

Generalized Susceptibility Theory I. Theories of Hypochromism*

WILLIAM RHODES,† MALCOLM CHASE

Department of Chemistry

and

Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida

A general theory is developed for the linear response of an interacting molecular system to an external field. The exact ground state of the system is expressed in terms of the uncoupled molecule (zeroth-order) state by means of adiabatic time-dependent perturbation theory. Including the external field to first order in the time-development operator leads to an infinite-order expansion of the linear response function for physical quantities such as current-charge density and electric-dipole polarization. Two basic approximations involving partial decorrelation of charge motion and spatial separability of the molecules allow the response function to be determined by a simplified Dyson-type equation, which can be put into closed form by further approximations. The approximate linear response function (susceptibility) so obtained is given in terms of the isolated molecule susceptibility and corresponds exactly to the results of classical, local field theory. Emphasis throughout is placed on the effect of molecular interaction on absorption spectra. Comparisons among theories of hypochromism show clearly that all previously reported theories are mutually compatible and are either equivalent to, or are contained in, the theory developed here. The relation of the present theory to a coupled equivalent oscillator model is discussed and the results are applied to a simple physical model.

I. INTRODUCTION

The effects of electronic coupling between molecules in geometrically ordered molecular systems on the various electronic spectral properties of the system as a whole is a subject of very wide interest. It is well known that in molecular systems, such as some dimers, polymers, and organic crystals, in which the monomers maintain their identity (i.e., effects of overlap of wave functions can be ignored) the absorption spectrum resembles that of the monomer with certain bands undergoing a splitting (or shift) and/or a change in intensity depending on the geometry of the system and the polarizations and intensities of the monomeric bands. The splitting of absorption bands is believed to be well understood in terms of molecular exciton theory. On the other hand, there has been considerable diversity of opinion in the literature regarding the theoretical interpretation of the changes in over-all absorption band intensity due to molecular interaction. This effect is of interest to many people in recent years because of the hypochromism of biological-type helical polymers, such as polypeptides and polynucleotides, which show a pronounced decrease in electronic absorption band ($\pi \rightarrow \pi^*$) intensities upon random coil to helix transformation.

This report develops and discusses a general theory of the effect of electronic coupling between molecules on the response of the system as a whole to an external electromagnetic field. The approach used here emphasizes the role of linear response functions for various physical quantities and their Fourier transforms, the

corresponding susceptibilities, in determining the spectral properties of the system. The method of using linear response functions is not original with us but has been developed extensively by Kubo.¹

The linear response of the system to an external field concerns processes involving one photon. This includes most processes of interest, such as ordinary light absorption and emission, light scattering, and rotatory dispersion, but not such phenomena as Raman scattering, biphotonic transitions, and other multiphoton processes. More specifically, we are interested here mainly in the effect of molecular interactions on absorption band shapes and intensities.

In addition to presenting a somewhat broader, more general theory than has been given in the past, we hope to be able to demonstrate convincingly the mutual compatibility of the various theories of hypochromism presented so far in the literature and to show that they are contained explicitly in the theory developed here. Each of these theories may be placed in one of three categories:

(1) *First-order perturbation theory* was first used by Tinoco,² later by Rhodes,³ and applied to helical polymers. The oscillator strength was determined to first order from the first-order wave functions of the helix using the unperturbed monomer states as a basis. Although exciton theory was used in the formalism, it is clear that there is no exciton effect on oscillator strength and that intensity changes result solely from borrowing among monomer bands.

(2) *Local field theories* are based on the idea that the electric field at the site of one monomer has a component due to the induced electric-dipole moments in neighboring monomers, the induced moment in any

* This work was supported (in part) by Public Health Service Research Grant GM-09202, by Public Health Service Research Career Program Award GM-8430, and by a contract between the Division of Biology and Medicine, U.S. Atomic Energy Commission, and the Florida State University.

† The work reported here was begun while the author (W. R.) was a National Science Foundation Senior Postdoctoral Fellow, visiting the Max Planck Institute for Physics and Astrophysics, Munich, Germany.

¹ R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954); R. Kubo, *ibid.* **12**, 570 (1957).

² I. Tinoco, Jr., *J. Am. Chem. Soc.* **82**, 4785 (1960).

³ W. Rhodes, *J. Am. Chem. Soc.* **83**, 3609 (1961).

monomer arising in turn from the combined external field and induced neighboring moments. This theory was first proposed by Bolton and Weiss⁴ who predicted a large hypochromic effect due to the induced field arising from the electric-dipole transition moments for a single transition in the monomer, i.e., for a two-state problem. While such an approach is valid in principle, the interpretations of Bolton and Weiss are grossly erroneous and incorrectly imply that hypochromism is primarily an exciton effect, originating from the self-interaction of a monomer band and leading to a violation of the Kuhn-Thomas sum rule.

Nesbet⁵ further developed the Bolton-Weiss theory for a molecular dimer in terms of the local scalar potential arising from charge-density response in the neighboring monomer in the presence of an external field. Nesbet also used an approximation whereby only one electronic transition was considered and obtained results corroborating those of Bolton and Weiss. In the meantime, DeVoe^{6,7} has pointed out clearly that these theories deal with point hypochromism at the frequency of maximum absorption in the monomer and if the shift in the absorption band is accordingly taken into account, there is indeed no over-all band hypochromism due to excitation resonance (exciton) interaction. DeVoe has put the local field approach in better perspective, using purely classical methods.

Nesbet's final results predict only a decrease in absorption intensity in the dimer, presumably, at all frequencies. However this conclusion is based on an approximation for the polarizability which makes it purely imaginary. Such an approximation is valid only at the frequency of maximum absorption and for a nonphysical model having a single narrow absorption band. Thiéry⁸ has modified Nesbet's results to include a more realistic complex polarizability, thereby leading to a theory which agrees in principle with DeVoe's.⁷

(3) *Second quantization methods* have been applied by Hoffmann,⁹ by which an approximate Hamiltonian for the system is expressed in terms of operators for the creation and destruction of excitations in the molecules. With use of a further approximation in the commutation relations for the excitation operators, the Hamiltonian can be diagonalized (for a finite number of excitations) by a Bogoliubov transformation, thus leading to an independent quasi-particle description of the excitation of the system. Hoffmann has solved the problem for a model which contains the ground state and two excited electronic states of the monomer. The calculated absorption intensity agrees closely with the first-order perturbation theory results for a double-stranded helix model.

We begin the development with a consideration

of the linear response function for a coupled molecular system. In the first part, coupling is taken through the field, so we examine the response of the components of the current-charge-density four-vector. Two approximations are made which put the theory in a form equivalent with that of Nesbet as modified by Thiéry. We next examine the direct coupling model in the dipole-dipole approximation. The exactly soluble coupled harmonic oscillator model is put into the framework of the present theory and its equivalence to the approximate molecular Hamiltonian in terms of excitation operators is discussed. It is shown that Hoffmann's results are contained implicitly in the present theory.

The theory presented here using linear response functions and their corresponding susceptibilities represents but one part of a general effort in the current literature to apply field theoretical techniques to problems of molecular electronic interactions. This trend has perhaps been stimulated by the appearance of books like those of Abrikosov, Gorkov, and Dzyaloshinski and Nozières,¹⁰ and the works cited therein. McLachlan¹¹ has applied susceptibility theory extensively to the problem of dispersion forces. Closely related work has been published recently by Herzenberg and Modinos,¹² who make use of the causal two-particle Green's function (density fluctuation propagator) in contrast to the linear response function used here, which is a retarded Green's function.

II. THE LINEAR RESPONSE FUNCTION

A. General Considerations

In the Schrödinger representation the exact state of the system Φ_s at time t is determined from the Schrödinger equation of motion, by the system Hamiltonian and the state at time t_0 . However, in dealing with problems in which the physical situation calls for the Hamiltonian to be split into two parts

$$H = H_1 + V_2,$$

where H_1 is time-independent and the interaction part V_2 may be time-dependent, it is convenient to use the interaction representation.¹³ The equation of motion for the state of the system is then

$$i(\partial\Phi_i/\partial t) = V_2^i(t)\Phi_i, \quad (1)$$

¹⁰ A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963); P. Nozières, *The Theory of Interacting Fermi Systems* (W. A. Benjamin, Inc., New York, 1964).

¹¹ A. D. McLachlan, Proc. Roy. Soc. (London) **A271**, 387 (1963).

¹² A. Herzenberg and A. Modinos, Proc. Phys. Soc. (London) **87**, 597 (1966).

¹³ S. S. Schweber, *Introduction to Relativistic Quantum Field Theory* (Harper and Row, Publishers, Inc., New York, 1961), Chap. 11.

⁴ H. C. Bolton and J. J. Weiss, *Nature* **195**, 666 (1962).

⁵ R. K. Nesbet, *Mol. Phys.* **7**, 211 (1964).

⁶ H. DeVoe, *Nature* **197**, 1295 (1963).

⁷ H. DeVoe, *J. Chem. Phys.* **41**, 393 (1964).

⁸ J. Thiéry, *J. Chem. Phys.* **43**, 553 (1965).

