THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 110, NO. 4 MAY 15, 1958

Specificity of Charge Fluctuation Forces. I

HERBERT JEHLE, JERROLD M. YOS,*† AND WILLIAM L. BADE†‡
Physics Department, University of Nebraska, Lincoln, Nebraska

(Received June 24, 1957)

The formation of van der Waals crystals, the formation of polymers, the properties of solubility, and several biological phenomena have raised the question what detailed role the van der Waals forces play in these cases. Given a mixture of several types of molecules or macromolecules contained in a liquid medium, the question at issue is whether van der Waals forces, more precisely and generally, forces due to the interaction of fluctuating charge distributions in one molecule with those in an adjacent molecule, will cause preferential association of identical molecules or macromolecules from among that mixture. The fluctuating charge distributions in question may be due to quantum-mechanical fluctuations of charge distribution of electronic oscillators, as considered by London, Eisenschitz, and Wang, and they may also be due to fluctuations of distributions of mobile protons as investigated by Kirkwood and Shumaker.

INTRODUCTION

OUT of the variety of intermolecular interactions the present paper will be concerned mainly with the interactions between molecules due to the circumstance that the molecules' representative oscillators always imply charge fluctuations. London, Eisenschitz, and Wang[1] first recognized this phenomenon; they had in mind the quantum-mechanical zero point fluctuations of electronic oscillators. Extending the types of charge fluctuations under consideration, Kirkwood and Shumaker[2] studied the corresponding effect due to fluctuations of mobile proton distributions over the surface of molecules when they are immersed in an aqueous medium. [As these fluctuations are comparatively slow, they contribute to what will be called the classical part $s_l=0$, $\mathcal{W}_0=-2R^{-3}\alpha_0$, Eq. (23), of the interaction.]

The property of these forces (which makes for association of identical molecules rather than nonidentical molecules) has first been given attention by the Dutch School, notably by H. C. Hamaker twenty years ago; and it has been subjected to a theoretical analysis in the present papers.

The implication of the property of association of identical molecules is basic for the problem of crystallization and polymerization. It is also basic for the problem of solubility, in particular for an understanding of the fact that structural similarity between solvent and solute molecules makes for good solubility (with the exception of solutes whose molecules have interactions among each other of a kind which they cannot have with a solvent molecule). And it is basic for the problem of specificity.

The notion of specificity designates a property of intermolecular interactions frequently encountered in biochemistry. It implies that a particular type of macromolecules can have a highly selective discriminatory interaction with just one other type of macromolecule which quite frequently is identical or nearly identical with the first one.

At this point we would like to give an idea about previous approaches[3] to the problem of specificity, different from our approach. Pauling[4] has looked into the prob-

---

* National Science Foundation predoctoral fellow 1954–1956.

† Present address: Research and Advanced Development Division, Avco Manufacturing Corporation, Lawrence, Massachusetts.

‡ National Science Foundation postdoctoral fellow 1956–1957.

[1] F. London, Discussions Faraday Soc. (1936), pp. 8–26; Z. physik. Chem. **B11**, 222 (1930); J. Phys. Chem. **46**, 305 (1942). R. Eisenschitz and F. London, Z. Physik **60**, 491 (1930); **63**, 245 (1930). S. C. Wang, Physik. Z. **28**, 663 (1927).

[2] J. G. Kirkwood and J. B. Shumaker, Proc. Natl. Acad. Sci. U. S. **38**, 855 and 863 (1952); Timasheff, Dintzis, Kirkwood, and Coleman, Proc. Natl. Acad. Sci. U. S. **41**, 710 (1955); J. Am. Chem. Soc. **79**, 782 (1957).

[3] An earlier attempt of explanation of specificity by P. Jordan [Physik. Z. **39**, 711 (1938); Z. Physik **113**, 431 (1939); Naturwissenschaften **29**, 89 (1941)] has been discussed by Linus Pauling and M. Delbrueck, Science **92**, 78 (1940).

[4] Linus Pauling, J. Am. Chem. Soc. **62**, 2643 (1940); Nature **161**, 707 (1948). F. Haurowitz, *Chemistry and Biology of Proteins* (Academic Press, Inc., New York, 1950), pp. 280 ff. and 326 ff.; F.

lem of biological specificity from the point of view of complementarity, following the lock-and-key concept of biological specificity. In particular, Pauling has shown that structures whose surfaces are closely complementary, i.e., which fit like a cast to its mold, prefer association simply because of the absence of empty interstices. This simply means that the general London-van der Waals attraction (between any kinds of atoms) prefer structures which have as few interstices as possible. Taking the complementarity principle in a somewhat different formulation, Crick and Watson,[5] to whom we owe the knowledge of the structure of the genetically all-important desoxyribose nucleic acid (DNA), have attempted to sketch a scheme of replica formation of DNA which implies that it is ripped into halves during each replication process.

Muller,[6] on the other hand, made another approach to the understanding of biological specificity by pointing to the instances in which association of similar or identical macromolecules is in evidence, and he pointed to a possibility of understanding the replication of genetic material, based on this principle of association of like molecules. This approach would permit the parent genes to stay intact, and not to be ripped apart during replication, and it would make their stability and the accuracy of their replication understandable. Under this view one may assume that molecules out of which genetic material can be assembled are available among other molecules in the surrounding medium.

The specificity of the van der Waals force, if strong enough, may cause the retention of medium molecules which happen to be identical with the constituent molecules of the parent genetic material, respectively, when these daughter molecules happen to come near their corresponding parent molecules. This will considerably facilitate the assembly of a replica.

The important physical phenomena which are at play in the processes to which attention has been drawn here, are the following: Brownian motion, which shuffles all molecules around so that like molecules in a mixture get introduced to each other; van der Waals attraction, which will be shown to have the property of being specific; and static electric repulsion between identical pairs—which can be regulated by changes of concentration of small ions in the medium[7]; these *gegen*-ions compensate the static electric charges without having much effect on fluctuating charges.

Only the London-van der Waals and Kirkwood attractions will be investigated here; the interacting molecules are assumed to be as somewhat globular, compact, and of a well-defined structure. The fluctuating charge distributions, electronic or protonic, are represented by oscillators l which, in the electronic case, show a well-defined distribution of their (static) polarizabilities α_l over the frequencies $\tilde{\omega}_l$ and over the oscillator orientations; the unit vector $\mathbf{u}_l$ indicates the orientation of the lth oscillator which is assumed to be one-dimensional.

