delta, \quad \kappa_{2I} = \kappa_{2II} = \kappa - \delta \quad (12.11)$$

$$H_1 = \kappa\delta(q_{1I}^2 + q_{1II}^2) - \kappa\delta(q_{2I}^2 + q_{2II}^2) + \lambda(\cdot) + \mu(\cdot)$$

For  $\kappa^2\delta^2 \gg \lambda^2$  we get

$$E_0^{(1)} = 0; \quad E_{10}^{(1)}, E_{11}^{(1)} = \{2\kappa\delta + \lambda^2/4\kappa\delta \pm \mu(1 + \lambda/2\kappa\delta)\}\hbar/2\kappa$$

$$E_{12}^{(1)}, E_{13}^{(1)} = \{-2\kappa\delta - \lambda^2/4\kappa\delta \pm \mu(1 - \lambda/2\kappa\delta)\}\hbar/2\kappa \quad (12.12)$$

and the attractive force

$$-kT \frac{d}{dR} \left( \frac{\mu}{\kappa^2} \right) \cdot \frac{\mu}{\kappa^2} \frac{\hbar\kappa}{kT} \left[ \frac{1}{2} \frac{\hbar\kappa}{kT} \left\{ \left( 1 + \frac{\lambda}{\kappa\delta} \right) \times \exp \left\{ - \left( 1 + \frac{1}{2\kappa^2} \left[ 2\kappa\delta + \frac{\lambda^2}{4\kappa\delta} \right] \right) \frac{\hbar\kappa}{kT} \right\} + \left( 1 - \frac{\lambda}{\kappa\delta} \right) \times \exp \left\{ - \left( 1 - \frac{1}{2\kappa^2} \left[ 2\kappa\delta + \frac{\lambda^2}{4\kappa\delta} \right] \right) \frac{\hbar\kappa}{kT} \right\} \right\} \right]. \quad (12.13)$$

Again the term (10.13) is missing; the present influence of  $\lambda$  is of a smaller order of magnitude than that in (10.12). The attractive force (10.12) is specific with respect to the changes  $B$ ,  $C$ ,  $D$  performed on the molecule pair. The absence of corresponding phase preferences causes the lack of strong attraction.

### XIII. DISCUSSION

The argument for specificity depends on the presence of a great number of identical pairs of vibrational modes (all with the same or commensurable frequencies) in a pair of rigid molecules. If the pair is not quite identical, because in one of the partners some change has been made, such change is likely to alter the set of phase-related vibrational modes of this molecule. Thus the changed molecule will no longer match the unchanged molecule and specificity will be lost.

An experimental test of the vibrational cause for specificity might be tried on this basis. The surrounding medium of a self-duplicating chromosome has, of course, to contain constituent molecules of the right chemical composition, but in some of these molecules one or several atoms may have been replaced by isotopes (e.g. isotopes at location where they do not walk out of the molecule or into it).<sup>14</sup> The resulting molecules will be chemically, but no longer vibrationally identical with the original ones. Thus they will be discriminated

against when it comes to being attracted by the original chromosome. The change of vibrational behavior by substitution of isotopes is, however, small compared to a change of vibrational behavior caused by a chemical or structural change of the molecule. Inactivation of viruses may perhaps be understood on the basis of a change of vibrational properties.

After a pair of molecules has come close together in the energetically most favorable orientation, the dipole field of the pair is altogether different from that of an individual molecule. It will make it difficult for them to match a third identical molecule which is alone. Hence triplets are not so easily formed. However, another *pair* may be attracted. This is in agreement with the fact that we observe only doublets, quadruplets, octuplets, etc. among chromosomes.

Also the mutual orientation of very large crystal-forming molecules may be influenced by this orientation effect. Figure 2 shows 8 molecules in such a preferential orientation. The whole crystal will be a multiple repetition of this octuplet. Such an orientation effect in crystals may show up provided the other intermolecular forces are too small to be influential.

Another fundamental phenomenon fits into this theory of self-duplication. This is the fact that laevo configurations of proteins always reproduce laevo. This has been a particular puzzle to the mould theory (explanation of specificity by steric effects) which tries to explain what is called a complementary structure. But it is evident from the orientation argument discussed above that a laevo configuration particularly strongly attracts another laevo configuration. A short discussion of various mutual orientations between laevo molecules and dextro molecules shows that they fail to be strongly attracted.