⁹ R. Hoffmann, *Radiation Res.* **20**, 140 (1963).

where

$$\Phi_i(t) = \exp [iH_1 t] \Phi_s(t)$$

and

$$V_2^i(t) = \exp [iH_1 t] V_2(t) \exp [-iH_1 t].$$

We use units in which $\hbar=c=1$. The solutions of (1) are given formally in terms of the unitary time-development operator, which may be expressed symbolically in the contracted form

$$U(t, t_0) = T \exp \left[-i \int_{t_0}^t V_2^i(t') dt' \right],$$

representing the infinite order expansion of the exponential. The chronological ordering operator T orders the operators in the expansion with increasing time to the left.

In this section we examine the response of the components of the current-charge density four-vector j_μ to an externally applied field. Throughout we deal with a molecular system, at zero absolute temperature, in which the individual molecular units are sufficiently separated so that overlap effects can be neglected. The case of nonzero temperature and the effects of overlap of molecular wave functions will be treated later.

The total system Hamiltonian can be expressed as the sum of H_1 , the Hamiltonian of the charge system and external field not interacting with each other, and the coupling between them

$$V_2^i(t) = - \int j_\nu(\mathbf{r}, t) A_0^\nu(\mathbf{r}, t) d^3\mathbf{r}.$$

The summation convention for repeated indices and a Lorentz gauge for the field is implied throughout. Repeated latin indices indicate summation only over spatial components. The four-vector scalar product is written in covariant-contravariant form with a metric tensor $g_{\mu\nu}$ such that $g_{\mu\nu}=0$ if $\mu \neq \nu$ and $g_{11}=g_{22}=g_{33}=-g_{00}=+1$. Therefore the scalar potential $\varphi=-A^0$. The response is always taken at $t=0$ with the external field turned on at some finite $t<0$, and the charge system is assumed to be in its ground state before the interaction is turned on. Thus,

$$\begin{aligned} \langle j_\mu \rangle &= \langle \Phi(0) | j_\mu(\mathbf{r}, 0) | \Phi(0) \rangle \\ &= \langle \Phi_i(t_0) | U^+(0, t_0) j_\mu(\mathbf{r}, 0) U(0, t_0) | \Phi_i(t_0) \rangle. \end{aligned} \quad (2)$$

If t_0 is taken to be prior to the interaction, $\Phi_i(t_0)$ represents the ground state of the charge system in the Heisenberg representation. We denote it by $\Phi(H_1)$. Expanding U and collecting terms to first order in A_0^ν , we get the linear response in j_μ

$$\begin{aligned} \Delta \langle j_\mu \rangle &= +i \int_{t_0}^0 dt' \int d^3\mathbf{r}' \\ &\times \langle \Phi(H_1) | [j_\mu(\mathbf{r}, 0), j_\nu(\mathbf{r}', t')] A_0^\nu(\mathbf{r}', t') | \Phi(H_1) \rangle, \end{aligned} \quad (3)$$

showing that the response to first order depends simply on unequal time commutators of the j 's with $j_\nu(t) = \exp[iH_1 t] j_\nu \exp[-iH_1 t]$. Since $\Phi(H_1)$ is an eigenfunction of H_1 , the expectation value of the commutator depends only on the time difference of the elements. We can therefore define the linear response function¹

$$\begin{aligned} K_{\mu\nu}(\mathbf{r}, \mathbf{r}', t-t') &= i\theta(t-t') \\ &\times \langle \Phi(H_1) | [j_\mu(\mathbf{r}, t), j_\nu(\mathbf{r}', t')] | \Phi(H_1) \rangle \end{aligned} \quad (4)$$

such that

$$\Delta \langle j_\mu \rangle = \int_{-\infty}^{\infty} K_{\mu\nu}(\mathbf{r}, \mathbf{r}', 0-t') A_0^\nu(\mathbf{r}', t') d^4x'.$$

Integration is carried out over all space-time. The time limits can be extended to infinity since $\theta(-t')=0$ for $t'>0$ and 1 for $t'<0$ and $A_0^\nu=0$ for $t'<t_0$.

The linear response function K is itself the response of j_μ at \mathbf{r} and $t=0$ to a δ -function field at the point (\mathbf{r}', t') . Causality is guaranteed by θ . The Fourier transform of K , given by

$$K_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) = \int_{-\infty}^{\infty} K_{\mu\nu}(\mathbf{r}, \mathbf{r}', t) \exp(i\omega t) dt,$$

is the corresponding generalized susceptibility and again the θ function (causality) demands that all poles lie in the lower half of the complex ω plane.¹⁴ It has the property that, when the external field consists of a single-frequency component, the linear response is

$$\Delta \langle j_\mu \rangle = \text{Re} \int d^3\mathbf{r}' K_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) A_0^\nu(\mathbf{r}', \omega) \exp[-i\omega t].$$

The mean rate of energy absorption by the charge system is

$$\bar{W} = - \left[\int A_0^\mu(\mathbf{r}, t) \Delta \langle j_\mu(\mathbf{r}, t) \rangle d^3\mathbf{r} \right]_{t \text{ average}},$$

which to first order for a single-frequency field, is easily shown to be

$$\begin{aligned} \bar{W}(\omega) &= (\omega/2) \int d^3\mathbf{r} \\ &\times \int d^3\mathbf{r}' A_0^{\mu*}(\mathbf{r}, \omega) K_{\mu\nu}''(\mathbf{r}, \mathbf{r}', \omega) A_0^\nu(\mathbf{r}', \omega), \end{aligned} \quad (5)$$

where K'' is the imaginary part of K and where the components A_0^μ are those of the external field and not the local field. Local field contributions are contained in K and are discussed in the next section.

B. The Decorrelation Approximation

The foregoing review of generally known results shows that the optical properties of a molecular system are determined, to first order, by the susceptibility

¹⁴ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publ. Co., Reading, Mass., 1958), Sec. 122.

function $K(\omega)$, of which the real part determines such properties as refractive index dispersion and the imaginary part the absorption spectrum of the system. For single-photon processes the theory can be regarded as essentially exact. This includes most processes of interest to molecular spectroscopists, at least those detectable in the presence of relatively weak external fields.

The problem then is to determine $K(\omega)$. This depends on the exact ground state in the absence of the external field, so we must use an approximation method. In this section an expression for K is developed in terms of the linear response function for the isolated molecule. The approximations to be used lead to a closed form for K which agrees with that obtained by a purely classical approach⁷ and which can be evaluated in terms of the corresponding isolated molecular quantities. The advantages of this approach lie in the simplicity and clarity of the formalism and in the fact that the points of introduction of, and the nature of, the approximations are clearly delineated.

The total Hamiltonian is expressed in the form

$$H = H_0 + V_1 + V_2, \quad (6)$$

where H_0 is the sum of all isolated molecule and external field Hamiltonians, V_2 is the coupling of the molecules with the external field (as above), and V_1 is the interaction among the molecules. Since the molecules are assumed to be spatially separated, the field components appearing in

$$V_1(t) = - \int j_\nu(\mathbf{r}, t) A^\nu(\mathbf{r}, t) d^3\mathbf{r}$$

are taken to be those arising from the charges in all molecules exclusive of the one containing the point \mathbf{r} . This assignment of electrons to molecules is the first, but probably not the most serious, approximation. It is necessary in order to transform the system K to the isolated molecule representation; i.e., to a basis con-

sisting of eigenfunctions of H_0 . To do this we allow V_1 to be turned on adiabatically with a factor $e^{\delta t}$, whereby the ground state of the system is evolved out of the ground state of the uncoupled molecule system from the infinite past.¹³

We use an interaction representation in terms of H_0 , in which all Schrödinger operators are transformed by the unitary operator $\exp[-iH_0t]$. Hereafter, we drop the index i . The state of the system at $t=0$ in the presence of the external field is given by

$$\Phi'(0) = U_1(0, -\infty)\Phi^0(H_0), \quad (7)$$

where the prime indicates the above "molecular cell" approximation for V_1 and

$$U_1(0, -\infty) = T \exp \left[-i \int_{-\infty}^0 (V_1(t) + V_2(t)) dt \right]. \quad (8)$$

Here $\Phi^0(H_0)$ is the ground state of the uncoupled system in the Heisenberg representation, since $\lim (V_1 + V_2) \rightarrow 0$ as $t \rightarrow -\infty$.

The expectation value of j_μ is

$$\begin{aligned} \langle j_\mu \rangle &= \langle \Phi^0(H_0) | U_1^+(0, -\infty) j_\mu(\mathbf{r}, 0) U_1(0, -\infty) | \Phi^0(H_0) \rangle. \end{aligned} \quad (9)$$

Since K is simply the value of $\Delta \langle j_\mu \rangle$ for a δ -function external field, we obtain K directly by making the substitution

$$\begin{aligned} V_2(t) &= - \int d^3\mathbf{r} j_\nu(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') \delta(t + \lambda) \\ &= -j_\nu(\mathbf{r}', t) \delta(t + \lambda) \end{aligned}$$

in (8), expanding U , and collecting terms to first order in V_2 . A technique like this has been used by McLachlan¹¹ to get the field response to third order. This gives a rather complicated expression which can be put into a simpler form of a commutator nest,¹¹ namely,

$$\begin{aligned} K_{\mu\nu}(\mathbf{r}, \mathbf{r}', \lambda) &= \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \theta(\lambda) T \int_{-\infty}^0 dt_1 \int_{-\infty}^0 dt_2 \cdots \int_{-\infty}^0 dt_n \\ &\quad \times \{ \langle [\cdots [j_\mu(\mathbf{r}, 0), V_2(t_1)], V_1(t_2)], \cdots], V_1(t_n)] \rangle \\ &\quad + \langle [\cdots [j_\mu(\mathbf{r}, 0), V_1(t_1)], V_2(t_2)], \cdots], V_1(t_n)] \rangle + \cdots \\ &\quad + \langle [\cdots [j_\mu(\mathbf{r}, 0), V_1(t_1)], V_1(t_2)], \cdots], V_2(t_n)] \rangle \} \quad (10) \end{aligned}$$

in which the single V_2 in each term appears progressively farther along the commutator chain. Henceforth the brackets indicate expectation values with respect to the zeroth-order state $\Phi^0(H_0)$.