MOLECULE PAIRS AND MOLECULE CONFIGURATIONS

The energy levels E_n of a pair of molecules depend on the separation R of their centers; the molecule pair occupies these levels according to a Boltzmann distribution. The interaction is characterized by the partition function Z or the Helmholtz free energy for a system of localizable particles, $A=-kT\ln Z$, and the attractive force is

$$F=\sum\nolimits_n(\partial E_n/\partial R)\exp(-E_n/kT)/Z=(\partial A/\partial R)_T. \quad (1)$$

For simplicity all that is needed is $\Delta A=-kT(\ln Z_R-\ln Z_\infty)$, denoted by $\Delta A_{\mathrm{I\ II}}$ when a molecule pair I-II is considered.

For molecules immersed in a medium, "buoyancy" effects (not against gravity) have to be included. This could be illustrated with the following scheme. Consider two identical macromolecules imbedded in an otherwise homogeneous isotropic medium of smaller molecules, and compare these two configurations

$$\begin{array}{ccccccccccc}
\mathrm{II} & \mathrm{II} & \mathrm{II} & \mathrm{II} & \mathrm{II} & & \mathrm{II} & \mathrm{II} & \mathrm{II} & \mathrm{II} & \mathrm{II} \\
\mathrm{II} & \mathrm{I} & \mathrm{I} & \mathrm{II} & \mathrm{II} & \text{and} & \mathrm{II} & \mathrm{I} & \mathrm{II} & \mathrm{I} & \mathrm{II} \\
\mathrm{II} & \mathrm{II} & \mathrm{II} & \mathrm{II} & \mathrm{II} & & \mathrm{II} & \mathrm{II} & \mathrm{II} & \mathrm{II} & \mathrm{II}.
\end{array}$$

Buoyancy is taken care of by grouping part of the medium molecules into aggregates II, each occupying the same volume as does a macromolecule I. In general

---

Breinl and F. Haurowitz, Z. physiol. Chem. **192**, 45 (1930); Stuart Mudd, J. Immunol. **23**, 423 (1932); D. H. Campbell, *Principles of Immunology* (McGraw-Hill Book Company, Inc., New York, 1957).

[5] F. H. C. Crick and J. D. Watson, Proc. Roy. Soc. (London) **A223**, 80 (1954).

[6] H. J. Muller, Am. Naturalist **56**, 32 (1922); Sci. Monthly **44**, 210 (1937); Cold Spring Harbor Symposia Quant. Biol. **9**, 290 (1941); Proc. Roy. Soc. (London) **B134**, 1 (1947); *Genetics in the 20th Century*, edited by L. C. Dunn (The Macmillan Company, New York, 1951), pp. 77 ff.

[7] P. Debye and E. Hückel, Physik. Z. **24**, 185 (1923); L. Onsager, Chem. Revs. **13**, 73 (1933); H. Kallmann and M. Willstaetter, Naturwissenschaften **20**, 952 (1932); J. Rubin Vinograd, in *Thixotropy*, edited by H. Freundlich (Hermann et Cie., Paris, 1935), Act. Sci. 267; J. H. De Boer, Trans. Faraday Soc. **32**, 21 (1936). H. C. Hamaker, Rec. trav. chim. **56**, 3 (1937); Chem. Weekblad **35**, 47 (1938). See also E. J. W. Verwey and J. Th. G. Oberbeek, *Theory of Lyophobic Colloids* (Elsevier Publishing Company, Inc., New York, 1948), pp. 161 and 162; or J. Th. G. Overbeek, in *Colloid Science*, edited by H. R. Kruyt (Elsevier Publishing Company, New York, 1952), Vol. I, pp. 276 and 277; E. J. W. Verwey and J. Th. G. Overbeek, Trans. Faraday Soc. **42B**, 117 (1946). J. Th. G. Overbeek, in *Colloid Science*, edited by H. R. Kruyt (Elsevier Publishing Company, New York, 1952), Vol. I, pp. 58, 115 ff., Vol. II, p. 184; in E. Verwey and J. Oberbeek, *Theory of Lyophobic Colloids* (Elsevier Publishing Company, New York, 1948); in Discussions Faraday Soc., Coagulation and Flocculation **18**, 9, 12, 52 (1954). S. Levine, Trans. Faraday Soc. **42B**, 102 (1946); **44**, 833 (1948). B. Derjaguin, Acta Physicochim. U.R.S.S. **10**, 333 (1939); **12**, 181 (1940); **12**, 314 (1940); Trans. Faraday Soc. **36**, 203 (1940); Discussions Faraday Soc., Coagulation and Flocculation **18**, 24, 85 (1954). B. Derjaguin and L. D. Landau, Acta Physicochim. U.R.S.S. **14**, 663 (1941); H. S. Harned and B. B. Owen, *Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1950); I. M. Klotz, in *The Proteins*, edited by H. Neurath and K. Bailey (Academic Press, Inc., New York, 1953), pp. 727 ff.; I. Progogine and A. Bellemans, in Discussions Faraday Soc., Nonelectrolytes **15**, 80 (1953).

this rearrangement corresponds to a free energy change

$$\Delta_4 A_{\mathrm{I\,II}} \equiv \Delta A_{\mathrm{I\,I}} + \Delta A_{\mathrm{II\,II}} - 2\Delta A_{\mathrm{I\,II}}. \tag{2}$$

For completeness one may assume the following, and thereby cover the case of several different types of macromolecules.[8] Assume (a) equality of the volume of these different, somewhat globular, molecules, and consider solely the nearest neighbor interactions, all at the same separation R (for two identical macromolecules I immersed in a homogeneous isotropic medium, as discussed above, this assumption is evidently satisfied automatically); (b) isotropy and additivity of the interactions; (c) entropy of mixing to be neglected; (d) numbers of nearest neighbors, statistically speaking, to be the same for every kind of macromolecule. Let n_{ij} be the number of molecules j which are nearest neighbors to molecules i. So $N_i = \sum_j n_{ij} =$ total number of all nearest neighbors to molecules of type i; because of (d), $0 = \delta N_i = \sum_j \delta n_{ij}$, for all i. The rearrangement free energy is

$$\begin{aligned}
&\tfrac{1}{2}\textstyle\sum_i \sum_j \delta n_{ij} \Delta A_{ij} \\
&\quad = \tfrac{1}{2}\textstyle\sum_i \sum_j \delta n_{ij} \Delta A_{ij} - \tfrac{1}{2}\sum_i \Delta A_{ii} \sum_j \delta n_{ij} \\
&\quad = \tfrac{1}{2}\textstyle\sum_i \sum_j \delta n_{ij} (\Delta A_{ij} - \Delta A_{ii}) \\
&\qquad\qquad\qquad \equiv \tfrac{1}{2}\textstyle\sum_j \sum_i \delta n_{ji} (\Delta A_{ji} - \Delta A_{jj}).
\end{aligned}$$

Because of $\delta n_{ij} = \delta n_{ji}$ and $\Delta A_{ij} = \Delta A_{ji}$, this becomes

$$-\tfrac{1}{4}\textstyle\sum_i \sum_j \delta n_{ij} (\Delta A_{ii} + \Delta A_{jj} - 2\Delta A_{ij}). \tag{3}$$

CLASSICAL AND QUANTUM OSCILLATORS

The London force may be pictured in terms of molecules each having a single isotropic oscillator of frequency $\tilde{\omega}$ (in contrast to ω which will later be used to indicate a normal mode frequency of a molecule *pair*).