While a constituent gene in the chromosome is attracting an identical gene, the pair of genes has the orientation described above (end of Section VII). The adjacent genes of the original chromosome may have already built up identical replicas from the surrounding medium. Now the genes of the daughter chromosomes, being close together, may be bound to each other by means of the chromosome material into which the genes are imbedded. This is done in just the same way as with the genes in the original chromosome. To establish this pearlstring alignment properly, the individual genes which are going to form the daughter chromosome either have each to turn  $180^\circ$  around the  $z$  axis (cf. Fig. 3), whereby they become oriented parallel to the genes of the original chromosome, or without changing their absolute orientation in space (cf. Fig. 3), they may align in antiparallel orientation. In the first case the  $x$  and  $y$  components of vibration cause repulsion after the rotation so that the strong attraction between the pair of genes is practically nullified. Let us now look into the second case (antiparallel  $xy$  alignment). If the chromosome section is elongated, such an alignment makes the distances be-

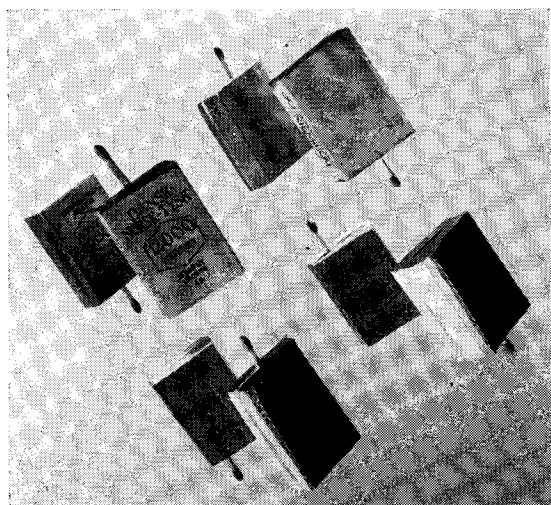


FIG. 2. Orientation of eight identical macromolecules if specific forces alone determine their orientation. The matches are used to indicate the top end of the pages.

<sup>14</sup> Experiments have been done in this direction by K. F. Bonhoeffer and collaborators. *Zeits. f. Physik. Chemie* 172A, 370-378 (1935); 175A, 459 (1936); 176A, 202 (1936); 180A. Among other problems, the influence of deuterium on the growth of yeast is investigated. Careful distinction is made between hydrogen atoms so located in the organic compounds of yeast that they are easily exchangeable (Austausch) with deuterium present in the surrounding  $D_2O$ , and hydrogen atoms at locations where they are built in (Einbau), i.e. not exchangeable with D if brought in contact with pure  $D_2O$ . The difficulty arose that even in the latter case such H atoms get occasionally exchanged with D atoms of compounds present in a nutrient solution.

tween corresponding genes very large and alters the angles of relative orientation of the lines connecting pairs of genes (new  $z$  axis) to the gene axes, so that the resulting attraction is diminished. If the chromosome section is not elongated, e.g. if we consider only one gene complex, the "or" configuration still results in some strong attraction. It might also be that the genes imbedded in the chromosome material can easily turn and so preserve the energetically most favorable orientation with respect to daughter genes.

Self-duplicated and synapsed chromosomes separate again at later stages in the respective processes. This may have various causes, e.g. changes in the constitution of the surrounding aqueous medium. The reorientation of the genes might help in permitting the chromosome pairs to go apart. Figure 3 illustrates the reorientation of genes in a daughter chromosome while the genes join together as in a string of beads. The strings are indicated by dotted lines; lines connecting corresponding genes are dashed. The original chromosome (consisting of 2 genes in this picture) is on the left, the daughter chromosome is on the right.

The theory requires us to regard the constituent molecules in a gene as being vibrationally independent units with little vibrational coupling between neighboring constituent molecules of the gene. This should be so because the molecule in the original gene is supposed to perform the same vibrations as the free molecule which is being attracted from the surrounding medium. That point should be understood more clearly.