We now treat the field as being quantized, meaning that $\Phi^0(H_0)$ is implied to contain the state of the non-interacting field (here the vacuum state) and the

A^ν are operators. Any term containing an odd number of A 's, therefore, vanishes because of the expectation value (the free field states are like harmonic oscillator states and the A 's are linear superpositions of photon creation and destruction operators). Only terms of odd n survive in expansion (10).

Equation (10) is still very cumbersome and almost

impossible to handle for problems in which it is desirable to include terms higher than third-order. In order to obtain a simpler form we use an approximation which partially decorrelates the motions of the electrons. This is accomplished by replacing each commutator of the j 's, as it appears in the expansion of the commutator

nest of each term, by its zeroth-order expectation value.

$$[j_\mu(t_1), j_\nu(t_2)] \rightarrow \langle [j_\mu(t_1), j_\nu(t_2)] \rangle.$$

To see the effect of this, we examine the integrand of the first of the third-order terms,

$$\langle \langle [[[j_\mu(\mathbf{r}, 0), j_\nu(\mathbf{r}', t_1) \delta(t_1 + \lambda)], j_\alpha(\mathbf{r}_2, t_2) A^\alpha(\mathbf{r}_2, t_2)], j_\beta(\mathbf{r}_3, t_3) A^\beta(\mathbf{r}_3, t_3)] \rangle \rangle.$$

Replacing the first commutator by its average value, a number, makes the whole term vanish. Any term vanishes identically unless the V_2 part appears at the end of the commutator nest. Thus, we have the approximate expression

$$\begin{aligned} \bar{K}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \lambda) = & \sum_{n=1}^{\infty} (i)^n \theta(\lambda) \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_n \\ & (\text{odd}) \\ & \times \int_{-\infty}^{\infty} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_{n-1} \langle [j_\mu(\mathbf{r}, 0), j_\alpha(\mathbf{r}_1, t_1)] \rangle \\ & \times [A^\alpha(\mathbf{r}_1, t_1), A^\beta(\mathbf{r}_2, t_2)] \langle [j_\beta(\mathbf{r}_2, t_2), j_\gamma(\mathbf{r}_3, t_3)] \rangle \cdots \\ & \times \langle [j_\rho(\mathbf{r}_{n-1}, t_{n-1}), j_\nu(\mathbf{r}', t_n)] \rangle \delta(t_n + \lambda). \end{aligned} \quad (11)$$

The unequal time commutators of the field components are c -number functions,¹⁵

$$i[A^\alpha(\mathbf{r}_1, t_1), A^\beta(\mathbf{r}_2, t_2)] = g^{\alpha\beta} R^{-1} \{ \delta(R-t) - \delta(R+t) \},$$

where $R = |\mathbf{r}_1 - \mathbf{r}_2|$ and $t = t_1 - t_2$, and can be replaced by their expectation values. The retarded Green's function, describing the free field linear response of A^α to an external current j_β , is consequently given by

$$\begin{aligned} D_0^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) &= i\theta(t_1 - t_2) \langle [A^\alpha(\mathbf{r}_1, t_1), A^\beta(\mathbf{r}_2, t_2)] \rangle \\ &= g^{\alpha\beta} R^{-1} \delta(R - t). \end{aligned} \quad (12)$$

Because of the time-ordered integrations in Eq. (11), each commutator may be multiplied by the corresponding θ function of the time difference and all integrations extended to $+\infty$. This leads to

$$\begin{aligned} \bar{K}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \lambda) = & \sum_{n=1}^{\infty} \int d^4x_1 \int d^4x_2 \cdots \int d^4x_n \\ & (\text{odd}) \\ & \times K_{\mu\alpha}^0(\mathbf{r}, \mathbf{r}_1, -t_1) D_0^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) K_{\beta\gamma}^0(\mathbf{r}_2, \mathbf{r}_3, t_2 - t_3) \cdots \\ & \times D_0^{\rho\sigma}(\mathbf{r}_{n-2}, \mathbf{r}_{n-1}, t_{n-2} - t_{n-1}) K_{\rho\nu}^0(\mathbf{r}_{n-1}, \mathbf{r}_n, t_{n-1} - t_n) \delta(\mathbf{r}_n - \mathbf{r}') \delta(t_n + \lambda). \end{aligned} \quad (13)$$

Summation over repeated indexes is implied. We thus find that, within the *decorrelation approximation*, the linear response function of the system as a whole appears as a space-time "convolution" of free-molecule and free-field response functions. This is equivalent to an iterative expansion of the integral equation

$$\bar{K}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \lambda) = K_{\mu\nu}^0(\mathbf{r}, \mathbf{r}', \lambda) + \int d^4x_1 \int d^4x_2 K_{\mu\alpha}^0(\mathbf{r}, \mathbf{r}_1, -t_1) D_0^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) \bar{K}_{\beta\nu}(\mathbf{r}_2, \mathbf{r}', t_2 + \lambda). \quad (14)$$

In expansion (13) λ can be shifted from the last to the first term by a sequential change of variables. The corresponding system susceptibility is the time Fourier transform of Eq. (14) and is given by a Dyson-type equation

$$\bar{K}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) = K_{\mu\nu}^0(\mathbf{r}, \mathbf{r}', \omega) + \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 K_{\mu\alpha}^0(\mathbf{r}, \mathbf{r}_1, \omega) D_0^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \omega) \bar{K}_{\beta\nu}(\mathbf{r}_2, \mathbf{r}', \omega). \quad (15)$$

Equations (14) and (15) are the principal results. The only approximations are (a) the "molecular cell" (molecule separability) approximation for V_1 in which it is assumed that each point in space belongs to a given molecule in order that j , and A^ν arise from different

molecules, and (b) the decorrelation approximation in which intermediate transitions between zeroth-order excited states of the system are neglected (Sec. IIIB).

¹⁵ P. A. M. Dirac, *Quantum Mechanics* (Clarendon Press, Oxford, England, 1958), Sec. 75.

Approximation (a) leads to a simple form for K^0 . It is zero unless \mathbf{r} and \mathbf{r}' are in the same molecule; hence, it is identically the isolated molecule susceptibility. On the other hand, the free-field susceptibility, given by the Fourier transform of Eq. (12), is

$$D_0^{\alpha\beta}(R, \omega) = g^{\alpha\beta} R^{-1} \exp [i\omega R] \quad (16)$$

and is understood to be zero unless \mathbf{r} and \mathbf{r}' (with $R = |\mathbf{r} - \mathbf{r}'|$) are in different molecules because of the elimination of self-interaction of the molecules by approximation (a).

Substituting in Eq. (15), we obtain a relatively simple integral equation,

$$\begin{aligned} \bar{K}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) &= K_{\mu\nu}^0(\mathbf{r}, \mathbf{r}', \omega) \\ &+ \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 K_{\mu\alpha}^0(\mathbf{r}, \mathbf{r}_1, \omega) (|\mathbf{r}_1 - \mathbf{r}_2|)^{-1} g^{\alpha\beta} \\ &\quad \times \exp [i\omega |\mathbf{r}_1 - \mathbf{r}_2|] \bar{K}_{\beta\nu}(\mathbf{r}_2, \mathbf{r}', \omega). \end{aligned} \quad (17)$$

which may be solved, in many cases, in terms of the geometry of the system and the optical properties of the isolated molecule.

Using the same approximations and procedure, we could have derived an expression for the susceptibility of the field in the presence of the molecular system in which the role of the field and charges are interchanged. Thus we have symbolically,

$$\bar{D} = D_0 + D_0 K^0 \bar{D}, \quad (18)$$

where the obvious indexes and integrations have been omitted. By comparison of Eqs. (15) and (18), $D_0 \bar{K} = \bar{D} K^0$ and, consequently,

$$\bar{K} = K^0 + K^0 \bar{D} K^0, \quad (19)$$

in which the interaction effects have been shifted to the field susceptibility.

