tive **39** and nicotinic acid,[11] little is known about the mechanism of their attachment other than its occurrence with decarboxylation at the carboxylated pyridine site. Furthermore, electrophilic substitution of simple pyridines is known to occur only under extreme, forcing conditions. If it be assumed that the transformations in the plant proceed *via* N-glycosylpyridine intermediates, a simple biosynthetic pathway can be envisaged (*vide infra*).[12]
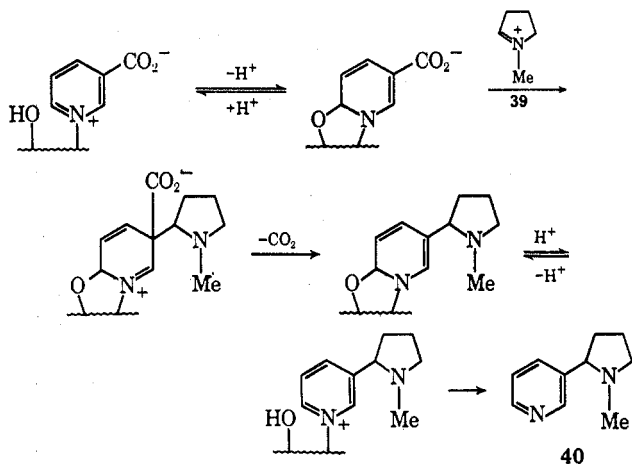

Although the starting materials of all above syntheses have been 1-alkyl-3-acylpyridinium salts whose nucleophilic centers resided uniformly on the N-alkyl substituents, there is no theoretical reason for such limitation in the general scheme of alkaloid synthesis. The following new method of synthesis of isoquinuclidines illustrates the utilization of an acylpyridine whose nucleophilic side chain does not radiate from the nitrogen position. Pyridine-3,5-dicarboxylic acid was converted by conventional means to the aldehydo ester **41**,

(11) T. J. Gilbertson and E. Leete, *J. Am. Chem. Soc.*, **89**, 7085 (1967), and previous work.

(12) This hypothesis was first propounded by the author at the Lecture of the Month, The Ullman Institute of Life Sciences, The Weizmann Institute of Science, Rehovoth, Israel, Jan 4, 1965.

whose condensation with acetone, ketalation, and hydrogenation led to the piperideine **42**. Acid-induced cyclization and hydrolysis yielded the isoquinuclidine **43**, a well-suited model of the *Iboga* alkaloids, e.g., **44**.[5]
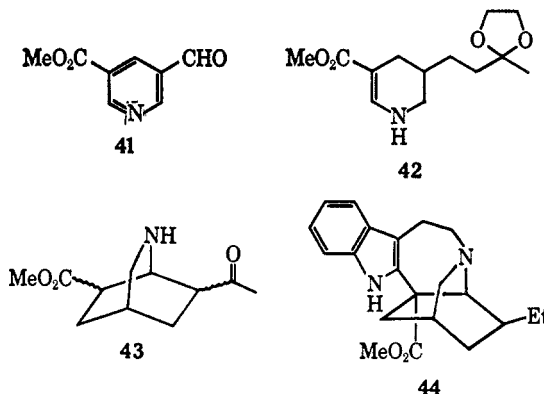
The accumulated body of evidence suggests strongly that the two-step scheme of construction of fused piperidines will be of general applicability in alkaloid synthesis. Much work remains in the utilization of the method for the preparation of the wide variety of virgin alkaloid structure types.[13]

(13) While only portions of the work presented in this review have appeared in print (see references), various phases of the research were presented at the following lectures: Frontiers of Chemistry Lecture, Western Reserve University, Cleveland, Ohio, March 23, 1963; Southeastern Regional American Chemical Society Meetings, Charlotte, N. C., Nov 14-16, 1963, and Atlanta, Ga., Nov 1-3, 1967; Chemistry Symposium, Rikagaku Kenkyusho (The Institute of Physical and Chemical Research), Tokyo, Japan, April 27, 1964; Natural Products Symposium, Israel Chemical Society Meeting, Jerusalem, Israel, Dec 29, 1964; Abbott Lecture, University of Sydney, Sydney, Australia, June 1, 1966; Barton Lecture, University of Oklahoma, Norman, Okla., Feb 2, 1967; Second Natural Products Symposium, University of the West Indies, Kingston, Jamaica, Jan 2-5, 1968.

Studies of the Electronic States of Simple Liquids

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Received May 22, 1967

A survey is presented of recent studies of conducting and nonconducting excited electronic states in simple liquids, e.g., He, Ar. Attention is focused on: (a) interpretation of the mobility of excess electrons in terms of the fundamental electron-atom potential and the structure of the liquid, (b) the difference between delocalized and localized excess electron states, (c) the nature of exciton states in the liquid and the form of the dispersion relation in terms of the structure of the liquid, (d) the role of intermolecular interactions in broadening and shifting the exciton spectrum of the liquid, and (e) possible modes of energy trapping and energy transfer. Wherever possible experiment and theory are compared, and directions where more work is needed are pointed out.

I. Introduction

Considerable effort has been devoted to studies of the electronic states of free molecules and of dielectric crystals. Spectroscopic studies of dilute gases, from

which information about the free molecule is deduced, are simplified by the absence of intermolecular interactions and hence of correlations between the positions of the molecules. Thus, any one molecule may be

regarded as isolated except for occasional binary collisions. Binary collisions, which decrease in frequency as the gas density is decreased, lead to a broadening and shift of the stationary states of the gas, and from this alteration of the spectrum there can be deduced information about the intermolecular potential.[1] A different simplification of description is possible in the case of crystalline solids. The long-range order of a crystalline lattice is a consequence of strict translational symmetry. In turn, the existence of strict translational symmetry, as well as the presence of other geometric symmetries within the unit cell, permits the use of a description in which independent collective coordinates are fundamental to the representation. These collective coordinates, of course, correspond to the exciton states of the crystal. What is a collective coordinate? In the dilute gas the coupling between molecules is sufficiently weak that the states of the gas (a many-body system) are essentially the same as the states of the free molecule. In the crystal (a different many-body system) intermolecular interactions are strong and the states of all molecules are mixed so as to produce distinct new states. For example, the vibrations of a crystal differ from those of the molecules composing the crystal by the existence of new motions, collective vibrations, in which the phases of the displacements of the atoms in the molecules are correlated. These are the normal modes of vibration of the crystal. In the case of optical excitation, the collective coordinates describe correlated oscillations of the electronic transition moments of the atoms and correspond to the exciton states of the crystal. Interaction between the exciton states and lattice vibrations leads to some alteration of the spectrum, and useful information may thereby be obtained.[2]

Now, a liquid has short-range structural order, but no long-range structural order. Because of the strong interactions between the molecules in a liquid, approximations suitable to the description of a gas are not useful. Furthermore, the lack of simple geometric symmetry in the short-range order of the liquid makes it necessary that the concepts of the exciton theory of crystals be extensively modified before they can be applied to the description of a liquid. It is my opinion that the development of a physically realistic and incisive interpretation of the electronic states of liquids and of other disordered systems is one of the most interesting and most challenging of contemporary scientific problems. One outgrowth of this contention is a program, initiated a few years ago at the University of Chicago, to study the electronic states of simple liquids. This report presents a short resumé of some of our work on the electronic properties of simple monatomic dielectric liquids, together with a description of what we now understand, do not understand, and where new concepts and constructs are needed.