The classical limit case of low frequencies implies an interaction of a pair of oscillators, $\Delta A_{\mathrm{I\,II}} = -3R^{-6} kT \alpha_{\mathrm{I}} \alpha_{\mathrm{II}}$. Thus

$$\Delta_4 A_{\mathrm{I\,II}} = -3R^{-6} kT (\alpha_{\mathrm{I}} - \alpha_{\mathrm{II}})^2 \leq 0. \tag{4}$$

This rearrangement free energy $\Delta_4 A_{\mathrm{I\,II}}$ depends on only one parameter, the polarizability difference.

An inequality in two variables α and $\tilde{\omega}$ has been discovered by de Boer[9] and Hamaker.[10] In the case of two isotropic oscillators whose $\tilde{\omega} \gg kT/\hbar$, the interaction free energy is

$$\Delta A_{\mathrm{I\,II}} = -\tfrac{3}{2} R^{-6} \alpha_{\mathrm{I}} \alpha_{\mathrm{II}} \hbar \tilde{\omega}_{\mathrm{I}} \tilde{\omega}_{\mathrm{II}} / (\tilde{\omega}_{\mathrm{I}} + \tilde{\omega}_{\mathrm{II}})$$

(London[1]; $\alpha =$ static oscillator polarizabilities). Therefore

$$\Delta_4 A_{\mathrm{I\,II}} = -\tfrac{3}{4} R^{-6} \hbar \frac{(\alpha_{\mathrm{I}} \tilde{\omega}_{\mathrm{I}} - \alpha_{\mathrm{II}} \tilde{\omega}_{\mathrm{II}})^2 + \tilde{\omega}_{\mathrm{I}} \tilde{\omega}_{\mathrm{II}} (\alpha_{\mathrm{I}} - \alpha_{\mathrm{II}})^2}{\tilde{\omega}_{\mathrm{I}} + \tilde{\omega}_{\mathrm{II}}} \leq 0. \tag{5}$$

The expression ($\hbar$ times an average of the frequencies) in the quantum-limit London formula essentially replaces kT in the classical formula.

To proceed to a more general case, let each molecule be represented by a set of oscillators: essentially no change occurs in the classical limit formulas, and one obtains an inequality involving again only one independent expression, the difference of the total polarizability of molecule I and that of molecule II, squared. A similar statement holds for the quantum limit formulas if all the oscillators have the same frequencies [(20) makes this evident]. On the other hand (5) and its generalization for many oscillators gets special importance if the oscillators cover a wide range of frequencies and have different polarizabilities and orientations.

In the quantum limit case the many-oscillator generalization (14) of the inequalities (5) contains a set of negative definite terms, i.e., a set of inequalities. One should point to the far-reaching implications which these inequalities have, and one should show how many effectively independent inequalities there are in a given situation, and one should demonstrate that specificity may be understood on this basis—after a definition of degree of specificity has been introduced.

Specific interaction refers to a type of high discrimination between different molecule-partners even though there is only a moderate spread in interaction free energies at stake. In the present theory this phenomenon is simply a consequence of the considerable number of effectively independent parameters upon which $\Delta_4 A_{\mathrm{I\,II}}$ depends.

The oscillator scheme is very convenient but not necessary; part II of these communications readily permits inclusion of anharmonicities, permanent electrical moments, and quadrupole interactions by treating the general quantum mechanical problem.

In order to cover the actual case, which certainly involves classical limit as well as quantum limit situations and much in between, and in order to define a measure of that discriminatory rearrangement, i.e., of the degree of specificity, it is necessary to calculate the partition function Z for molecule pairs. These calculations were done before the authors knew of the work of the Dutch school.

OSCILLATOR PAIR INTERACTIONS IN THE GENERAL CASE

The molecules I and II may have N_{I} and N_{II} oscillators, respectively. The normal mode frequencies $\omega_l/2\pi$ of the pair I–II depend on the intermolecular distance R. The partition function and Helmholtz free

---

[8] J. M. Yos, Ph.D. thesis, University of Nebraska, 1956 (unpublished).

[9] J. H. de Boer, Trans. Faraday Soc. 32, 118 (1936).

[10] H. C. Hamaker, Physica 4, 1058 (1937). We are deeply indebted to H. T. Epstein for having drawn our attention to these papers, and to T. Y. Wu for a comment on this inequality.

energy of the pair are

$$Z=\prod_{l=1}^{N_{\mathrm{I}}+N_{\mathrm{II}}}[2\sinh(\hbar\omega_l/2kT)]^{-1}, \tag{6}$$

$$\begin{aligned}A&=-kT\ln Z\\&=kT\sum_l[\tfrac{1}{2}\ln V_l'+\sum_{s=1}^{\infty}\ln(1+V_l'/s^2\pi^2)+\ln 2],\end{aligned} \tag{7}$$

where $V_l'=\hbar^2\omega_l^2/4k^2T^2$ are the eigenvalues of a potential energy matrix V whose diagonalized form will be denoted by V'. Equation (7) permits expansion in powers of the intermolecular interaction, an expansion which is convergent for all positive V_l'. The matrix V can be written in the form

$$\begin{aligned}V=\begin{pmatrix}\mathcal{V}_{\mathrm{I}} & 0\\ 0 & \mathcal{V}_{\mathrm{II}}\end{pmatrix}+\begin{pmatrix}0 & \mathcal{U}\\ \mathcal{U}^T & 0\end{pmatrix}&=V_\infty+U\\&=V_\infty(I+V_\infty^{-1}U),\end{aligned} \tag{8}$$

where T means transposition. V_∞ and U usually do not commute. The summation over l in (7) can be written as the trace of the function $kT[\;]$ of the diagonal matrix V'. This trace is invariant under the transformation which beings V into diagonal form. Thus

$$\begin{aligned}A=kT\,\mathrm{tr}\{&\tfrac{1}{2}\ln[V_\infty(I+V_\infty^{-1}U)]\\&+\sum_{s=1}^{\infty}\ln\{(I+V_\infty/s^2\pi^2)\\&\qquad\times[I+(I+V_\infty/s^2\pi^2)^{-1}U/s^2\pi^2]\}+I\ln 2\}.\end{aligned} \tag{9}$$