C. Comparison with Previous Theory

The molecule separability approximation of the previous section implies that we are dealing with a local field theory. This is obvious from the fact that our theory is developed in the representation of the isolated molecule and the molecular interaction part of the Hamiltonian density at any point \mathbf{r} consists of the interaction of the current density of the molecule "containing" the point \mathbf{r} with the potential arising from the rest of the system. From this and the decorrelation approximation, the resulting system susceptibility, given by expressions (14)–(19), gives a simple picture of the interplay between the field and the charges in the linear response to an external field. The external field induces a local response in current fluctuation which then produces an induced field in the rest of the system. The induced field in turn produces a current response at each point and the cycle is repeated to infinite order. That part of the total induced current which is linear in the external field A_0^ν is thus given by

$$\Delta \langle j_\mu(\mathbf{r}) \rangle_\omega = \int d^3\mathbf{r}' \bar{K}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) A_0^\nu(\mathbf{r}', \omega). \quad (20)$$

The total induced field linear in A_0^ν is determined solely by the induced current and the free-field susceptibility, namely,

$$A_i^\rho(\mathbf{r}, \omega) = \int d^3\mathbf{r}' D_0^{\rho\sigma}(\mathbf{r}, \mathbf{r}', \omega) \Delta \langle j_\sigma(\mathbf{r}') \rangle_\omega. \quad (21)$$

Substitution of the integral from (15) into (20) gives

$$\begin{aligned} \Delta \langle j_\mu(\mathbf{r}) \rangle_\omega &= \int d^3\mathbf{r}' [K_{\mu\nu}^0(\mathbf{r}, \mathbf{r}', \omega) + \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 K_{\mu\alpha}^0(\mathbf{r}, \mathbf{r}_1, \omega) D_0^{\alpha\sigma}(\mathbf{r}_1, \mathbf{r}_2, \omega) \bar{K}_{\sigma\nu}(\mathbf{r}_2, \mathbf{r}', \omega)] A_0^\nu(\mathbf{r}', \omega) \\ &= \int d^3\mathbf{r}' K_{\mu\nu}^0(\mathbf{r}, \mathbf{r}', \omega) [A_0^\nu(\mathbf{r}', \omega) + A_i^\nu(\mathbf{r}', \omega)], \end{aligned} \quad (22)$$

showing how, within the framework of our approximations, the response depends on the net local field and the unperturbed molecule susceptibility. Expressions (20) and (22) may be regarded as alternative pictures in which the interaction effects appear, respectively, in the molecular susceptibility and the field.

In order to make comparisons with a previous theory,⁵ we first obtain an integral equation for the linear response of the induced field to the external field. Substitution of Eq. (22) into Eq. (21) gives

$$A_i^\rho(\mathbf{r}, \omega) = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 D_0^{\rho\sigma}(\mathbf{r}, \mathbf{r}_1, \omega) K_{\sigma\nu}^0(\mathbf{r}_1, \mathbf{r}_2, \omega) [A_0^\nu(\mathbf{r}_2, \omega) + A_i^\nu(\mathbf{r}_2, \omega)]. \quad (23)$$

The isolated molecule susceptibility can be put into the standard representation by inserting an intermediate resolution of the identity over eigenstates of the unperturbed molecule into the commutator in $K^0(t)$. This leads to the familiar form

$$K_{\sigma\nu}^0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_k \left[\frac{j_\nu(\mathbf{r}_2)_{0k} j_\sigma(\mathbf{r}_1)_{k0}}{\omega + \omega_{k0} + i\delta} - \frac{j_\sigma(\mathbf{r}_1)_{0k} j_\nu(\mathbf{r}_2)_{k0}}{\omega - \omega_{k0} + i\delta} \right], \quad (24)$$

where $\omega_{k0} = E_k - E_0$, the excitation energy of the isolated molecule. The limit $\delta \rightarrow +0$ is understood throughout.

Insertion of expressions (16) and (24) into Eq. (23) gives a detailed equation for the linear response of any component A_i^r to the total external field. At this point we follow Nesbet,⁵ however, and consider only the response of the scalar potential to an external vector potential, neglecting any induced vector potential effects. Thus we have

$$(\mathbf{r}\varphi_i, \omega) = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\exp [i\omega |\mathbf{r} - \mathbf{r}_1|]}{|\mathbf{r} - \mathbf{r}_1|} \sum_k \left[\frac{j_b(\mathbf{r}_2)_{0k} \rho(\mathbf{r}_1)_{k0}}{\omega + \omega_{k0} + i\delta} - \frac{\rho(\mathbf{r}_1)_{0k} j_b(\mathbf{r}_2)_{k0}}{\omega - \omega_{k0} + i\delta} \right] A_0^b(\mathbf{r}_2) - \left[\frac{\rho(\mathbf{r}_2)_{0k} \rho(\mathbf{r}_1)_{k0}}{\omega + \omega_{k0} + i\delta} - \frac{\rho(\mathbf{r}_1)_{0k} \rho(\mathbf{r}_2)_{k0}}{\omega - \omega_{k0} + i\delta} \right] \varphi_i(\mathbf{r}_2, \omega) \quad (25)$$

which is identical to Nesbet's Eq. (22) except for the form of the damping factors introduced arbitrarily by him. The latter appear to have the wrong sign and lead to a violation of causality. We see that Nesbet's theory is a local field theory with the molecule separability and the decorrelation approximations implied. The advantages of the present method are the simplicity by which one obtains equations such as (25) from the general, formal relations (14)–(19) and the fact that \bar{K} may be used directly to examine the spectral properties of the system.

In order to determine the absorption spectrum [Eq. (5)] of the coupled molecular system in terms of the spectral properties of the isolated molecule, we seek a closed form solution of Eq. (15). This would be accomplished if the individual terms in the iterative expansion of Eq. (15) could be arranged in such a way that we have a power series in some determinable quantity. The problem in doing this can perhaps best be understood by inspection of the first-order term of $\bar{K}_{\mu\nu}(\mathbf{r}, \mathbf{r}')$,

$$\sum_{k,l} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \left[\frac{j_\alpha(\mathbf{r}_1)_{0k} j_\mu(\mathbf{r})_{k0}}{\omega + \omega_{k0} + i\delta} - \frac{j_\mu(\mathbf{r})_{0k} j_\alpha(\mathbf{r}_1)_{k0}}{\omega - \omega_{k0} + i\delta} \right] g^{\alpha\alpha} \left[\frac{\exp(i\omega |\mathbf{r}_1 - \mathbf{r}_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \left[\frac{j_\nu(\mathbf{r}')_{0l} j_\alpha(\mathbf{r}_2)_{l0}}{\omega + \omega_{l0} + i\delta} - \frac{j_\alpha(\mathbf{r}_2)_{0l} j_\nu(\mathbf{r}')_{l0}}{\omega - \omega_{l0} + i\delta} \right].$$

This term is the amplitude for the propagation of an "impulse" from the point \mathbf{r}' to the point \mathbf{r} via all intermediate points \mathbf{r}_1 and \mathbf{r}_2 and all intermediate states k and l . It can be factored into a product, or a simple sum of products (finite matrix form), only by means of further approximations. The two approximations that are immediately obvious are (1) to limit the number of intermediate states, and (2) to make a multipole expansion of $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ and consider only leading terms; e.g., dipole-dipole interactions. The former has been used by Nesbet⁵ and improved by Thiéry.⁸ For the purpose of comparison we describe it briefly here, but a greater emphasis is placed on the latter approximation.

As above, we neglect induced vector potential effects and consider only coupling through the scalar field. The external field is assumed to vary negligibly over the space of the individual molecule, so we may express, somewhat artificially, the external field as a scalar field,⁵

$$\varphi_0(\mathbf{r}, \omega) = -\mathbf{r} \cdot \mathbf{E}_n(\omega), \quad (26)$$

where n labels the molecule and

$$\mathbf{E}_n = i\omega \mathbf{A}_n.$$

These approximations enable us to express \bar{K} entirely in terms of charge densities. The states of the uncoupled system may be taken to be real, thus $\rho_{0k} = \rho_{k0}$ and

$$K_{00}^0(\mathbf{r}, \mathbf{r}', \omega) = \sum_k \rho_{0k}(\mathbf{r}) \rho_{k0}(\mathbf{r}') g_k(\omega), \quad (27)$$

where g_k is the complex function of frequency in Eq. (24). We next assume $\rho_{0k}(\mathbf{r}) = \rho_{0f}(\mathbf{r}) \chi_{0k}$, which leads to

$$K_{00}^0(\mathbf{r}, \mathbf{r}', \omega) = \rho_{0f}(\mathbf{r}) \rho_{f0}(\mathbf{r}') \sum_k \chi_{0k} \chi_{k0} g_k(\omega) = \rho_{0f}(\mathbf{r}) \rho_{f0}(\mathbf{r}') G(\omega). \quad (28)$$

This is Nesbet's single-band approximation, by which only one electronic band ($0 \rightarrow f$) of the isolated molecule is included and summation is over vibronic sublevels associated with the electronic state f . Therefore, it amounts to the Born-Oppenheimer approximation, with χ_{0k} being the Franck-Condon factor. Expression (28) is substituted into the expansion of \bar{K} , each $\rho_{0f}(\mathbf{r})$ is labeled according to the molecule in which \mathbf{r} is located, and integrations are taken over all intermediate \mathbf{r} 's. This gives a matrix equation for \bar{K} of which a typical element is

$$[\bar{K}_{00}(\mathbf{r}, \mathbf{r}')]_{nn'} = \sum_{s=0}^{\infty} \sum_{i,j,\dots,q} (-1)^s \rho_{0f}(\mathbf{r})_n V_{ni} V_{ij} \dots V_{qn'} \times \rho_{f0}(\mathbf{r}')_{n'} G^{s+1}(\omega). \quad (29)$$

The number of V 's in each term equals the order s , and the interaction V is

$$V_{ij} = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \rho_{0f}(\mathbf{r}_1)_i \frac{\exp [i\omega |\mathbf{r}_1 - \mathbf{r}_2|]}{|\mathbf{r}_1 - \mathbf{r}_2|} \rho_{f0}(\mathbf{r}_2)_j,$$

the excitation exchange integral coupling molecules i and j . Symbolically, \bar{K} may be expressed as the

matrix expansion

$$\begin{aligned}\bar{K}_{00} &= \sum_{s=0}^{\infty} \rho_{0f} (-VG)^s \rho_{f0} G \\ &= \rho_{0f} (1+VG)^{-1} \rho_{f0} G.\end{aligned}\quad (30)$$

The derivation shows that the zeroth-order term is zero unless \mathbf{r} and \mathbf{r}' are in the same molecule; i.e., K^0 is locally diagonal. The transition densities are part of the matrix in such a way that ρ_{0f} and ρ_{f0} are associated with the molecules labeling the row and column, respectively.