We might remark in concluding that the problem of specific attraction between identical or almost identical macromolecules certainly has several aspects of which vibrational compatibility seems to be the most important. But one should understand clearly the limitations of this phenomenon and attempt some experimental investigations of it. It would go beyond the scope of this note if we would discuss the possible relations of this specific attraction phenomenon to polymerization, antigen antibody specificity and related fields.<sup>14</sup>

## APPENDIX

### Frequencies, Velocities, and Amplitudes of the Low Frequency Vibrations in Macromolecules

The highest frequencies in molecular vibrations are known to be of the order  $\nu = 10^{14}$  to  $10^{13}$  sec.<sup>-1</sup>. This is above the equipartition value  $kT/h = 0.6 \cdot 10^{13}$  sec.<sup>-1</sup>, and is important for specific interactions.

In this Appendix we should like to get oriented about the thermal excitation of the lower frequency vibrations of a "constituent molecule" of a gene. We can imagine such a macromolecule as vibrating as a solid does in Debye's theory of specific heats. Let us calculate

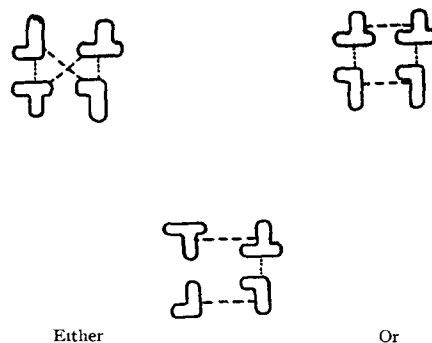


FIG. 3. Above: Orientation before daughter genes are strung up. Below: Orientation afterwards.

velocities and amplitudes of vibrations of smaller and larger parts of the macromolecule. These low frequency vibrations usually do not play the predominant role in specific interaction.

Let  $m_0$  be the average atomic weight of the atoms in the "constituent molecule" and let  $M$  be the total mass of the molecule, measured in atomic units, and let  $m$  (in the same units) be the mass of a part of this molecule, a part in whose motion as a subunit we are interested. For simplicity, let us imagine  $M$  and  $m$  to be cubical in shape, and let us assume that practically all thermal energy is vibrational.

### First approach

Since we are interested in the average motion of the atoms of a certain part of the molecule, we assume that this part moves as an independent unit, performing vibrations of such a form as if it were a section  $\lambda/2$  of a standing wave, whereas the rest of the molecule moves differently and there were no interdependence between the motion of the different "parts" of the molecule. A hydrogen atom with kinetic energy  $\frac{1}{2}kT$  (considering the motion in one direction, say  $x$  direction) has a velocity of 160,000 cm/sec. Therefore, our part  $m$  has a thermal root mean square velocity

$$\sim 160,000/m^{\frac{1}{2}} \quad (\text{A1})$$

("mean" over space and time).

If we approximate the motion of our part by a harmonic motion, the equivalent frequency with which this part moves may be about that of an acoustic vibration whose  $\lambda/2$  is about equal to the linear extension of the part *viz.*

$$\lambda/2 \sim (m/\dot{m}_0)^{\frac{1}{2}} 2 \cdot 10^{-8}.$$

Therefore, the equivalent frequency  $\nu$  becomes

$$\nu \sim 10^5/\lambda \sim 0.15 \cdot 10^{13} (m_0/m)^{\frac{1}{2}}.$$

And the vibrational amplitude = time maximum of velocity/ $2\pi\nu = 2^{\frac{1}{2}}$  root mean square velocity/ $2\pi\nu$

$$\sim 2^{\frac{1}{2}} 160,000 / 2\pi \cdot 0.25 \cdot 10^{13} m_0^{\frac{1}{2}} m^{\frac{1}{6}}. \quad (\text{A2})$$

<sup>14</sup> P. Jordan, Naturwiss. 29, 89 (1941).



*Second approach*

Instead of considering the part of the molecule which we are interested in as moving independently, we calculate its velocity and amplitudes by adding up, with random phases, velocities and amplitudes of the normal modes of vibrations of the whole molecule. We add up only those normal modes which actually contribute to the motion of our part  $m$  as a whole and we assume that to the motion of the part  $m$  as a subunit only those modes contribute whose  $\lambda/2$  are larger than the linear extension  $(m/m_0)^{1/3} \cdot 10^{-8}$  of the part  $m$ . The modes of shorter wave-length contribute to internal differential motions inside the part  $m$ . We are not interested in them. Let us calculate the r.m.s. velocity and amplitude of vibration in one mode. As the whole molecule participates in the mode, the thermal r.m.s. velocity

$$\sim 160,000/M^{1/2}.$$

And its vibrational amplitude

$$= 2^{1/2} \text{ r.m.s. velocity} / 2\pi\nu \sim 2^{1/2} 160,000 / 2\pi\nu M^{1/2}.$$