From the Baker-Haussdorff theorem, or by direct calculation ($\mathrm{tr}\ln X=\ln\det X$), two noncommuting matrices X, Y are seen to satisfy $\mathrm{tr}\ln(XY)=\mathrm{tr}\ln X+\mathrm{tr}\ln Y$. Therefore, with the abbreviation

$$(s^2\pi^2I+V_\infty)^{-1}U\equiv U_s, \tag{10}$$

one gets

$$\begin{aligned}\Delta A=A-A_\infty&=\tfrac{1}{2}kT\,\mathrm{tr}\sum_{s=-\infty}^{+\infty}\ln(I+U_s)\\&=\tfrac{1}{2}kT\,\mathrm{tr}\sum_{s=-\infty}^{+\infty}\{-\tfrac{1}{2}U_s^2-\cdots\}.\end{aligned} \tag{11}$$

The oscillators are distributed all over the volume occupied by each molecule. If they are shifted into the centers of the molecules, quadrupole, etc., terms arise. The assumption of an interaction matrix (8) is equivalent to neglecting quadrupole and higher multipole terms in the expansion in terms of R. The results of this paper are simple because they are based on dipole interactions; "large" separations R would, in view of this, be a desirable assumption. Besides, for "large R" one has the added advantage of being entitled to break off the expansion (11) with the term U_s^2, which means neglect of R^{-12} terms. The assumption of "large R" is evidently a compromise for the sake of achievement of easily interpretable simple results; the actually interesting situation is one of close approach where sizable interactions occur.

REARRANGEMENT INEQUALITIES

At this point a new assumption must be introduced, *viz.*, that the intermolecular interaction $\mathcal{U}$ in Eq. (8) can be written as a product of two matrices, one depending on molecule I only, the other on II: $\mathcal{U}=\mathcal{U}_{\mathrm{I}}\mathcal{U}_{\mathrm{II}}^T$. Dipole interactions evidently satisfy this assumption; $\mathcal{U}_{\mathrm{I}}$ is an N_{I} by three matrix (17). Introducing the abbreviated notations for the three by three matrices

$$\mathcal{W}_{s\mathrm{I}}\equiv\mathcal{U}_{\mathrm{I}}^T(s^2\pi^2I+\mathcal{V}_{\mathrm{I}})^{-1}\mathcal{U}_{\mathrm{I}}, \tag{12}$$

one can write

$$\mathrm{tr}U_s^2=\mathrm{tr}\begin{pmatrix}(s^2\pi^2I+\mathcal{V}_{\mathrm{I}})^{-1}\mathcal{U}(s^2\pi^2I+\mathcal{V}_{\mathrm{II}})^{-1}\mathcal{U}^T & 0\\ 0 & (s^2\pi^2I+\mathcal{V}_{\mathrm{II}})^{-1}\mathcal{U}^T(s^2\pi^2I+\mathcal{V}_{\mathrm{I}})^{-1}\mathcal{U}\end{pmatrix}=2\,\mathrm{tr}(\mathcal{W}_{s\mathrm{I}}\mathcal{W}_{s\mathrm{II}}). \tag{13}$$

Here s is an integer, positive, negative, or zero. Dropping higher powers of U_s^2, the rearrangement free energy (2) becomes (as the $\mathcal{W}_{sI\mu\nu}$ are symmetric).

$$-\Delta_4A_{\mathrm{I\,II}}=\tfrac{1}{2}kT\sum_{s=-\infty}^{+\infty}\sum_{\mu,\nu=1}^{3}[(\mathcal{W}_{s\mathrm{I}}-\mathcal{W}_{s\mathrm{II}})_{\mu\nu}]^2. \tag{14}$$

This trace is positive definite if $(\mathcal{W}_{s\mathrm{I}}-\mathcal{W}_{s\mathrm{II}})$ has real eigenvalues for every s and any pair I–II, that is, if $\mathcal{W}_{s\mathrm{I}}$ and $\mathcal{W}_{s\mathrm{II}}$ are Hermitean matrices. That provides a sufficient condition for the specificity theorem:

$$\Delta_4A_{\mathrm{I\,II}}\leq 0, \tag{15}$$

to hold in the limit of large R.

As $(s^2\pi^2I+\mathcal{V}_{\mathrm{I}})$ is a symmetric matrix, $\mathcal{W}_{s\mathrm{I}}$ and $\mathcal{W}_{s\mathrm{II}}$ are, by (12), symmetric matrices. The Hermiticity condition for $\mathcal{W}_{s\mathrm{I}}$, $\mathcal{W}_{s\mathrm{II}}$ therefore implies that all elements of $\mathcal{W}_{s\mathrm{I}}$ and $\mathcal{W}_{s\mathrm{II}}$ are real. Since $(s^2\pi^2I+\mathcal{V}_{\mathrm{I}})^{-1}$ has only real matrix elements, and as $\mathcal{U}=\mathcal{U}_{\mathrm{I}}\mathcal{U}_{\mathrm{II}}^T$ is real, $\mathcal{W}_{s\mathrm{I}}$ and $\mathcal{W}_{s\mathrm{II}}$ will be real if the elements of $\mathcal{U}_{\mathrm{I}}$ and $\mathcal{U}_{\mathrm{II}}$ are either all purely imaginary or all real. There are therefore two different sufficient conditions for the inequality (15).

Let molecules I and II be referred to the same axes (x,y,z), where the z axis connects the centers of the molecules. (8) becomes in detail

$$\begin{aligned}\mathcal{U}_{kj}=(\hbar^2/4k^2T^2)\epsilon_km_k^{-\frac{1}{2}}\epsilon_jm_j^{-\frac{1}{2}}R^{-3}&\\\times[u_{kx}u_{jx}+u_{ky}u_{jy}-2u_{kz}u_{jz}].&\end{aligned} \tag{16}$$

The ϵ_j's are charges, the m_j's are masses, and the $\mathbf{u}_j$'s are orientation vectors of the oscillators. The oscillator orientations can be referred to axes fixed in the molecule, e.g., the axes of the permanent moments.