For systems having simple geometry, Eq. (30) can be handled easily. We consider, as an example, a molecular dimer in which the molecules are translationally equivalent. The system is assumed to be sufficiently small that, at optical frequencies, the retardation term, $\exp[i\omega R]$, and the variation of the external field can be neglected. The total rate of energy absorption is then

$$\begin{aligned}\bar{W}(\omega) &= (\omega/2) \mathbf{E}^*(\omega) \cdot \int d^3\mathbf{r} \int d^3\mathbf{r}' \\ &\quad \times \mathbf{r} [\rho_{0f}(\mathbf{r}) (1+VG)^{-1} G \rho_{f0}(\mathbf{r}')]'' \mathbf{r}' \cdot \mathbf{E}(\omega) \\ &= \sum_{nn'} (\omega/2) \mathbf{E}^* \cdot [\mathbf{r}_{0f} (1+VG)^{-1} G \mathbf{r}_{f0}]''_{nn'} \cdot \mathbf{E}.\end{aligned}\quad (31)$$

The double prime stands for the imaginary part and \mathbf{r}_{0f} is the electric-dipole matrix element. In this case the two-dimensional matrix V has only two nonzero terms, $V_{12} = V_{21}$. Therefore, in the expanded form, Eq. (30), it is easily seen that the diagonal elements of \bar{K} contain only even terms, while the off-diagonal elements contain only odd terms in powers of V (a molecule interacts with itself only through an even number of V 's).

Expressing the odd and even expansions in closed form and summing the matrix elements in Eq. (31), we obtain the result

$$\bar{W}(\omega) = \omega \frac{\mathbf{E}^* \cdot \mathbf{r}_{0f} \mathbf{r}_{f0} \cdot \mathbf{E} G''(\omega)}{|1 + V_{12}G|^2}.\quad (32)$$

The numerator is exactly the absorption by two non-interacting molecules; all interaction effects are contained in the denominator term.

Equation (32) is essentially of the same form as the result of Nesbet⁵ using the same model. The only difference is in the frequency term G . Since G is a polarizability (here associated with one electronic transition), it is necessarily a complex quantity which can have at most isolated zeros in either the real or imaginary part. Nesbet used an approximation for G which makes it purely imaginary and consequently predicts an intensity decrease (hypochromism) at all frequencies. This is clearly an improper approximation since it violates the requirement that the Kronig-Kramers transformation be satisfied (causality).

Examination of the denominator term in Eq. (32) shows that the direction of intensity change, at any frequency, depends on the sign of the real part of $V_{12}G$. Since the sign changes somewhere in the absorption band, we have the result that the interaction contained in Eq. (32) causes a shift and, possibly, a change in shape, but the overall intensity remains constant. This has been pointed out also by Thiéry,⁸ who corrected Nesbet's theory by including an appropriate G .

For translationally nonequivalent molecules the matrix elements \mathbf{r}_{0f} are not identical for the two molecules. The diagonal and off-diagonal terms in Eq. (31) must be treated separately, thus leading to a description of "exciton splitting" of the monomer band. The derivation of the two-term expression similar to Eq. (32) is straightforward so is not included here.

From the above and previous^{7,8} discussions we see that *excitation resonance (exciton) interaction* (more generally, the "self interaction" of any band system, inclusive of off-resonance interactions) *does not lead to a net change in absorption intensity*. In order to describe over-all intensity changes within a given band system, resulting from molecular interactions, we must include other excited states outside the absorption band system in question. This could be done by an extension of the matrix formulation leading to Eq. (31) to include more than one excited electronic state per molecule. This is rather cumbersome, however, so it is preferable to use another method which takes into account, in a simple way, all states of the system.

III. POLARIZATION RESPONSE

We now discuss the second method for approximating \bar{K} as a power series expansion which can be put into closed form. As above, we neglect induced vector potential effects resulting from charge motion and consider only charge density fluctuations caused by the induced scalar potential, an approximation which is probably satisfactory for small molecules in which the electrons are highly localized. The expanded form of Eq. (15) for \bar{K}_{00} , as before, may be written symbolically

$$\bar{K}_{00} = K_{00}^0 + K_{00}^0 D_{00}^0 K_{00}^0 + \dots,\quad (33)$$

containing only transition densities, ρ_{0k} , and free-field susceptibilities,

$$D_0^{00}(\mathbf{r}_1, \mathbf{r}_2, \omega) = g^{00} \{ \exp[i\omega |\mathbf{r}_1 - \mathbf{r}_2|] / |\mathbf{r}_1 - \mathbf{r}_2| \}.$$

Expansion in a multipole series about the center of charge on each molecule gives for the dipole-dipole part

$$D_0^{00} = \mathbf{r}_1 \cdot (3\mathbf{e}_{12}\mathbf{e}_{12} - \mathbf{I}) \cdot \mathbf{r}_2 R_{12}^{-3} \exp[i\omega R_{12}],\quad (34)$$

where \mathbf{e}_{12} and R_{12} are the unit vector and distance between the charge centers of the molecules, and now \mathbf{r}_1 and \mathbf{r}_2 are measured from the charge centers.

Substituting into Eq. (33) and carrying out all integrations over intermediate \mathbf{r}' , as indicated by Eq. (15), leads to the matrix form

$$\bar{\alpha}_{nn'}(\omega) = \alpha_{nn'}^0(\omega) \delta_{nn'} + \alpha_{nn}^0(\omega) d_{nn'}(\omega) \alpha_{n'n}^0(\omega) + \alpha_{nn}^0(\omega) d_{nj}(\omega) \alpha_{jj}^0(\omega) d_{jn'}(\omega) \alpha_{n'n}^0(\omega) + \dots, \quad (35)$$

where, in anticipation of using relation (26), we have defined the system polarizability,

$$\bar{\alpha}_{nn'}(\omega) = \int_n d^3\mathbf{r} \int_{n'} d^3\mathbf{r}' \mathbf{r} \cdot \bar{K}_{00}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{r}'. \quad (36)$$

Indices now label molecules. In Eq. (35) summation is implied over repeated indices (other than n and n') and use has been made of the fact that α^0 connecting different molecules is zero.

The integrations in Eq. (36) extend only over the space of molecules n and n' . Thus, the system polarizability, defined by Eq. (36), takes the form of a matrix of dimension equal to the number of molecules in the system and is given in terms of the isolated molecule polarizability,

$$\alpha^0(\omega) = e^2 \sum_k \mathbf{r}_{0k} \mathbf{r}_{k0} [(\omega + \omega_{k0} + i\delta)^{-1} - (\omega - \omega_{k0} + i\delta)^{-1}]$$

and the dipole field susceptibility

$$d_{ij} = (3\mathbf{e}_{ij}\mathbf{e}_{ij} - \mathbf{I}) R_{ij}^{-3} \exp[i\omega R_{ij}].$$

In matrix form we then have

$$\begin{aligned} &= \alpha^0 + \alpha^0 \mathbf{d} \alpha^0 + \alpha^0 \mathbf{d} \alpha^0 \mathbf{d} \alpha^0 + \dots \\ &= \alpha^0 (\mathbf{I} - \mathbf{d} \alpha^0)^{-1}. \end{aligned} \quad (37)$$

The matrix element $\bar{\alpha}_{nn'}$ is the dipole response (ω component) at molecule n to a unit electric field at molecule n' . Each matrix element is itself a three-dimensional tensor; therefore, we may let each index represent both the spatial component and the molecule, making $\bar{\alpha}$ a $3N$ dimensional matrix for an N molecule system. α^0 and \mathbf{d} are then $3N$ dimensional such that α^0 is block diagonal with three-dimensional blocks and \mathbf{d} contains three-dimensional blocks of zeros on diagonal.

Equation (37) is equivalent to the result obtained by DeVoe⁷ from a purely classical starting point. This means that the molecular separability and decorrelation approximations have made the theory essentially a classical one.

A. Coupled Harmonic Oscillator Model

In order to better understand the significance of the decorrelation approximation, we examine briefly the exactly soluble problem of the polarization linear response function for a system of coupled harmonic oscillators and show how the above results, as well as those obtained from the usual second quantized Hamiltonian, are equivalent to using a coupled oscillator model.

The system consists of a set of harmonic oscillators with coordinates X_n and fundamental frequencies ω_n , coupled linearly by the constants d_{nm} , so the interaction among them may be expressed as

$$V_1 = -\frac{1}{2} \sum_{nm, (n \neq m)} X_n X_m d_{nm}.$$

The total system Hamiltonian, including interaction with an external electric field, is

$$H = H_0 - \frac{1}{2} \sum_{nm} X_n X_m d_{nm} - \sum_m X_m E_m. \quad (38)$$

The interaction representation is used for the Hamiltonian of the uncoupled system, H_0 ; thus, all operators have the form

$$X_n(t) = \exp[iH_0 t] X_n \exp[-iH_0 t].$$

As in Sec. II, the coupling between the oscillators is assumed to be turned on adiabatically, while the external field is turned on at a finite $t < 0$. The response of X_n at $t=0$ is exactly

$$\begin{aligned} \langle X_n \rangle &= \langle \Phi(0) | X_n(0) | \Phi(0) \rangle \\ &= \langle \Phi^0(H_0) | U^+(0, -\infty) X_n(0) U(0, -\infty) | \Phi^0(H_0) \rangle, \end{aligned}$$

where $\Phi^0(H_0)$ is the ground-state eigenfunction of H_0 and U contains all interactions.