II. Excess Electron States in Monatomic Dielectric Liquids

A. Free Electron States. As a first step in our study of the electronic states of simple liquids we consider the behavior of an excess electron in a liquid composed of neutral, closed shell atoms (*e.g.*, He, Ar, Kr). There are two reasons for studying this system. First, adding an electron to a liquid populates a conducting state of the liquid, and conducting states may be studied experimentally. Second, the nonconducting states of the liquid are related to and influenced by the conducting states, so that knowledge of the behavior of conduction electrons is also important for the description of bound excited states of the liquid. Studies of the excess electron states of a simple liquid are analogous to studies of the conduction electrons of a metal. The most important questions to be answered are: (a) What is the nature of the electron wave function, *i.e.*, is the electron best described as free (in which case the wave function is a plane wave) or is the electron trapped by a group of atoms in the liquid (in which case the electron wave function is localized in the trap)? (b) If the electron is almost free, how large is the mean free path? (c) What is the binding energy of the electron to the liquid?

Because the interaction between an electron and a neutral atom is both weaker and of shorter range than the interaction between an electron and an ion, it is tempting to suppose that an excess electron in a simple liquid behaves very much like a free electron. Of course, the fact that the electron–atom interaction is nonzero suggests that scattering phenomena cannot be totally neglected, and that the free electron spectrum of states will be perturbed by the presence of fluid atoms.

I have already mentioned that adding an extra electron to a dielectric liquid leads to a state which conducts electricity. Now, the number of electrons that can be introduced into a dielectric liquid is very small. In the experiments thus far performed, typical electron densities are of the order of magnitude of 10^5 to 10^8 cm^{-3}. Because of the low concentration of electrons, electron–electron interaction is negligibly small. Indeed, the Coulomb energy of a pair of charges separated by the average distance between charges is less than the thermal energy k_BT (where k_B is the Boltzmann constant). When the average Coulomb energy is less than k_BT it is experimentally feasible to separate positive and negative charges in a macroscopic region, and thus study how, say, only the electrons respond to an electric field. The mobility of the electron, defined as the drift velocity in a field of 1 V/cm, then measures the resistance to electron motion arising from scattering of the electron by fluid atoms. If the drift velocity is not linearly dependent on the field strength additional information about the electron

(1) There is an extensive literature dealing with the theory of line broadening. As an example of the modern approach see U. Fano, *Phys. Rev.*, **131**, 259 (1963).

(2) There is also an extensive literature dealing with the theory of exciton–phonon coupling. A good overall view of the field can be obtained from: Y. Toyazawa, *Progr. Theoret. Phys.* (Kyoto), **20**, 53 (1958); *ibid.*, **27**, 89 (1961); *J. Phys. Chem. Solids*, **25**, 59 (1964).
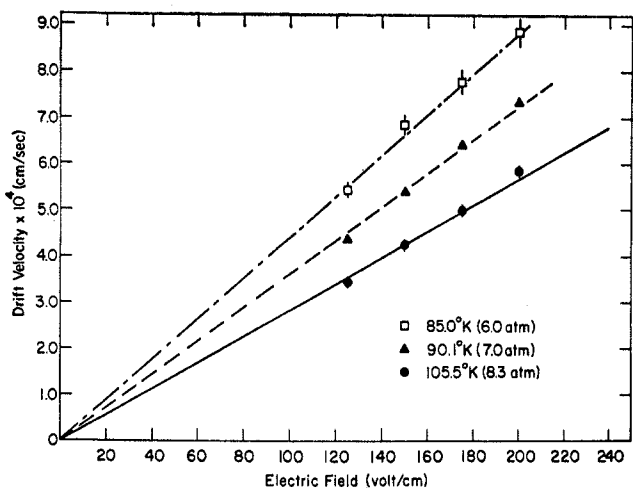
Figure 1.   Low-field drift velocity of electrons in liquid Ar.

Figure 2.   Temperature dependence of the mobility of electrons in liquid Ar.

Figure 3.   Pressure dependence of the mobility of electrons in liquid Ar.

atom interaction may be deduced. Referring the reader elsewhere for detailed descriptions of the experimental techniques,[3] we display in Figures 1, 2, and 3 the results of mobility measurements made in a time-of-flight instrument at very low electron concentrations (10^5 cm^{-3} $\sim$ 10^{-18} M). These data clearly show how the mobility of an excess electron in liquid Ar is decreased by increasing temperature (for $T < 115°$K) and increased by increasing pressure. Also, for $T < 115°$K, the drift velocity is proportional to the electric field strength.

Given the information cited, what can be said about the excess electron states of a simple liquid? We consider the development of a microscopic theory to explain these data. Clearly, before (a), (b), and (c) can be answered there are (at least) two major problems to be solved: (i) What is the effective atomic potential scattering the electron? (ii) Given the scattering potential, how do we determine the electron mobility and other transport properties?

An electron a distance R from an isolated atom of polarizability α induces on it a dipole of strength $\alpha e/R^2$ which, in turn, attracts the electron with a force of magnitude $2\alpha e^2/R^5$. Because of other electron–atom forces, the interaction of an atom and electron does not increase indefinitely as $R \rightarrow 0$. A convenient form for the electron–atom potential which accounts approximately for exchange forces and other short ranged interactions is

$$u_\alpha{}^0 = -\tfrac{1}{2} \frac{\alpha e^2}{(R^2 + R_\alpha{}^2)^2} \qquad (1)$$

where R_α is a measure of the strength of short ranged correlation and exchange forces. The value of R_α may be determined from the electron–atom scattering cross section in the limit of zero incident energy of the electron (scattering length). Lekner[4] has shown that when R_α is fixed in this fashion, the electron drift velocity as a function of field strength in gaseous Ar is very accurately reproduced up to electron energies of several volts.

(3) H. C. Schnyders, S. A. Rice, and L. Meyer, *Phys. Rev.*, **150**, 127 (1966).