Refer the two molecules to right-handed coordinate systems $(x_{\mathrm{I}},y_{\mathrm{I}},z_{\mathrm{I}})$ and $(x_{\mathrm{II}},y_{\mathrm{II}},z_{\mathrm{II}})$, respectively, whose

z axes are parallel and x and y antiparallel, then the interaction matrix $\mathcal{U}_{\mathrm{I}}\mathcal{U}_{\mathrm{II}}{}^T$ has the value (16) if

$$\mathcal{U}_{\mathrm{I}}=(\hbar/2kT)R^{-\frac{3}{2}}\begin{bmatrix} \cdot\,, & \cdot\,, & \cdot \\ i\epsilon_l m_l{}^{-\frac{1}{2}}u_{lx}, & i\epsilon_l m_l{}^{-\frac{1}{2}}u_{ly}, & i\sqrt{2}\epsilon_l m_l{}^{-\frac{1}{2}}u_{lz} \\ \cdot\,, & \cdot\,, & \cdot \\ \cdot\,, & \cdot\,, & \cdot \end{bmatrix}. \tag{17}$$

$\mathcal{U}_{\mathrm{II}}$ is made up in a corresponding fashion. With this convention, $\mathcal{U}_{\mathrm{I}}\mathcal{U}_{\mathrm{I}}{}^T$ represents the interaction matrix of a molecule I located at the origin I with a molecule II at origin II whose dipole distribution referred to $(x_{\mathrm{II}},y_{\mathrm{II}},z_{\mathrm{II}})$ is exactly the same as the dipole distribution of I with respect to $(x_{\mathrm{I}},y_{\mathrm{I}},z_{\mathrm{I}})$. II is rotated 180° around the z axis with respect to I, otherwise identical; this is the energetically most advantageous orientation. With that definition of pairs of identical molecules I–I and II–II, the matrices $\mathcal{W}_{s\mathrm{I}}$ and $\mathcal{W}_{s\mathrm{II}}$ are Hermitian, a statement which implies (15).

Suppose the two molecules are referred to two mirror image coordinate systems whose z axes are antiparallel, and x and y axes parallel. The interaction matrix $\mathcal{U}_{\mathrm{I}}\mathcal{U}_{\mathrm{II}}{}^T=\mathcal{U}$ is of the form (16) if $\mathcal{U}_{\mathrm{I}}$ is given by $-i$ times (17), and similarly for $\mathcal{U}_{\mathrm{II}}$. In that case, $\mathcal{U}_{\mathrm{I}}\mathcal{U}_{\mathrm{I}}{}^T$ denotes the interaction of one molecule with another which is the mirror image of the first one with respect to a plane parallel to the xy plane; this is the orientation of lowest free energy for these molecules. The inequality (15) holds again. In this mirror case, the interaction may no longer be specific, however, if the representative oscillators are anharmonic, or for other reasons have permanent dipole moments.

The static polarizatilities and the dynamic polarizability tensor are defined by

$$\alpha_l=\epsilon_l{}^2/m_l\tilde{\omega}_l{}^2,\quad \boldsymbol{\alpha}(\omega)=\textstyle\sum_l \alpha_l\mathbf{u}_l\mathbf{u}_l/[1-(\omega/\tilde{\omega}_l)^2]. \tag{18}$$

$\mathbf{u}_l\mathbf{u}_l$ is the dyadic product of orientation vectors. The $\tilde{\omega}_l$ are normal-mode frequencies of the isolated molecules; that is, the eigenvalues of $\mathcal{V}_{\mathrm{I}}$ are $\hbar^2\tilde{\omega}_l{}^2/4k^2T^2$. Equations (12), (17), and (18) give

$$(\mathcal{W}_{s\mathrm{I}})_{zz}=-R^{-3}\{\sum_{l=1}^{N_{\mathrm{I}}}\alpha_l/[1+(2\pi kT/\hbar\tilde{\omega}_l)^2s^2]\}2u_{lz}{}^2. \tag{19}$$

$\mathcal{W}_{s\mathrm{I}}$ is essentially the dynamic polarizability analytically continued into the purely imaginary argument $\omega=is2\pi kT/\hbar$. Experimental data about dispersion and absorption gives α_l, $\tilde{\omega}_l$, and $\mathbf{u}_l$ because the partial fraction expansion (18) is unique. $\mathcal{W}_{s\mathrm{I}}$ then follows from these quantities. The Appendix shows how the classical- and the quantum-limit London formulas are derived from (11), (13), and (19).

(15) actually represents six inequalities for every $|s|$, one for each component μ, ν of the symmetric sum $-\Delta_4A_{\mathrm{I\ II}}$ in (14). Equation (14) means that $\Delta_4A_{\mathrm{I\ II}}=0$ if and only if the molecules I, II have the same set of $(\mathcal{W}_s)_{\mu\nu}$ values; i.e., according to (19), if they have the same dynamic polarizability ellipsoid as function of frequency. This defines "identical" molecules in regard to charge fluctuation forces.

For the attainment of specificity, strong oscillator polarizabilities distributed over a wide frequency region, including the quantum region, are necessary. The question might be brought up why one could not deal with the present problem by the use of the ground state alone rather than dealing with the entire partition function. The answer is that only the present complete calculation will properly delimit the importance of low-frequency oscillators, and of only a small range of distribution of frequencies of the oscillators, for attainment of specificity.

The use of the full partition function turns out to be mathematically more elegant and convenient than ground-state calculations; it shows the rearrangement free energy to be of the form of the square of a Euclidean distance (14) in a $\mathcal{W}_s$ space [the s originally provided for the series expansion (7)]. The rearrangement free energy (14) is a sum over s, and not a sum over the normal modes l. This is evident from

$$-\Delta_4A_{\mathrm{I\ II}}=\tfrac{1}{2}kT\sum_s 4R^{-6}\Bigg[\sum_{l=1}^{N_{\mathrm{I}}}\frac{\alpha_l}{1+(2\pi kT/\hbar\tilde{\omega}_l)^2s^2} - \sum_{l=N_{\mathrm{I}}+1}^{N_{\mathrm{I}}+N_{\mathrm{II}}}\frac{\alpha_l}{1+(2\pi kT/\hbar\tilde{\omega}_l)^2s^2}\Bigg]^2, \tag{20}$$

the result for one-dimensional oscillators oriented in the z direction.