We now follow the procedure in Sec. II by considering the linear response of X_n to an impulse electric field of unit strength at X_m (the interaction with the field becomes $-X_m \delta(t+\lambda)$, with $\lambda > 0$), expanding U and collecting terms into a commutator nest. This gives $K_{nm}(\lambda)$ directly in an expanded form exactly like Eq. (10), the only difference being that every commutator involves only X 's. The unequal time commutator,

$$[X_j(t), X_k(t')] = -2i | X_{01} |^2 \delta_{jk} \sin \omega_k(t-t') \quad (39)$$

is not an operator, but is simply a classical function of time and the transition matrix element between the ground and first excited oscillator states. This property makes the problem exactly soluble. The only nonzero term in each perturbation order is the one with the external field coupling term located at the outer terminal position of the commutator nest [cf. Eq. (10)]. All commutators are then of the form $[X_j(t), X_k(t') X_l(t'')]$, which are linear in the X 's. Therefore, without the decorrelation approximation, each commutator may be replaced by its average value as it appears during the expansion of the commutator nest.

The uncoupled oscillator linear response function is defined by

$$\begin{aligned} K_{jk}^0(t-t') &= i\theta(t-t') \langle [X_j(t), X_k(t')] \rangle \\ &= +2\delta_{jk}\theta(t-t') | X_{01} |^2 \sin \omega_k(t-t'). \end{aligned} \quad (40)$$

Making use of the θ dependence in the expansion of K , we obtain

$$K_{nm}(\lambda) = \sum_{s=0}^{\infty} \int \cdots \int dt_1 \cdots dt_s K_{nn}^0(-t_1) d_{nj} \times K_{jj}^0(t_1-t_2) d_{jk} \cdots K_{mm}^0(t_{s-1}-t_s) \delta(t_s+\lambda) \quad (41)$$

with summation taken over all intermediate indices. The corresponding susceptibility for the coupled system is

$$\begin{aligned} K_{nm}(\omega) &= \sum_{s=0}^{\infty} K_{nn}^0(\omega) d_{nj} K_{jj}^0(\omega) d_{jk} \cdots K_{mm}^0(\omega) \quad (Sd^s) \\ &= K_{nn}^0(\omega) + K_{nn}^0(\omega) d_{nj} K_{jm}(\omega). \end{aligned} \quad (42)$$

This is exact. That such is the case is not surprising, since the linearly coupled harmonic oscillator problem can be solved exactly by a normal mode transformation. However, the important thing is that the solution is of the same form as that for the molecular system obtained by use of the decorrelation approximation. A comparison of Eqs. (35) and (42) shows clearly that $\bar{\alpha}$ is the susceptibility of a system of coupled harmonic oscillators, provided that in α^0 we make the usual substitution,

$$\mathbf{r}_{0k} \mathbf{r}_{k0} = (2m\omega_k)^{-1} \mathbf{f}_{0k},$$

in terms of oscillator strength, whereby α^0 for the ground state of each molecule is that for a set of equivalent oscillators.

The reason that K_{nm} has the simple form (42), and a physical picture of the interaction effects, can best be seen by inspection of terms in the expansion. Each term is an expectation value taken with respect to the unperturbed ground state of the uncoupled system; and the term of order S , since it contains S interactions, is composed of $2S+2$ virtual transitions. From the origin of the term in the expansion, it is clear that every possible sequence of $2S+2$ transitions (other than those coming from oscillator self-interaction) which begin and end with the system in the ground state contribute, while all others give zero identically. Thus, each term is the total of all transition probabilities mediated by S interactions.

The interesting point is that none of the terms in expansion (42) allow an oscillator to be excited above the first excited state, i.e., all amplitudes containing transitions to higher states cancel. This results simply from the fact that the susceptibility of the harmonic oscillator is independent of the state; thus, transitions involving the ground states are sufficient to describe the problem.

The contribution of terms through third order are shown schematically by the diagrams in Fig. 1. The open circles represent oscillators, while the external photon and the coupling between oscillators are represented by light, external and heavy, internal dashed

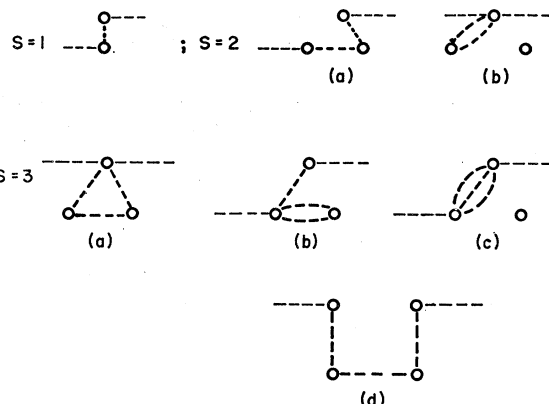


FIG. 1. Diagrams representing contributions of interactions, in various perturbation orders, to system susceptibility.

lines, respectively. At each vertex a field line causes a transition in the oscillator to its first excited state, followed by a transition back to the ground state with emission of a field line. Therefore each vertex, must have an even number of field lines. These are not propagator diagrams (except in the sense that each diagram represents a forward scattering amplitude for the incident photon), but serve only to show the types of interactions for each perturbation order. For example, the first-order term is nondiagonal, leading to absorption of energy by one oscillator due to the field at another.

Equation (42) is easily solved for a model in which every oscillator is coupled only to one "central" oscillator. Expansion (42) then becomes a power series, which for the diagonal element is

$$\begin{aligned} K_{nn}(\omega) &= K_{nn}^0 \sum_{s=0}^{\infty} \left(\sum_k d_{nk} K_{kk}^0 d_{kn} K_{nn}^0 \right)^s \\ &= K_{nn}^0 \left(1 - \sum_k d_{nk}^2 K_{kk}^0 K_{nn}^0 \right)^{-1}. \end{aligned} \quad (43)$$

and for a non-diagonal element is

$$K_{nm}(\omega) = K_{nn}^0 d_{nm} K_{mm}^0 \left(1 - \sum_k d_{nk}^2 K_{kk}^0 K_{nn}^0 \right)^{-1},$$

where n refers to the given "central" oscillator. In Fig. 1 only diagram 2b contributes to K_{nn} and only diagrams 1, 3b and 3c contribute to K_{nm} . The diagonal element is equivalent to the results of Huber and Van Vleck,¹⁶ who have applied this model to a study of line broadening using the same Green's function but a different approach.

B. Approximate Molecular Hamiltonian

In this section we consider the Hamiltonian for an interacting molecular system in terms of the operators for creation and annihilation of excitations to various states of the individual molecules of the system and

¹⁶ D. L. Huber and J. H. Van Vleck, *Rev. Mod. Phys.* **38**, 187 (1966).

show how its use in formulating the system susceptibility is equivalent to use of the molecular separability and decorrelation approximations.

In the point dipole-dipole approximation a typical matrix element for the interaction of molecules n and m is

$$V_{nm}^{sr} = \langle (no)(mr) | V_{nm} | (ns)(mo) \rangle = -e^2 \mathbf{r}_{ns} \cdot \mathbf{d}_{nm} \cdot \mathbf{r}_{mr}, \quad (44)$$

where $| (ns)(mo) \rangle$ is the zeroth-order (noninteracting) state in which molecule n is in excited state s , molecule m (and all others) is in the ground state and d_{nm} is the dipole coupling tensor in Eq. (37). The molecule states are taken to be real, so that

$$\mathbf{r}_{ns} = \langle (no) | \mathbf{r} | (ns) \rangle = \langle (ns) | \mathbf{r} | (no) \rangle.$$

The system Hamiltonian is then taken to be

$$H = H_0 - \frac{1}{2} e^2 \sum_{n \neq m} \sum_{r,s} V_{nm}^{sr} (a_{ns}^+ + a_{ns}) (a_{mr}^+ + a_{mr}) \quad (45)$$

in which H_0 is the Hamiltonian of noninteracting molecules; a^+ and a create and annihilate excitations as labeled for the molecules and states. This is the Hamiltonian used by Agronovich¹⁷ in his extensive work on molecular exciton theory and dispersion in molecular crystals. As an approximation it neglects (1) "static" interactions between molecules, (2) all transitions between excited states of the molecules, and (3) processes involving transfer of charge between molecules. The dipole approximation (44), which neglects overlap-exchange effects, is also included by us. These approximations are essentially the same as those used above in obtaining Eq. (35).

The effect of using excitation operators is to reduce the problem to a multifold two-state problem. They satisfy the commutation relations

$$\begin{aligned} [a_{ns}, a_{mr}^+] &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \delta_{nm} \delta_{sr} \\ [a_{ns}, a_{mr}] &= [a_{ns}^+, a_{mr}^+] = 0, \end{aligned} \quad (46)$$

in a two-state space, so they may be referred to as Pauli operators. Matrix elements connecting different excited states of the nondiagonal type

$$\langle (ns) | [a_{nr}, a_{ns}^+] | (nr) \rangle = -1$$

are not considered. Consequently, the excitations are to be regarded as "quasi-particles" which obey neither boson nor fermion type commutation relations, but rather obey mixed relations.