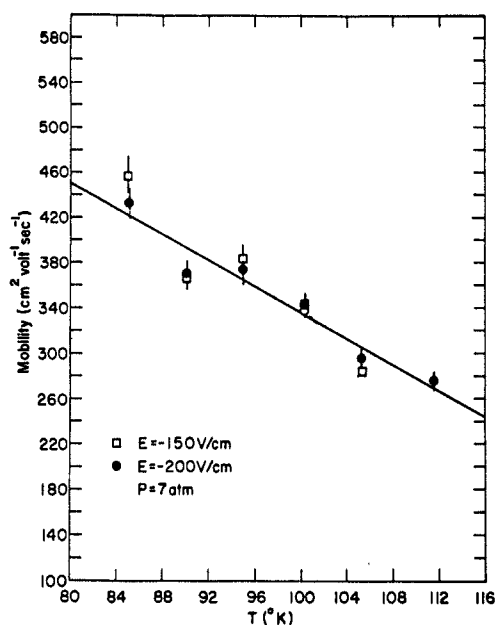(4) J. Lekner, *ibid.*, **158**, 130 (1967).
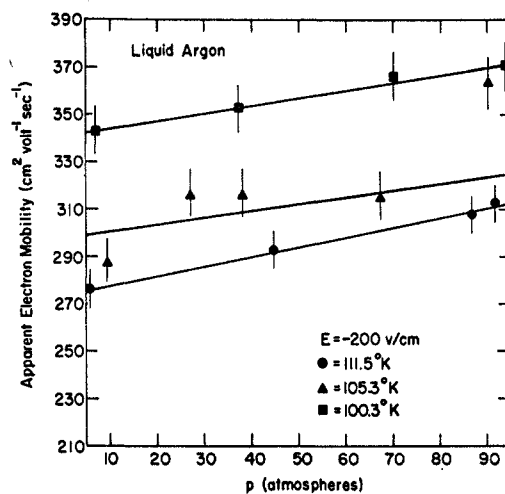
What is the polarization interaction between an electron and a particular atom in a liquid? To answer this question we must find the local field acting on the atom, which consists of the direct field and the sum of all other fields arising from dipoles induced on neighboring atoms. The problem is simplified by the fact that $v_A \ll v_e \ll v_{Ae}$, where v_A, v_e, and v_{Ae} are typical velocities of atoms in the liquid, of excess electrons, and of the bound atomic electrons. Because of the large differences between these velocities the motion of the atoms can be ignored in calculating the mutual screening effect of neighbors, and the motion of the excess electrons may be ignored in calculating the induced polarizations of the atomic electrons.

Consider, now, a point charge, $-e$, in a liquid composed of atoms of polarizability α. In the absence of other nearby atoms the electric field acting on an atom at R would be e/R^2 (see Figure 4). We define the average local field acting on the atom at R, and along
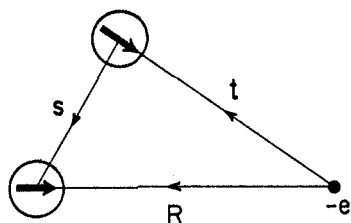
Figure 4. Relationships between the dipoles induced by a point charge in a simple liquid.

R, by $(e/R^2)f(R)$. But this local field is equal to the direct field (e/R^2), plus the contribution to the field arising from all the other induced dipoles in the liquid. Given that an atom is located at some point in the liquid, the probability of finding another atom in the volume element dt at distance s from the first is defined to be $\rho g(s)dt$, where ρ is the number density of atoms and $g(s)$ is the pair correlation function (radial distribution function). The field acting on this second atom is $(e/t^2)f(t)$, so that it carries an induced dipole of average strength $\alpha(e/t^2)f(t)$. After calculation of the component along **R** of the field at **R** arising from this dipole, and integration over all possible positions of the second atom, it is found that $f(t)$ must satisfy the equation[4]

$$f(R) = 1 - \pi\rho\alpha \int_0^\infty \frac{ds}{s^2} g(s) \int_{|R-s|}^{R+s} \frac{dt}{t^2} f(t)\Theta(R,s,t),$$

$$\Theta(R,s,t) = \frac{3}{2s^2}(s^2 + t^2 - R^2)(s^2 + R^2 - t^2) +$$

$$(R^2 + t^2 - s^2) \quad (2)$$

The function $g(s)$ includes the effects of induced dipole–induced dipole interaction. The solution of the linear integral equation (eq 2) gives the required self-consistent ensemble averaged local field. In deriving (2) it is assumed that the average effect of the dipole at **t** is the same as the effect of the average dipole at **t**, i.e., that fluctuations are negligible. It is also assumed that the atomic polarizability, α, is constant with distance, and that the atoms act as point dipoles. These restrictions are easily removed, but will not be considered herein. The solution of eq 2 for a realistic liquid structure is shown in Figure 5.[4] The variation of shielding with distance is particularly noteworthy. It is easy to show that the screening effects are contained entirely in the local field and therefore that the electron–atom polarization interaction in the liquid is, in place of (1)

$$u_\alpha(R) = -\frac{1}{2}\frac{\alpha e^2 f(R)}{(R^2 + R_\alpha^2)^2} \quad (3)$$

Of course, the total electron–atom potential is a sum of the polarization and Hartree (atomic) potentials. For a liquid like Ar the Hartree potential is little influenced by the state of aggregation, and we may assume that R_α in eq 1 and 3 is the same.

Because of the overlapping of potential fields in the liquid, the electron is never in field free space. Now, the average total potential near an atom at R_i is the sum of the atomic potential centered at R_i and the
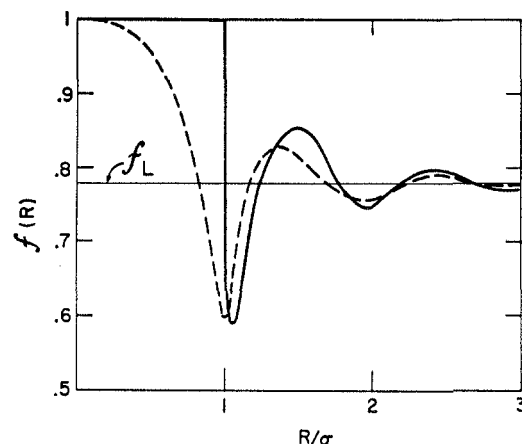