SPECIFICITY[10a]

Specificity refers to the sharp discrimination which a certain type of macromolecule (I) exerts in its preferential association with a particular macromolecule, e.g., its like. The point is that this discrimination rejects an enormous number of different types of macromolecules II even though the energies $\Delta_4A_{\mathrm{I\ II}}$ are quite moderate. When one talks about specificity, one is thinking of a property of a manifold of macromolecule types II, in particular about the following question: for how many types II out of this manifold is the quantity

$$-\Delta_4A_{\mathrm{I\ II}}=\tfrac{1}{2}kT\textstyle\sum_s(\mathcal{W}_{s\mathrm{II}}-\mathcal{W}_{s\mathrm{I}})^2 \tag{21}$$

(forgetting about the anisotropy subscripts μ, ν) greater than the thermal energy kT? Choosing as molecule I an average molecule out of the manifold, the question is: what is the measure of the subset of molecule types for which the signal,

$$-\Delta_4A=\tfrac{1}{2}kT\textstyle\sum_s(\mathcal{W}_s-\langle\mathcal{W}_s\rangle_{\mathrm{Av}})^2>kT, \tag{22}$$

[10a] Henry Quastler, *Information Theory in Biology* (University of Illinois Press, Urbana, 1953), p. 41.

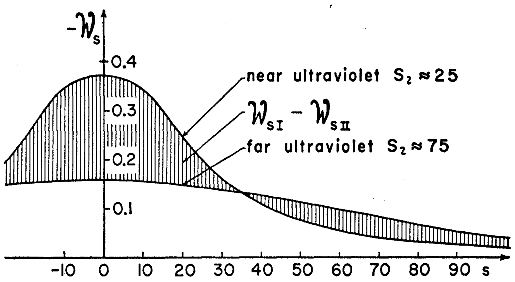

FIG. 1. Representation of the rearrangement free energy [Eqs. (2) and (14), (21)] showing the discrimination between two hypothetical molecule types I and II, one of which has its principal polarizabilities in the far ultraviolet, the other in the near ultraviolet.

i.e., is greater than the noise? That measure, if it is close to unity (unity is chosen as the measure of the total set of molecule types), indicates specific discrimination.

The quantity $-\Delta_4 A$ is made up of positive definite terms. They are not independent for all s. If one considers $\mathcal{W}_s$ as function of s for two simplified *very* different kinds of molecules, one of which has strong polarizabilities only in a narrow region in the far ultraviolet ($s_l \approx 75$), the other only in the near ultraviolet ($s_l \approx 25$), their $\mathcal{W}_s$,

$$-\mathcal{W}_s = 2R^{-3} \sum_l \alpha_l / (1 + s^2/s_l^2), \tag{23}$$

(where $|s_l| = \hbar\bar{\omega}_l / 2\pi kT$) would have distributions like the two which are represented in Fig. 1. If the molecules of the manifold were characterizable by two parameters, their polarizability in the far ultraviolet and their polarizability in the near ultraviolet, they could be represented by the two-parametric manifold of dots on the left-hand side of Fig. 2. $-\Delta_4 A$ [Eq. (22)] is given by the square of the Euclidean distance of the representative dot from the origin of the coordinates. The circle quadrant indicates the noise limit.

If, on the contrary, another manifold had its polarizabilities only in a fixed narrow frequency region, a one-parametric manifold would ensue (right side of Fig. 2). In the case that, for comparison's sake, the two kinds of manifolds had the same values $\langle -\Delta_4 A \rangle_{\mathrm{Av}}$ [Eq. (22)], one would immediately realize that for the two-dimensional manifold the measure of the discriminated subset is much closer to unity than for the one-dimensional manifold.

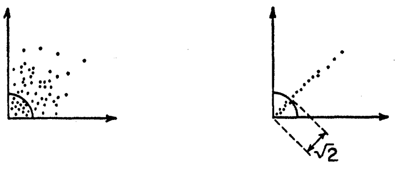

FIG. 2. Comparison of a two-parametric manifold of molecule types with an effectively one-parametric manifold.

$$\text{Abscissas} = \{(\mathcal{W}_0 - \langle \mathcal{W}_0 \rangle_{\mathrm{Av}})^2 + 2(\mathcal{W}_1 - \langle \mathcal{W}_1 \rangle_{\mathrm{Av}})^2 + \cdots + 2(\mathcal{W}_{35} - \langle \mathcal{W}_{35} \rangle_{\mathrm{Av}})^2\}^{\frac{1}{2}};$$

$$\text{ordinates} = \{2(\mathcal{W}_{36} - \langle \mathcal{W}_{36} \rangle_{\mathrm{Av}})^2 + 2(\mathcal{W}_{37} - \langle \mathcal{W}_{37} \rangle_{\mathrm{Av}})^2 + \cdots\}^{\frac{1}{2}}.$$

Qualifying details may be omitted here, but it may be appropriate to remark that anisotropy terms increase the number of effective parameters, and that the Kirkwood-Shumaker fluctuations bring about an important contribution towards the term $\mathcal{W}_0$ (from low-frequency oscillators $s_l \approx 0$), thus adding another important parameter on which the $\mathcal{W}_s$ distribution depends.

The order of magnitude of the interaction energies should be estimated.[10b] If one uses atomic polarizabilities (ground state contributions only) and adds their effect according to Eq. (19), one arrives at a low estimate. That estimate is roughly obtained if one takes 50% of the electrons in the valence shells and assigns to each of those electrons static polarizabilities α_l according to (18) where ϵ_l = charge of the electron and $\hbar\bar{\omega}_l$ = ionization energy. [Or one takes all electrons in the valence shells and includes an oscillator strength $f = 0.5$ into the formula (18) for the polarizability α_l of such an electron.] The dependence of the strength of interaction upon the average electronic oscillator frequencies $\bar{\omega}$ can already be inferred from the London formula (28): as $\sum \alpha = \sum f\epsilon^2 / m\bar{\omega}^2$, one gets $\Delta A \propto (\sum \alpha)^2 \bar{\omega} \propto (\sum f)^2 / \bar{\omega}^3$ where $\sum f$ is limited by the number of electrons in the valence shells per molecule (Thomas-Reiche-Kuhn). Actually the polarizabilities for macromolecules are higher than the low estimates obtained with atomic far ultraviolet $\bar{\omega}$ values: they are specially strong if high electron mobilities arise. The presence of thermally excited states often involves strong electron mobility. The low-limit estimates give about the following contributions for pair interactions $\Delta A_{\mathrm{I\,II}}$: if the pair of interacting molecules is at their closest approach, the electronic contribution of mostly far ultraviolet polarizabilities (London-Eisenschitz-Wang) amounts to a $\Delta A_{\mathrm{I\,II}}$ at least of the order of kT and the mobile proton contribution (Kirkwood-Shumaker) amounts also at least to something of the order of kT. Both these estimates refer to the case of fairly small groups like aminoacid side chains. For pairs of larger spherical molecules, again at closest approach, their total polarizabilities squared might cautiously be taken as proportional to the square of the molecular volume. R^{-6} just compensates that, so one may again get kT or a few kT for the interaction.