In order to solve problems using Hamiltonian (45), these commutation relations must somehow be modi-

fied. Krugler *et al.*,¹⁸ have been able to transform them into fermion operators for the two-state case of a linear chain with only nearest-neighbor interactions and cyclic boundary conditions. The resulting Hamiltonian can then be diagonalized by a Bogoliubov-type transformation. On the other hand, for handling more general cases, Agronovich¹⁷ has chosen to approximate the excitation operators as boson type by taking $[a_{ns}, a_{mr}^+] = \delta_{nm} \delta_{rs}$ thereby allowing H to be diagonalized, by a Bogoliubov transformation, for the case in which only a few molecular states are included.

We prefer to use the boson approximation. The error introduced is twice the amount, q , of excited state character in the exact ground state of the system. This is easily seen from the identity

$$[a_{ns}, a_{ns}^+] = 1 - 2a_{ns}^+ a_{ns},$$

the expectation value of which is $1 - 2q$, since $a_{ns}^+ a_{ns}$ is the number operator for excitation ns . In molecular systems where the other approximations contained in Hamiltonian (44) are reasonable, we expect this error to be small.

For simplicity of notation we now define the dipole polarization operator

$$\mathbf{P}_{ns} = e \mathbf{r}_{ns} (a_{ns}^+ + a_{ns}). \quad (47)$$

In the interaction representation for H_0 these operators become $\mathbf{P}_{ns}(t) = \exp [iH_0 t] \mathbf{P}_{ns} \exp [-iH_0 t]$ and, with the boson approximation, have the unequal time commutator

$$[\mathbf{P}_{ns}(t), \mathbf{P}_{mr}(t')] = -2ie^2 \mathbf{r}_{ns} \mathbf{r}_{mr} \delta_{nm} \delta_{sr} \sin \omega_s(t-t'), \quad (48)$$

where ω_s is the excitation energy to state s . Thus, the polarization operator has the properties of the displacement coordinate of a harmonic oscillator and it becomes obvious that the second quantized Hamiltonian (45) leads to the results obtained in the beginning of Sec. III.

The molecular polarization operator may be defined as

$$\mathbf{P}_n = \sum_s \mathbf{P}_{ns}$$

and has the commutator

$$[\mathbf{P}_n(t), \mathbf{P}_m(t')] = -2ie^2 \sum_s \mathbf{r}_{ns} \mathbf{r}_{ms} \delta_{nm} \sin \omega_s(t-t'). \quad (49)$$

When multiplied by $i\theta(t-t')$, this becomes the polarization linear response function, the Fourier transform of which is the isolated molecule polarizability, $\alpha^0(\omega)$, given above Eq. (37). Using Hamiltonian (45) and the procedure of Sec. IIB to determine the linear response functions for \mathbf{P}_n in the exact (interacting) ground state of the system, we obtain Eq. (35).

¹⁷ V. M. Agronovich, Zh. Eksperim. i Teor. Fiz. **37**, 430 (1960), and [English transl.: Soviet Phys.—JETP **10**, 307 (1960)], later papers.

¹⁸ J. I. Krugler, C. G. Montgomery, and H. M. McConnell, J. Chem. Phys. **41**, 2421 (1964).

Therefore the approximation contained in the second quantized Hamiltonian used by Agronovich and others, together with the boson approximation for the excitation of operators, are entirely equivalent to the molecule separability and decorrelation approximations used here. As seen in the previous section, the latter give us a coupled equivalent oscillator picture. This is accomplished here by the boson approximation. The -1 appearing in $[a, a^+]$ means simply that for a two-state problem any susceptibility of the system in the upper state is of opposite sign to that in the ground state. Changing this sign (boson approximation) converts the two-state system into a fictitious oscillator, the susceptibility of which is state-independent [Eq. (48)]. The result is that Eq. (35) is equivalent to representing the molecular system by a system of coupled harmonic oscillators consisting of an infinite number of mutually uncoupled oscillators at each molecular site (having the frequency and oscillator strength distribution of the molecular spectrum), each of which is coupled to the oscillators of every other site.

Hoffmann⁹ applied Hamiltonian (45) and the boson approximation to a study of interaction effects on the absorption intensity of double-stranded helical polynucleotides. He restricts consideration to three states (i.e., two types of excitation operators) in the monomer and, with the dipole-dipole interaction approximation, puts the Hamiltonian in diagonal form with a Bogoliubov transformation. This gives a quasi-particle (mixed exciton) picture for the electronic excitations of the system, in which all possible multiply excited (zeroth-order) states are mixed. It is not a perturbation expansion, so it contains such mixing to infinite order. The above discussion shows however, that limitation to three states, or any finite number of states, is not necessary. Hoffmann's results are contained explicitly in Eq. (35) as a further approximation.

IV. DISCUSSION OF THE CLOSED FORM

The molecular system polarizability given by Eq. (35) is the most applicable result of the theory. We turn now to the problem of finding its solution for systems with simple geometry and, in particular, of comparing absorption intensities with those of the isolated molecule. Equation (52) below is the classical form obtained by DeVoe⁷ and the solutions which follow have been discussed already by him. We repeat the major features using our notation and terminology, in order to emphasize the origin of absorption intensity effects.

From Eqs. (5), (26), and (36) the rate of energy absorption is

$$\bar{W}(\omega) = (\omega/2) \sum_{nm} \mathbf{E}_n^*(\omega) \cdot \bar{\alpha}_{nm}''(\omega) \cdot \mathbf{E}_m(\omega), \quad (50)$$

where \mathbf{E}_m is the external field at molecule m . The prob-

lem of evaluating this expression is one of spatial dispersion, since the matrix elements depend on the positions, \mathbf{R}_n and \mathbf{R}_m , of the molecules (and their orientations in space). In general, the problem is quite complex and is best handled by examining special cases. If the matrix elements $\bar{\alpha}_{nm}''(\omega)$ depend only on the distance between the molecules, a solution is found by transformation to k -space, giving

$$\bar{W}(\omega) = N(\omega/2) \mathbf{E}^*(\mathbf{k}, \omega) \cdot \bar{\alpha}''(\mathbf{k}, \omega) \cdot \mathbf{E}(\mathbf{k}, \omega), \quad (51)$$

for an N molecule system. Since \mathbf{E} is the external photon field, $\bar{W}=0$ unless $k=\omega$. [The k -space for the photon field is taken to be continuous, while that of $\bar{\alpha}$ is finite and discrete. This distinction is not important for systems containing a large number of molecules, or for small systems in which the molecules are closely spaced compared to the wavelength of the photon. The simple k dependence of Eq. (51) does imply that the basis functions for the k -spaces are of the same type, i.e., the molecular system has periodic boundary conditions.]

By rearranging Eq. (37), we have the equivalent form⁷

$$\bar{\alpha}^{-1}(\omega) = (\alpha^0)^{-1} - \mathbf{d}. \quad (52)$$

As discussed in Sec. III, this is a matrix equation of dimension $3N$ for an N molecule system, and the problem consists of finding a transformation to diagonal form.

We take as a model a linear chain of identical, translationally equivalent molecules. The coordinate system is chosen so that α^0 is diagonal. In \mathbf{d} the three spatial coordinates are not coupled to one another; therefore, the similarity transformation which puts \mathbf{d} into diagonal form also diagonalizes $\bar{\alpha}^{-1}$ (and, accordingly, $\bar{\alpha}$). The solution then becomes

$$\bar{\alpha}_{ii}(\mathbf{k}, \omega) = \alpha_{ii}^0(\omega) [1 - d_i^k \alpha_{ii}^0(\omega)]^{-1}, \quad (53)$$

where the index i labels the spatial component and d_i^k is an eigenvalue of the dipole field susceptibility. Extracting the imaginary part gives

$$\alpha_{ii}''(\mathbf{k}, \omega) = \frac{\alpha_{ii}^{0''}(\omega)}{(1 - d_i^k \alpha_{ii}^{0'}(\omega))^2 + (d_i^k \alpha_{ii}^{0''}(\omega))^2}, \quad (54)$$

in which the prime denotes the real part. For simplicity, we have neglected retardation term in \mathbf{d} , assuming that the wavelength of the photon is large compared to the distance of significant interaction. The identification of the system \mathbf{k} with the field \mathbf{k} in Eq. (51) implies periodic boundary conditions, so we have

$$d_T^k = -2l^{-3} \sum_{n>0} n^{-3} \cos 2\pi knN^{-1}$$

$$d_L^k = 4l^{-3} \sum_{n>0} n^{-3} \cos \pi knN^{-1} \quad (55)$$

for the transverse and longitudinal components, where l is the distance between molecules.