Figure 5a. The shielding function $f(R)$ in liquid Ar. The dashed line refers to the interaction of a point charge with neutral atoms, the solid line to the interaction of a charge with diameter equal to the atomic diameter.
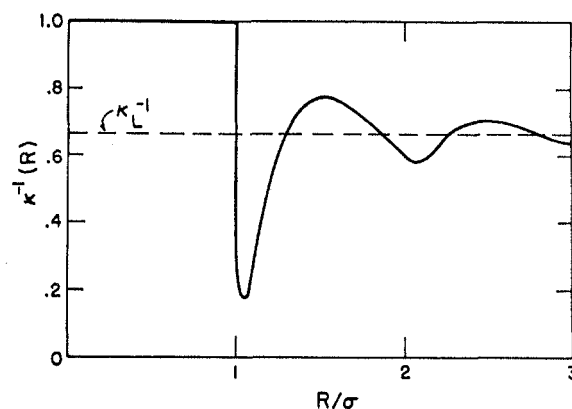

Figure 5b. The effective dielectric constant as a function of charge–charge separation in liquid Ar.

potential averaged over the positions of all other atoms (see Figure 6a). The effective potential for the electron scattering arises from deviations from the average potential and is defined by

$$u_{eff} = \langle u(R)\rangle - u_0; \quad R < R_m$$

$$= 0; \quad R > R_m$$

$$\left(\frac{\partial\langle u\rangle}{\partial R}\right)_{R=R_m} = 0$$

$$\langle u(R_m)\rangle \equiv u_0 \quad (4)$$

The drift velocity of an electron is determined by the cross section for momentum transfer. In Figure 6b we compare electron–atom momentum transfer cross sections calculated for the potential of eq 1 (labeled u_{gas}), for the potential of eq 2 (labeled u_1), and for the potential of eq 4 (labeled as u_{eff}). We notice that the cross sections corresponding to u_{gas} and u_1 vary considerably as the energy of the incident electron varies, whereas the cross section corresponding to u_{eff} is nearly independent of the electron energy. The cross sections corresponding to u_{gas} and u_1 lead to a drift velocity which depends more than linearly on the field strength at fields as small as 1–10 V/cm, whereas that corresponding to u_{eff} leads to a drift velocity which is linear
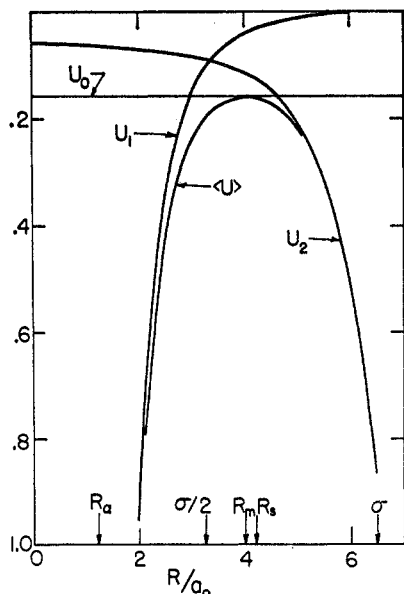
Figure 6a. Atomic potentials in liquid Ar. u_0, u_1, $\langle u \rangle$ as defined in text. u_2 is the average potential at R arising from all atoms other than that at R_1. R_s is defined by $4\pi R_s^3/3 = 1/\rho$.
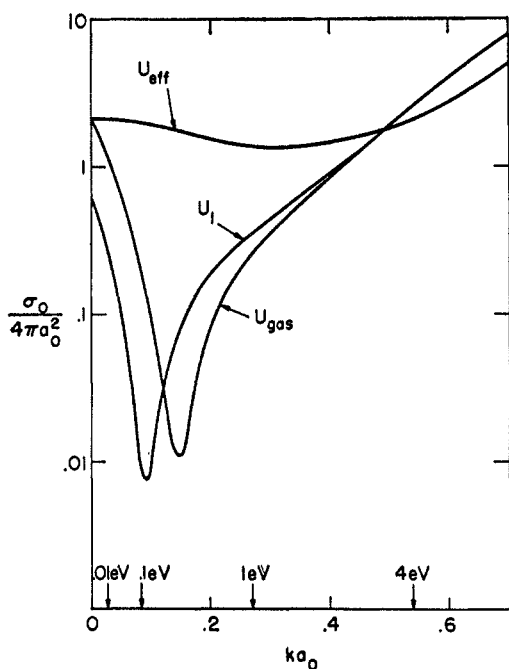
Figure 6b. The momentum transfer cross sections for the potentials defined by eq 1 (u_{gas}), eq 2 (u_1), and eq 4 (u_{eff}).

in the field strength up to much higher field strengths. As mentioned previously, the potential u_{gas} accounts for the drift velocity of electrons in gaseous Ar with high precision. The data presented in Figure 1 show that u_{gas} or u_1 will be inadequate to describe the liquid. In making these latter statements we are anticipating the results of the dynamical analysis of electron–atom scattering in the liquid. What is important to note is that, with the calculation of u_{eff}, we have answered question (i) to the accuracy required for our present purposes.

To answer question (ii) we adopt the single scattering

approximation, i.e., the scattered amplitude at any point is the coherent sum of amplitudes scattered from individual atoms, with neglect of the sum of amplitudes multiply scattered from different atoms. The wave incident on each atom is a wave packet which is approximated by a plane wave. The single scattering approximation is valid when the mean free path, Λ, is large compared with the de Broglie wavelength of the wave packet.

As a result of scattering, a particle-wave moving through a liquid transfers energy to all collective excitations of the system. In the single scattering approximation all the necessary information about the excitations is contained in the function that describes the probability of finding a molecule at R' at time t' given that a selected molecule was at R at time t. This function is called the Van Hove space–time pair correlation function, and its Fourier transform, denoted $S(\mathbf{k},\omega)$, is called the spectral function.[5] The probability of an electron scattering with loss of momentum $\hbar\mathbf{k}$ and energy $\hbar\omega$, say by creating a density fluctuation of momentum $\hbar\mathbf{k}$ and energy $\hbar\omega$, is proportional to the product of the single atom–electron differential scattering cross section and the spectral function. Now, the spectral function has certain general properties which are of use to us. First, the detailed balancing condition requires that

$$S(-\mathbf{k},-\omega) = e^{-\hbar\omega/k_B T} S(\mathbf{k},\omega) \qquad (5)$$

Equation 5 relates the cross sections for momentum and energy changes $\hbar\mathbf{k}$, $\hbar\omega$ and $-\hbar\mathbf{k}$, $-\hbar\omega$. Second, the integration of $S(\mathbf{k},\omega)$ over all ω leads to

$$\int d\omega\, S(\mathbf{k},\omega) = S(\mathbf{k}) \qquad (6)$$

Equation 6 simply states that the probability of scattering with momentum transfer $\hbar\mathbf{k}$, averaged over all possible energy transfers, is proportional to the structure factor $S(\mathbf{k})$, which is itself just the Fourier transform of the static excess pair correlation function $G(\mathbf{R},0)$ [$G(\mathbf{R},0) \equiv g(R) - 1$]. This is, then, just the same result as embodied in the familiar formula for the intensity of X-ray scattering from a liquid.[5] Equation 6 can be thought of as the average value of $(\omega)^0 = 1$, with respect to the function $S(\mathbf{k},\omega)$. The average value of ω

$$\hbar^2 \int d\omega\, \omega S(\mathbf{k},\omega) = \frac{\hbar^2 k^2}{2M} \qquad (7)$$

states that the average energy transfer in an interaction is exactly equal to the free-atom recoil energy for the same momentum transfer, independent of structure or thermal motion. Finally, the average value of ω^2

$$\int d\omega\, \omega^2 S(\mathbf{k},\omega) \cong 2k_B T \langle\omega\rangle \qquad (8)$$

is only approximately structure independent. Omitted from (8) are structure-dependent terms which are smaller by the ratio of the energy transferred in a collision ($m\epsilon/M$, where ϵ is the electron energy and