The order of magnitude of the interaction is strong enough to bring about a high degree of specificity, in particular in a situation like the following:

Consider protein α helixes (Pauling, Corey, and Branson[11]), with a variety of L-aminoacid side chains. Two identical ones of those helixes may lie in parallel, side by side, so that corresponding side chains of the

---

[10b] H. A. Kramers and R. de L. Kronig, Z. Physik **48**, 174 (1928); E. M. Lifshitz, Zhur. Eksptl. i Teoret. Fiz. **29**, 94 (1955); Doklady Akad. Nauk S.S.S.R. **97**, 643 (1954); **100**, 879 (1955); Derjaguin, Abrikosova, and Lifshitz, Quart. Revs. (London) **10**, 259 (1956).

[11] Pauling, Corey, and Branson, Proc. Natl. Acad. Sci. U. S. **37**, 205 (1951).

two helixes interlock in such a fashion that corresponding, pairwise identical side chains come to lie next to each other. One gets a particularly strong specificity due to the interaction of pairs of side chains which, by the way, have the energetically favorable orientation with respect to each other. The rearrangement free energy $\Delta_4 A$ is made up from a sum of expressions (14), due to the side group pair interactions; all interaction terms have the same signature and thus one has to do with a many-parametric specificity.

Imagine, on the other hand, a right-handed protein helix being confronted with a left-handed protein helix, both built from the same sequence of amino acids,[12] all amino acids being of the laevo type. The helixes can roll over each other, exert specific interaction, and provide for an extremely rapid recognition. The motion is a rotational Brownian motion, hindered by some occasional big side chains. It is to be anticipated that such a mechanism might also be an ideal tool for the synthesis of protein helixes along the lines indicated in the introduction.

An α helix can, in a very oversimplified manner, illustrate the replica formation. Suppose the surrounding medium supplies all kinds of activated amino acids, and Brownian motion shuffles them around. They will preferentially be retained next to the corresponding amino acids of the parent helix, in a mantle region surrounding that helix. The formation of the replica helix may occur after a change of *p*H, permitting the amino acids from the mantle region to be unrolled with simultaneous peptide bond formation between them. Another possible mechanism would be a similar assembly process of activated amino acids around a nucleoprotein helix, or of nucleotides around a nucleic acid helix. Or else, extended chains might be all that is involved.[13]

The charge fluctuation effects which have been discussed in this paper differ from static electrostatic interactions of polarized side chains insofar as the static charge distributions are readily compensated by small *gegen*-ions from the medium. That compensation depends very much upon the ionic concentration of the medium. Decreases of that ionic concentration permit the repulsive forces between identical pairs of groups or molecules to become predominant over the attraction due to charge fluctuation forces. Because of their rapidity, the charge fluctuation forces are not much influenced by *gegen*-ions from the medium.

One may return briefly to the question of the relationship of the approach to specificity outlined in this paper to the approach on the basis of complementarity. In the present approach a particular model of interlocking pairwise identical side chains has been envisaged. There are plenty of empty spaces between these interlocking molecules which are randomly filled with smaller molecules from the medium. The space-filling principle is thus satisfied in a statistical fashion, but the cumulation of positive definite terms in $-\Delta_4 A$ is responsible for the specific association of identical macromolecules. In the complementarity approach the space filling is somehow attempted to be made complete.

APPENDIX: LONDON FORMULAS

The pair interaction formulas are special cases of the present matrix calculation results (11), (13), i.e.,

$$\Delta A_{\mathrm{I\ II}} = -\tfrac{1}{2}kT \sum_{s=-\infty}^{+\infty} \mathrm{tr}(\mathcal{W}_{s\mathrm{I}}\mathcal{W}_{s\mathrm{II}}), \tag{24}$$

and of (19), i.e.,

$$(\mathcal{W}_{0\mathrm{I}})_{zz} = -2R^{-3}\sum_{l=1}^{N_{\mathrm{I}}} u_{lz}{}^2\alpha_l = -2R^{-3}\sum_{l=1}^{N_{\mathrm{I}}} u_{lz}{}^2\epsilon_l{}^2/\kappa_l, \tag{25}$$

$$(\mathcal{W}_{s\mathrm{I}})_{zz} = -2R^{-3}\sum_{l=1}^{N_{\mathrm{I}}} (\hbar\tilde{\omega}_l/2kT)^2 u_{lz}{}^2\alpha_l/[s^2\pi^2 + (\hbar\tilde{\omega}_l/2kT)^2]. \tag{26}$$

$\kappa_l = \tilde{\omega}_l{}^2 m_l$ indicates the force constants; the polarizabilities (18) are $\alpha_l = \epsilon_l{}^2/\kappa_l$. That means that $2\,\mathrm{tr}(\mathcal{W}_{0\mathrm{I}}\mathcal{W}_{0\mathrm{II}})$ is independent of $\hbar$ and the masses for given force constants. The part $s=0$ of the series (11), i.e., for $N_{\mathrm{I}} = N_{\mathrm{II}} = 1$,

$$\Delta A_{\mathrm{I\ II}} = -\tfrac{1}{2}kT\,\mathrm{tr}(\mathcal{W}_{0\mathrm{I}}\mathcal{W}_{0\mathrm{II}}) = -2kTR^{-6}\alpha_{\mathrm{I}}\alpha_{\mathrm{II}} \tag{27}$$

gives the classical part of the interaction free energy and is the one-dimensional equivalent of the formula given before (4). The corresponding quantum limit case is obtained by replacing the sum over s by an integral. s_{I} and s_{II} are defined below (23).

$$\begin{aligned}\Delta A_{\mathrm{I\ II}} &= -\tfrac{1}{2}kT\,\mathrm{tr}(\mathcal{W}_{0\mathrm{I}}\mathcal{W}_{0\mathrm{II}}) \\ &\quad\times\int_{-\infty}^{+\infty}[1+(s/s_{\mathrm{I}})^2]^{-1}[1+(s/s_{\mathrm{II}})^2]^{-1}ds \\ &= -\tfrac{1}{2}kT(\mathcal{W}_{0\mathrm{I}})_{zz}(\mathcal{W}_{0\mathrm{II}})_{zz}\pi s_{\mathrm{I}}s_{\mathrm{II}}/(s_{\mathrm{I}}+s_{\mathrm{II}}) \\ &= -R^{-6}\alpha_{\mathrm{I}}\alpha_{\mathrm{II}}\hbar\tilde{\omega}_{\mathrm{I}}\tilde{\omega}_{\mathrm{II}}/(\tilde{\omega}_{\mathrm{I}}+\tilde{\omega}_{\mathrm{II}}),\end{aligned} \tag{28}$$

i.e., the one-dimensional London formula.