Figure 2 gives the results of calculations for a linear

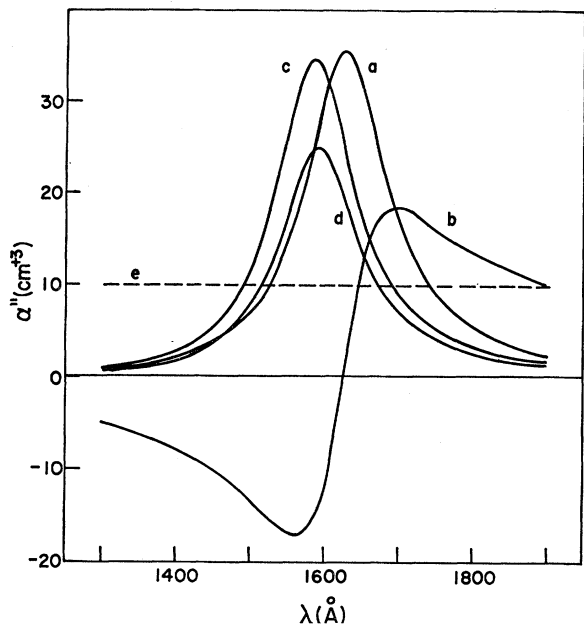


FIG. 2. Calculated absorption spectra for model linear chain of ethylene molecules. Curve (a)—imaginary part of α^0 for the isolated molecule (from Ketteler-Helmholtz formula); Curve (b)—real part of α^0 corresponding to curve (a); Curve (c)—imaginary part of α for linear chain, including contributions from only curves (a) and (b); Curve (d)—similar to curve (c), but including also contributions from curve (e); Curve (e)—real part of background α^0 .

chain of ethylene molecules in which the principal molecular axis is perpendicular to the chain axis. The intermolecular distance is taken to be 4.0 Å. A single absorption band [curve (a)] is considered, having the frequency, $\epsilon(\text{max})$, and bandwidth of the lowest energy $\pi \rightarrow \pi^*$ band of ethylene, but following a Ketteler-Helmholtz dispersion. This enables us to separate $(\alpha^0)'$ into two parts, that [curve (b)] arising from the absorption band and a background part [curve (e)], taken to be constant in this region and arising from all other transitions of the isolated molecule. Since the wavelength is large compared to l , the value $k=0$ is taken in d_T^k . Curve (c), which includes the contribution only of curve (b) to $(\alpha^0)'$, shows that the absorption band is shifted with no change in total intensity (since \bar{W} has a factor ω). On the other hand, including both parts of $(\alpha^0)'$ [curve (d)] results in a smaller band shift but a large decrease in intensity.

Figure 2 illustrates the previous conclusion, therefore, that over-all intensity changes arise only from interactions with states outside of the band system in question, and within the framework of the decorrelation approximation, are determined by the real part of the background polarizability. It is a matter of intensity borrowing with conservation of total intensity (Kuhn-Thomas sum rule), if absorption due to *all* transitions throughout the entire spectrum is considered.

The shift of curve (c) to higher frequency is in ac-

cordance with excitation resonance (exciton) interaction. The inclusion also of the background $(\alpha^0)'$ gives a shift back to lower frequency. This is the expected effect of dispersion forces and may be a factor in explaining the observed hypochromism with small frequency shifts in polynucleotides.^{8,12}

These results, based on Eq. (35), are more general than those presented earlier^{2,3} in terms of first-order perturbation theory. However, it is easy to show⁷ that the first-order term in expansion (35) is identical to the previous first-order perturbation theory results, provided an average is taken over the orientation of the molecular system relative to the incident field. (Such averaging was taken also in the previous theory.) This means that the decorrelation approximation does not come into play until the second-order term, as is apparent from the diagram representation in Fig. 1. Only those diagrams having more than two field lines connected to any one molecule are involved in the decorrelation approximation; thus it is contained in less than half the second-order terms (for a system of more than three molecules).

By way of summary, we have developed, starting with an exact quantum-mechanical formulation, a theory for the susceptibility of an interacting molecular system. The approximations used enable us to express the system susceptibility in closed form in terms of the isolated molecule susceptibility and the coupling between the molecules. One of the advantages of using such a Green's function approach lies in the simplicity with which the theory can be developed in a formal way, allowing one to keep an over-all view of the observables in the problem and to pinpoint the places where approximations arise.

There are two basic approximations: (1) the decorrelation approximation, which *partially* decouples the motions of the electrons on different molecules, and (2) the molecular separability approximation, which enables us to assign current-charge density at each space-time point to a particular molecule; and several less crucial ones: (3) the neglect of induced vector potential effects, (4) either the restriction to a few electronic states (as in Sec. IIC) or restriction to the point dipole-dipole term in a multipole expansion (as in Sec. III), and (5) (frequently) the neglect of the retardation term, $\exp[i\omega R]$, in making numerical calculations. The extent of validity of all but, perhaps, the first depends greatly on the geometry of the individual molecules and their spacings in the system. The first approximation, necessary to put the theory in closed form, is difficult to assess. It is hoped that an alternative approach in terms of single-particle Green's function techniques will be helpful.

The theory developed here leads to an expression for the absorption dispersion which entirely agrees with earlier local field theories and the results obtained from second quantization with the boson approximation. The original first-order perturbation theory for hypo-

chromism is identical to the first-order term of the present theory [Eq. (35)]. Hoffmann's results are contained, as an approximation, in the present theory. For completeness, we point out discussions of the hypochromism problem by McLachlan and Ball,¹⁹ Fowler,²⁰ and Bullough,²¹ whose conclusions are in general agreement with ours.

¹⁹ A. D. McLachlan and M. A. Ball, *Mol. Phys.* **8**, 581 (1964).

²⁰ G. N. Fowler, *Mol. Phys.* **8**, 383 (1964).

²¹ R. G. Bullough, *J. Chem. Phys.* **43**, 1927 (1965).

The theory, therefore, contains nothing which is basically new, but does serve to coordinate previous theories under one "theoretical roof". We feel that, because of the generality, directness, and completeness of the approach, the use of linear response (retarded) Green's functions will point the way to better approximation methods.

The same method should be readily applicable to other optical phenomena, besides absorption, such as rotatory dispersion and molecular crystal reflection.

Electrodynamics of a Semiclassical Free-Electron Gas*

M. G. CALKIN, P. J. NICHOLSON

Dalhousie University, Halifax, Nova Scotia, Canada

This article presents a simplified treatment of the high density, collisionless, free-electron gas, based on the ideas of a wave number and frequency-dependent conductivity and dielectric constant. The formalism is applied to solve a number of problems: the screening of the electrostatic potential of a foreign point charge placed in the electron gas, the rate of energy loss of a charged particle moving through the electron gas, plasma oscillations, the reflection of electromagnetic waves from the electron gas, and ultrasonic attenuation in metals due to the interaction of the sound waves with the conduction electrons. In a final section it is indicated how the methods may be generalized. Explicit expressions for the conductivity of the electron gas are obtained in an appendix.

INTRODUCTION

In recent years the quantum theory of the electron gas has attracted the attention of a large number of investigators, with the result that many features of such a system are now well understood. Although the power and generality of the quantum-mechanical approach cannot be denied, there are times when a simplified analysis is desired, if only to introduce concepts and aid the intuition. Thus motivated, this article presents a semiclassical treatment of a series of problems, which can be classified under the heading: the electrodynamics of an electron gas. Most of the results have been obtained previously, and are available, for example, in the works of Lindhard,¹ Rukhadze and Silin,² Pines,³ Kittel,⁴ Ziman,⁵ and Pippard.⁶ It is

* This research was supported by the National Research Council.

¹ J. Lindhard, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.* **28**, No. 8 (1954).

² A. A. Rukhadze and V. P. Silin, *Usp. Fiz. Nauk* **74**, 223 (1961); **76**, 79 (1962) [English transl.: *Soviet Phys.—Uspekhi* **4**, 459 (1961); **5**, 37 (1962)].

³ D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1961); *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963).

⁴ C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963).

⁵ J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, England, 1960); *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, England, 1964).

⁶ A. B. Pippard, *Rept. Progr. Phys.* **23**, 176 (1960); in *Low Temperature Physics, Les Houches*, 1961, C. DeWitt, B. Dreyfus, and P. G. DeGennes, Eds. (Gordon and Breach, Science Publishers, Inc., New York, 1962).

hoped, however, that the following treatment will prove a useful introduction, serving to bridge the gap between the old-fashioned and more modern pictures.

Although the ideas can be applied to, and in some cases derive from, the study of a low-density electron gas at high temperatures, this article is primarily concerned with the high-density electron gas at low temperatures. That is, in the absence of any perturbing electric field, the system considered consists of a gas of electrons, moving without collisions through a uniform, smeared out distribution of positive charge, with charge density equal and opposite to that of the electrons. It is further assumed that the electrons obey Fermi statistics, and that the temperature is zero. The average number of electrons in a volume $d^3\mathbf{x}$ with velocities in the range $d^3\mathbf{v}$ is thus $(3n_0/4\pi v_F^3)d^3\mathbf{x}d^3\mathbf{v}$ for $v < v_F$ and 0 for $v > v_F$. The Fermi velocity v_F is given by $(\hbar/m)(3\pi^2n_0)^{1/3}$.

The results obtained are used to describe the behavior of the conduction electrons in a metal. In most cases this application should be regarded as a crude approximation to the true state of affairs. Firstly, the periodicity of the lattice changes the unperturbed electron states, leading, for example, to nonspherical and in some cases multiply-connected Fermi surfaces. The modifications to the theory presented here to allow for these effects are described by Pippard.⁷ Secondly, the theory is valid only if the mean Coulomb inter-

⁷ A. B. Pippard, *Ref. 6*.