(5) D. Pines and P. Nozieres, "Quantum Liquids," Vol. I, W. Benjamin and Co., New York, N. Y., 1965.

m, *M* the electron and atom masses) to the thermal energy of an atom, k_BT, and hence negligible for our case.

Conditions (5), (6), (7), and (8) can now be used to derive a kinetic equation descriptive of the electron–liquid system. The important idea is that because the electron–atom mass ratio, m/M, is so small, an electron colliding elastically with an atom undergoes large deflections, but suffers only very small changes in energy. In the presence of an electric field we may expect a distortion of the distribution function for the electrons. The direction of the external field defines the axis about which distortion occurs. Let f($\mathbf{p},\mathbf{R}$) d$\mathbf{p}$d$\mathbf{R}$ be the number of electrons with momentum between $\mathbf{p}$ and $\mathbf{p} + $ d$\mathbf{p}$ in the volume d$\mathbf{R} = 4\pi R^2 dR$ about the point $\mathbf{R}$. If the electric field strength is $\mathbf{E}$ an accelerating force $e\mathbf{E}$ acts on each electron. This accelerating force is balanced by the forces arising from electron–atom collisions. As a result of this force balance a steady state is set up in which the number of electrons which have their momenta and positions changed so that they are no longer in the ranges $\mathbf{p}$ to $\mathbf{p} + $ d$\mathbf{p}$ and $\mathbf{R}$ to $\mathbf{R} + $ d$\mathbf{R}$ is just equal to the number of electrons whose momenta and positions are changed to be within $\mathbf{p}$ to $\mathbf{p} + $ d$\mathbf{p}$ and $\mathbf{R}$ to $\mathbf{R} + $ d$\mathbf{R}$.

By counting the number of electrons lost and gained by a volume element in phase space (d$\mathbf{p}$d$\mathbf{R}$) one finds the kinetic equation[6]

$$e\mathbf{E}\,\frac{\partial f}{\partial \mathbf{p}} = \rho\hbar \int d\Omega' \int d\omega\,\frac{p'}{p}$$

$$\sigma(\epsilon - \frac{\hbar\omega}{2},\theta)S(\mathbf{k},\omega)\,[e^{-\hbar\omega/k_BT}f(\mathbf{p}') - f(\mathbf{p})]\quad(9)$$

with $\sigma(\epsilon,\theta)$ the differential scattering cross section at energy ϵ, and θ the angle between $\mathbf{p}$ and $\mathbf{p}'$. It is found that the rate of transfer of energy is determined by a mean free path

$$\Lambda_\epsilon{}^{-1} = 2\pi\rho \int_0^\pi \sin\theta(1 - \cos\theta)\sigma(\epsilon,\theta)\quad(10)$$

which is independent of structure, while the rate of transfer of momentum is determined by a mean free path

$$\Lambda_p{}^{-1} = 2\pi p \int_0^\pi d\theta\,\sin\theta(1 - (\cos\theta))\times$$

$$\sigma(\epsilon,\theta)S(2k\sin\theta/2)\quad(11)$$

which does depend on the liquid structure. For thermal electrons, for which $2k\sin\theta/2 \approx 0.01$ Å^{-1}, the efficiency of energy transfer is greater than that of momentum transfer by the factor $1/S(0)$, which is very large in a liquid. In Ar at 84°K, $\Lambda_p \approx 140$ Å, while $\Lambda_\epsilon \approx 7$ Å.

The predicted drift velocity as a function of field strength is displayed in Figure 7. Good agreement between theory and experiment is obtained.[4]

A different test of the theory is provided by measuring the work required to inject an electron into the liquid (the binding energy of the electron). The

(6) J. Lekner and M. H. Cohen, *Phys. Rev.*, **158**, 305 (1967).
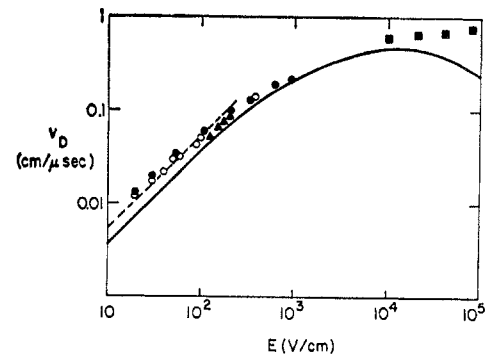

Figure 7. Drift velocity of electrons in liquid Ar as a function of the applied field strength. The solid curve is the prediction of the theory described in the text.
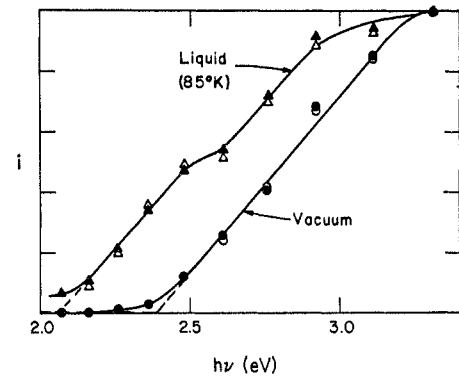

Figure 8. Photo-injected electron current in liquid Ar as a function of the illuminating photon energy. The surface from which the electrons come is Ba–Cs.

difference in energy resulting from the transfer of an electron from the vacuum to a liquid is just the mean potential acting on the electron in the liquid. By measuring the work function for emission of electrons into vacuum and into a liquid, Lekner, Halpern, Gomer, and Rice[7] find (see Figure 8) that the energy in the liquid is -0.33 eV relative to the vacuum. The theoretical calculations sketched lead to the prediction that this energy change is -0.46 eV.

The preceding considerations suggest that a conduction electron in liquid Ar is nearly free, and that the scattering can be described in terms of the combined effects of the collective polarization field and the superposed atomic fields, at least in the first approximation. As we shall see, a necessary condition for the validity of this deduction is that the electron–atom interaction be sufficiently small that geometric reorganization in the liquid is not energetically favored.