In the summation of the contributions of the various modes, the mode with lowest frequency is determined by

$$\begin{aligned} \lambda_l/2 &= (M/m_0)^{1/3} \cdot 10^{-8} \\ \nu_l &\sim 10^5/\lambda_l = 0.25 \cdot 10^{13} (m_0/M)^{1/3}, \end{aligned}$$

the highest frequency mode by

$$\begin{aligned} \lambda_h/2 &= (m/m_0)^{1/3} \cdot 10^{-8} \\ \nu_h &\sim 0.25 \cdot 10^{13} (m_0/m)^{1/3}. \end{aligned}$$

There are altogether  $3(4\pi/3 \cdot 8) \cdot (\nu_h/\nu_l)^3$  modes between  $\nu_l$  and  $\nu_h$ , the factor 3 stands for 2 transverse plus 1 longitudinal modes; only  $\frac{1}{3}$  of these modes have motion in the  $x$  direction, so we have to add  $(\pi/6)(\nu_h/\nu_l)^3$  modes' contributions with random phases. To calculate the thermal r.m.s. velocity of the part  $m$ , each contribution has the same amount,  $160,000/M^{1/2}$ . Therefore the sum with random phases is thermal r.m.s. velocity of  $m$

$$\begin{aligned} &\sim (160,000/M^{1/2}) \left( \sum_{\nu_l}^{\nu_h} 1^2 \right)^{1/2} \\ &= (160,000/M^{1/2}) [(\pi/6)(\nu_h/\nu_l)^3]^{1/2} \\ &= (160,000/M^{1/2}) (\pi/6)^{1/2} (M/m)^{1/6} \\ &= (\pi/6)^{1/2} 160,000/m^{1/6}. \quad (\text{A3}) \end{aligned}$$

For such an approximate calculation this is a good agreement with the previous calculation (A1). In a similar way we calculate, by the method of the second approach, the resulting amplitude. The contributions of the various modes,  $2^{1/2} 160,000 / 2\pi\nu M^{1/2}$  are different for the different modes. The summation with random phases is given, as above, by the evaluation of

$$(2^{1/2} \cdot 160,000 / 2\pi M^{1/2}) \left( \sum_{\nu_l}^{\nu_h} (1/\nu^2) \right)^{1/2}.$$

In the interval  $\nu$  to  $\nu + \nu_l$  there are about  $(4\pi/8)(\nu/\nu_l)^2$  modes contributing to motion in the  $x$  direction. Therefore

$$\begin{aligned} \sum_{\nu_l}^{\nu_h} \left( \frac{1}{\nu} \right)^2 &= \int \frac{1}{\nu^2} \frac{4\pi}{8} \frac{\nu^2}{\nu_l^2} \frac{d\nu}{\nu_l} \\ &= \frac{\pi}{2} \frac{\nu}{\nu_l^3} \Big|_{\nu_l}^{\nu_h} = \frac{\pi}{2\nu_l^2} \left( \frac{\nu_h}{\nu_l} - 1 \right) \sim \frac{\pi\nu_h}{2\nu_l^3}. \end{aligned}$$

Thus we get for the vibrational amplitude

$$\begin{aligned} &\sim (2^{1/2} \cdot 160,000 / 2\pi M^{1/2}) (\pi\nu_h / 2\nu_l^3)^{1/2} \\ &= (\pi/2)^{1/2} 2^{1/2} 160,000 / 2\pi \cdot 0.25 \cdot 10^{13} m_0^{1/3} m^{1/6} \quad (\text{A4}) \end{aligned}$$

(cf. (A2)). Particularly interesting in this result is the small dependence of the vibrational amplitude upon the mass  $m$  of the part of the molecule.

Accordingly the thermal velocities of vibration and amplitudes of vibration assume the following orders of magnitude ( $m$  is the mass of the part of the molecule whose vibration as a subunit we consider)

$m$ in atomic mass units	10	100	1000	10000
thermal velocity in cm/sec	$3 \cdot 10^4$	$10^4$	$3 \cdot 10^3$	$10^3$
amplitude in cm	$4 \cdot 10^{-9}$	$3 \cdot 10^{-9}$	$2 \cdot 10^{-9}$	$1.4 \cdot 10^{-9}$

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