ACKNOWLEDGMENTS

We should like to thank the Research Corporation, the National Science Foundation (grant G627), the National Cancer Institute (grant C3304BBC), and the

---

[12] L. Pauling and R. B. Corey, Istituto Lombardo di Scienze e Lettre **89**, 20 (1955).

[13] H. Jehle, Proc. Natl. Acad. Sci. U. S. 44 (1958).

University of Nebraska Research Council for their generous support of this investigation. We have received a great deal of valuable criticism and important help from many colleagues and friends to whom we wish to give thanks, in particular Dr. N. H. Cromwell, Dr. H. T. Epstein, Dr. Th. Jorgensen, Dr. W. G. Leavitt, Dr. A. S. Skapski, and most of all Dr. S. T. Epstein, Dr. H. J. Muller, and Dr. Linus Pauling. They have given us encouragement, inspiration, and friendship through the years.

PHYSICAL REVIEW VOLUME 110, NUMBER 4 MAY 15, 1958

Specificity of Charge Fluctuation Forces. II

Jerrold M. Yos*
Physics Department, University of Nebraska, Lincoln, Nebraska

(Received June 24, 1957)

With intermolecular interactions due to fluctuating charge distributions (van der Waals-London-Kirkwood), a system of molecules has some interesting properties as regards its rearrangement free energies. They have been investigated in the preceding paper. It was found desirable to look into the corresponding results on the basis of a general quantum mechanical model for the molecules.

NEED FOR A MORE GENERAL QUANTUM MECHANICAL CALCULATION

THE foregoing calculations[1] have all been based on the representation of a molecule by an oscillator model. In the following, a general quantum mechanical model is used to consider the problem anew.

The harmonic dipole oscillator model had the advantage of ease of calculation and it was readily possible to evaluate the effects in terms of polarizabilities, orientations, and frequencies of the oscillators. The general quantum mechanical calculations are needed because the foregoing oscillator calculations are based on some rather drastic assumptions. The following reasons show the desirability of these general calculations.

(1) The assumed level scheme and the transition matrix elements for a set of *harmonic* oscillators are quite different from those of an actual molecule. In the quantum limit of high oscillator frequencies, this difference may not be of much importance. In the general case when many levels are in thermal reach (this general case is the object of the present investigation) and when we have to deal with a complicated set of strong and weak transition matrix elements, it is wise, however, to find out what the calculation based on an arbitrary level—and transition—scheme has to tell.

(2) The foregoing oscillator calculations started with the consideration of the intermolecular interaction between a pair of molecules and assumed that this interaction can be expressed as part of a potential energy matrix of a pair of *dipole* oscillator sets. The calculations took advantage of the simplicity of matrix calculations based on that potential energy matrix which implies the interaction to be bilinear in the oscillator amplitudes of the two molecules. An actual molecule, even if representable by a set of oscillators, has these oscillators distributed all over the molecule. Such a distribution is equivalent to a set of oscillators, located at the center of the molecule, but there appear quadrupole, octupole, etc. terms because of the displacements of the dipole oscillators. (Evidently, a general time-dependent charge distribution in a molecule can always be expanded into charge, and dipole moments, quadrupole moments, etc.).[2] Intermolecular interaction which takes these quadrupole terms, etc., into account, can no longer be handled by the simple matrix methods which had been used so far.

(3) The question also might arise whether higher order perturbation theory may be needed, in cases where the linear polarizability theory is inadequate.

HAMILTONIAN FOR A MOLECULE PAIR

The Hamiltonian for a pair of interacting molecules is of the form

$$H=\mathcal{H}_{\mathrm{I}}(q_{\mathrm{I}})+\mathcal{H}_{\mathrm{II}}(q_{\mathrm{II}})+\mathcal{U}_{\mathrm{I\,II}}(q_{\mathrm{I}},q_{\mathrm{II}}), \qquad (1)$$

where $\mathcal{H}(q)$ is a shorthand notation for a Hamiltonian $\mathcal{H}(q,i\hbar^{-1}\partial q)$ and $\mathcal{H}_{\mathrm{I}}(q_{\mathrm{I}})$, $\mathcal{H}_{\mathrm{II}}(q_{\mathrm{II}})$ are the Hamiltonians of the two isolated molecules. The symbols q_{I} and q_{II} represent the whole set of independent variables for the molecules I and II, respectively. H, $\mathcal{H}_{\mathrm{I}}(q_{\mathrm{I}})$, and $\mathcal{H}_{\mathrm{II}}(q_{\mathrm{II}})$ have the usual properties of Hamiltonians; namely, they are Hermitean and have complete sets of eigenfunctions over their respective function spaces. Since the theory will be applied to cases in which the operators $\mathcal{H}_{\mathrm{I}}(q_{\mathrm{I}})$, $\mathcal{H}_{\mathrm{II}}(q_{\mathrm{II}})$, and $\mathcal{U}_{\mathrm{I\,II}}(q_{\mathrm{I}},q_{\mathrm{II}})$ are "real" (i.e., produce real functions whenever they operate on real functions) and in which $\mathcal{U}_{\mathrm{I\,II}}(q_{\mathrm{I}},q_{\mathrm{II}})$ is a "pure"

---

* National Science Foundation predoctoral fellow 1954–1956. Present address: Research and Advanced Development Division, Avco Manufacturing Corporation, Lawrence, Massachusetts.

[1] Jehle, Yos, and Bade, Phys. Rev. **110**, 793 (1958), preceding paper.

[2] For an elegant method, see J. Frenkel, *Elektrodynamik* (Verlag Julius Springer, Berlin, 1926), Vol. 1, pp. 98 ff, or Z. Physik **21**, 1 (1924).