B. Bound Excess Electron States. When the properties of an excess electron in liquid He are studied,[8] it is found that the electron mobility is very much less than anticipated, *i.e.*, of the order of 10^{-2} cm^2 sec^{-1} V^{-1}. Furthermore, a study of the electron mobility as a function of density reveals that there is a drastic change as the density is increased toward the liquid

(7) J. Lekner, B. Halpern, S. A. Rice, and R. Gomer, *ibid.*, **156**, 351 (1967).

(8) F. Reif and L. Meyer, *ibid.*, **123**, 727 (1961); L. Meyer and F. Reif, *ibid.*, **119**, 1164 (1960); G. Careri, F. Scaramuzi, and J. O. Thomson, *Nuovo Cimento*, **13**, 186 (1959).
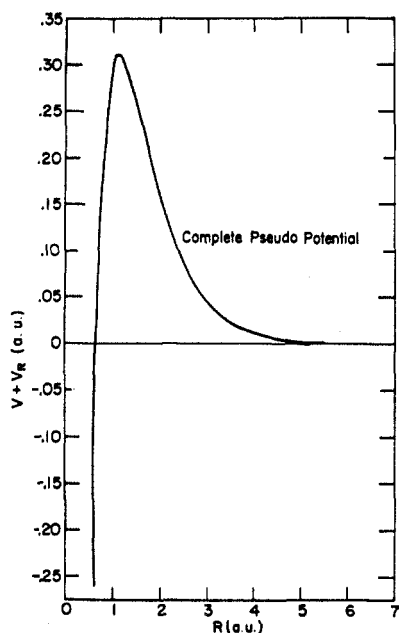
Figure 9. The effective electron–He atom repulsion.

Figure 10. The dependence of the electron mobility on gas density in He.

density (see Figure 9).[9] Examination of the electron–atom interaction reveals,[10] in this case, a very strong repulsion (see Figure 10), which in turn suggests that the quasi-free electron state may be of higher free energy than other excess electron states. What other configuration might be more stable than the free electron state? Note that the very need for consideration of new atomic configurations is a characteristic of the liquid state. Solids have a rigid lattice structure and can support shear stresses, whereas a liquid cannot support such stresses. Furthermore, the ease of atomic motion in a liquid is very much greater than in a solid. One measure of the difference in ease of motion is the self-diffusion coefficient. Typical values of this coefficient are 10^{-4} cm²/sec for a liquid and 10^{-8} cm²/sec for the corresponding solid near the melting point. Thus, it is to be expected that the structure of a liquid in the neighborhood of a force center will be different from that elsewhere in the fluid. Indeed, if the energy of interaction of an atom with the force center is large relative to the thermal energy, $k_B T$, large geometric rearrangements may be expected. Such rearrangements are not generally possible in solids where the crystal lattice corresponds to near close packing. In the case under consideration, an electron in liquid He, the electron–atom repulsion is as large as 10 eV, i.e., corresponds to $k_B T$ when T is 100,000°K. We are thereby led to consider the free energy of the state wherein radial repulsion of atoms by the electron creates a void surrounding the electron. Actually, the electron–atom repulsion in He is so large that even in solid He the state with a void probably has lower free energy than does the free-electron state. On the
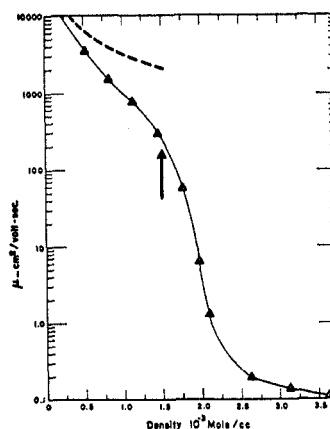
other hand, we have already shown that in liquid Ar the effective electron–atom interaction is attractive, and hence the free-electron state is of lower free energy than a void configuration.

We have now introduced the speculation that the bubble configuration is of lower or higher free energy than other configurations, depending on the substance. To verify this speculation we must compute the free energies of the several possible configurations of the system. This has already been done for the free electron in the last section. The work required to create a bubble around an electron depends on the volume of the bubble, the effective surface tension of the liquid (new surface area is created when a bubble is formed), and the increase in electron kinetic energy because of localization inside the bubble. Of course, the electron–atom repulsion is reduced as a result of enclosing the electron in a void, and whether or not bubble formation is thermodynamically favored depends on the balance between all the factors mentioned. The bubble model was first suggested by Careri and Feynman[11] and has since been studied by several other investigators. The most sophisticated calculations are those of Hiroike, Kestner, Rice, and Jortner,[12] who use the mathematical isomorphism between a pair product form of the wave function and the pair distribution function of a classical liquid in an external field to avoid the introduction of a surface tension, etc. All calculations are in agreement that: (a) Void formation is only favored at high density (see Figure 11). (b) The qualitative features of the trapped state are independent of whether or not the bubble boundary is fuzzy or sharp (see Figure 12) and of the gross magnitude of the surface energy (see Figure 13). In the calculations of Jortner, Rice, Kestner, Hiroike, and Cohen[12] the electron–atom interaction was calculated from pseudopotential theory. In quantitative terms, these calculations account for: (c) The mobility of the electron,

(9) J. Levine and T. M. Sanders, *Phys. Rev. Letters*, **8**, 159 (1962); *Phys. Rev.*, **154**, 138 (1967).
(10) N. R. Kestner, J. Jortner, M. H. Cohen, and S. A. Rice, *ibid.*, **140A**, 56 (1965).

(11) G. G. Kuper, *ibid.*, **122**, 1007 (1959); R. A. Ferrell, *ibid.*, **108**, 167 (1957); R. P. Feynman (quoted by C. G. Kuper); G. Careri, *Progr. Low Temp. Phys.*, **3**, 58 (1961).
(12) J. Jortner, N. R. Kestner, S. A. Rice, and M. H. Cohen, *J. Chem. Phys.*, **43**, 2614 (1965); K. Hiroike, N. R. Kestner, S. A. Rice, and J. Jortner, *ibid.*, **43**, 2625 (1965).
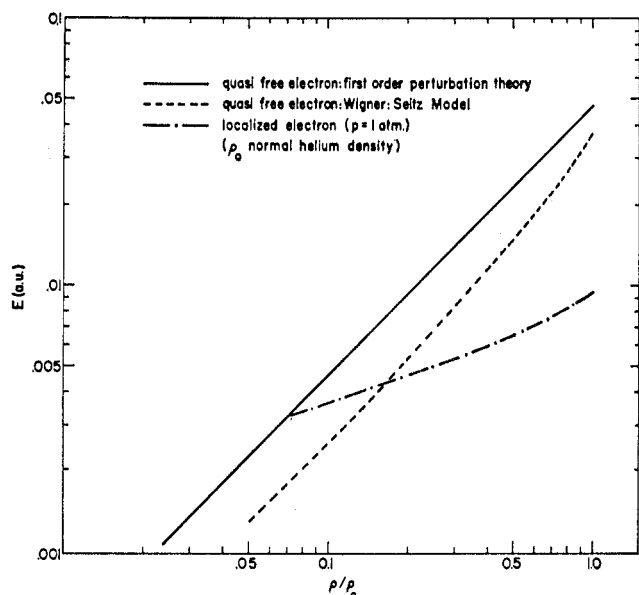
Figure 11. The free energies of a free electron and a bound (bubble) electron in He as a function of density. Note that the density at which the curves cross is close to the density marked by an arrow in Figure 10.

and its pressure and temperature dependence[13] (see Table I). (d) The energy required to inject an electron into liquid He (theory 1.07 eV, observed 1.05 eV).[14] (e) The density at which the transition from delocalized to localized electron states occurs (see Figure 10). (f) The size of the void as measured by electron–vortex line trapping experiments[15] (Table I).

Thus, in contrast to the case of liquid Ar, in the case of liquid He the excess electron states are nothing at all like free-electron plane wave states. We see, then, that the excited states of a simple liquid are complex and depend very strongly on the nature of the electron–atom interaction. It is just because the lack of a rigid lattice permits easy geometric readjustment of the local structure that the electronic states are so strongly coupled to the translational states of the liquid. We may anticipate a rich variety of behavior of excess electron (conduction electron) states, dependent on details of the electron–molecule interaction and perhaps on the nature of the internal states of the host molecules. We are only at the very threshold of understanding what these states are like or how they behave under external perturbation.

Thus far in sections IIA and IIB we have discussed those properties of the conduction electron states which are, at least qualitatively, understood. Examples of phenomena that are not understood include the following.

(13) L. Meyer, H. T. Davis, S. A. Rice, and R. J. Donnelly, *Phys. Rev.*, **126**, 1927 (1962); R. J. Donnelly, *Phys. Rev. Letters*, **14**, 39 (1965); B. E. Springett, *Phys. Rev.*, **155**, 139 (1967).
(14) M. A. Woolf and G. W. Rayfield, *Phys. Rev. Letters*, **15**, 235 (1965); W. T. Sommer, *ibid.*, **12**, 271 (1964).
(15) G. Careri, W. D. McCormick, and F. Scaramuzzi, *ibid.*, **1**, 61 (1962); B. E. Springett, D. J. Tanner, and R. L. Donnelly, *ibid.*, **14**, 585 (1965); R. L. Douglas, *ibid.*, **13**, 791 (1964); *Phys. Rev.*, **141**, 192 (1966); G. Careri, S. Consolo, P. Mazzoldi, and M. Santini, *Phys. Rev. Letters*, **15**, 932 (1965); G. W. Rayfield and F. Reif, *Phys. Rev.*, **136**, 1194 (1964); L. Bruschi, B. Maraviglia, and P. Mazzoldi, *ibid.*, **143**, 84 (1966).

Table I

Experimental and Theoretical Determinations of the Size of the Trapped Electron in Liquid He

(a) p = 0 atm

T, °K	R, Å	Comment
4.2	14.0	Exptl: from mobility measurements[a]
3.0	12.7	
1.7	14.5–16.0	Exptl: from trapping lifetime for negative ions by vortex lines[b]
1.9	13 ± 4	Exptl:[c] A. J. Dahm and T. M. Sanders
4.2	20	Theory: simple bubble model neglecting kinetic energy corrections[d]
0	12.5	Theory: full quantum mechanical calculation using pseudo-potential and pair wave function[e]
0	12.5	Theory: δ function pseudo-potential[f]

(b) Pressure Dependence at T = 1.7°K[g]

p, atm	R_{exptl}, Å	R_{theory}, Å
.0	16.0	(16.0)
4	13.3	13.7
8	12.2	12.6
12	11.4	11.8
16	10.8	11.2
20	10.2	11.0

(c) Temperature Dependence at p = 0 atm[h]

T, °K	$\mu(T)\eta(T)/\mu(4.2)\eta(4.2)_{exptl}$	$\mu(T)\eta(T)/\mu(4.2)\eta(4.2)_{theory}$
⁴He 4.2	1.00	1.00
3.0	1.19	1.22
2.0	1.37	1.32

T, °K	$\mu(T)\eta(T)/\mu(3.2)\eta(3.2)_{exptl}$	$\mu(T)\eta(T)/\mu(3.2)\eta(3.2)_{theory}$
³He 3.2	1.00	1.00
1.2	1.67	1.60

[a] L. Meyer, H. T. Davis, S. A. Rice, and R. J. Donnelly, *Phys. Rev.*, **126**, 1927 (1962). [b] P. E. Parks and R. J. Donnelly, *Phys. Rev. Letters*, **16**, 45 (1966). [c] A. J. Dahm and M. T. Sanders, *ibid.*, **17**, 126 (1966). [d] J. Jortner, N. Kestner, S. A. Rice, and M. H. Cohen, *J. Chem. Phys.*, **43**, 2614 (1965). [e] K. Hiroike, N. R. Kestner, S. A. Rice, and J. Jortner, *ibid.*, **43**, 2625 (1965). [f] R. C. Clark, *Phys. Rev. Letters*, **16**, 42 (1966). [g] Calculations based on use of the variational principle (B. E. Springett, M. H. Cohen, and J. Jortner, *Phys. Rev.*, in press). [h] Based on Stokes law analysis, hence representation as Walden product. Theory predicts that $\mu\eta$ is proportional to $\gamma^{1/4}$ where μ is the mobility, η is the viscosity, and γ the surface tension.

(a) In liquid Ar above T = 115°K and in liquid Kr for all temperatures thus far studied, the temperature dependence of the drift velocity is opposite to that expected (see Figures 14 and 15).[3] If it is a valid argument that the polarization field in the liquid sums to an almost constant field which does not influence the scattering, one cannot invoke a Ramsauer effect to explain these data. The fact that the drift velocity depends on the field strength more than linearly suggests that some feature of the scattering process is not properly accounted for in the analysis thus far developed.
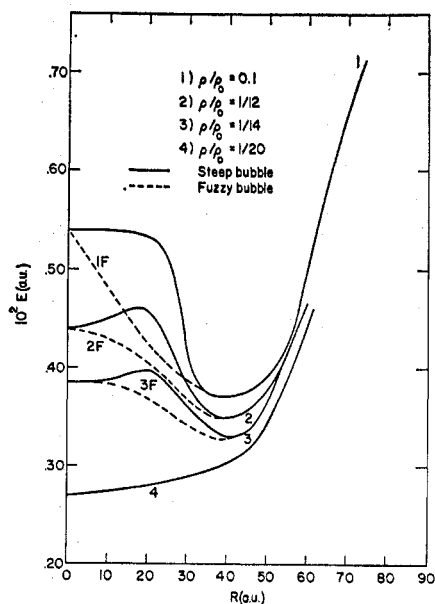
Figure 12. The effect of altering the bubble boundary density (fuzzy boundary) on the stability of the bubble configuration in He.
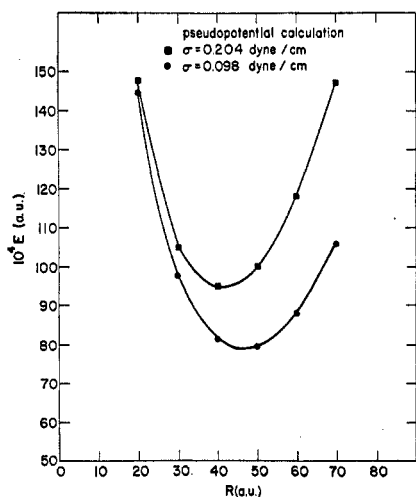
Figure 13. The effect of surface tension on the stability of the bubble configuration in liquid He.
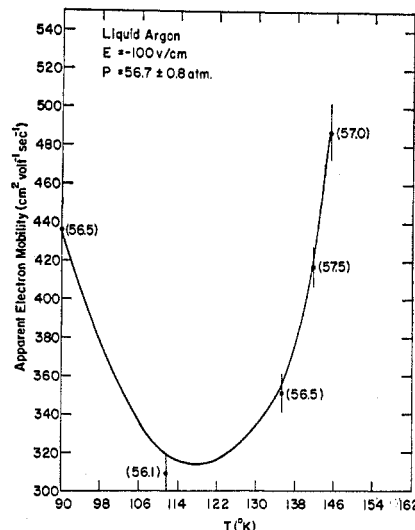
Figure 14. The effective mobility as a function of temperature in liquid Ar.

(b) There is observed to be a transition from localized excess electron states to delocalized excess electron states in systems such as Na in molten NaCl.[16] The nature of this transition is intimately related to the interplay between electron–electron and electron–ion (or atom) interactions. Many theoretical studies of the nonmetal–metal transition have been made,[17] and there is relevant experimental data from studies of impurity conduction in doped semiconductors.[18] However, these studies do not describe the role of the local ion or atom structure, and more particularly the possibility of local deformation, in determining the transition, since all use a lattice model with an assumed random distribution of impurity centers. It is possible that the differences between the electronic structures of the doped solid and liquid are as great as those between a pure solid and liquid. There are also studies of the properties of liquid metals,[17] but these use approximations not necessarily valid in dielectric liquids.

The solution of these and other problems may require new constructs and lead to new and more in-
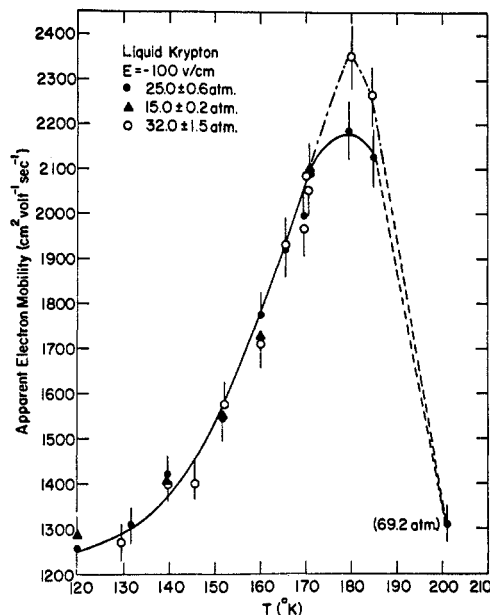

Figure 15. The effective mobility as a function of temperature in liquid Kr.

cisive understanding of the conduction electron states of all media. The problems which will be raised when systems with internal states are studied, e.g., polyatomic molecules, polymers, etc., can now only be foreseen with difficulty, but they too should be of great intrinsic interest and value in the construction of a complete theory of the electronic properties of matter.

III. Exciton States in a Monatomic Dielectric Liquid

We now examine some of the properties of the bound excited states of a simple liquid. It is convenient to consider several interrelated questions: (a) Do exciton states exist in a liquid? If such states do exist, what is

(16) H. R. Bronstein and M. Bredig, J. Am. Chem. Soc., 80, 2077 (1958); D. O. Raleigh, J. Chem. Phys., 38, 1677 (1963).

(17) There is an extensive literature on this subject. Some pertinent references are: H. M. James and A. S. Ginzberg, J. Phys. Chem., 57, 840 (1953); E. H. Kerner, Phys. Rev., 95, 687 (1954); P. Aigrain, Physica, 20, 978 (1954); M. Lax and J. C. Phillips, Phys. Rev., 110, 41 (1958); H. L. Frisch and S. P. Lloyd, ibid., 120, 1175 (1960); N. F. Moh and D. Twose, Advan. Phys., 11, 107 (1961); S. F. Edwards, Phil. Mag., 6, 617 (1961); T. Matsubara and Y. Toyazawa, Progr. Theoret. Phys. (Kyoto), 26, 739 (1961); H. Matsuda, ibid., 27, 811 (1962); S. F. Edwards, Proc. Roy. Soc. (London), A267, 518 (1962); R. Klauder, Ann. Phys., 14, 43 (1963); I. M. Lifshitz, Advan. Phys., 13, 483 (1964); F. Yonezawa, Progr. Theoret. Phys. (Kyoto), 31, 357 (1964); F. Yonezawa and T. Matsubara, ibid., 35, 357 (1966); ibid., 35, 759 (1966). T. Matsubara and T. Kaneyoshi, ibid., 36, 695 (1966); A. I. Gubanov, "Quantum Electron Theory of Amorphous Conductors," Consultants Bureau, New York, N. Y., 1965.

(18) H. Fritzsche and M. Cuevas, Phys. Rev., 119, 1238 (1960); H. Fritzsche, ibid., 99, 406 (1955); J. Phys. Chem. Solids, 6, 69 (1958); Phys. Rev., 120, 1120 (1960); 119, 1899 (1960).

the nature of the spectrum? (b) How do intermolecular interactions alter the spectrum of stationary states? (c) How is energy transferred in a liquid? (d) What is the nature of the relationship between the bound electron states and free electron states in the liquid? Clearly, questions (a) and (b) are intimately coupled to one another. Nevertheless, it is useful to proceed by first considering the properties of the bound states in the absence of scattering, and then to examine how the spectrum of states is altered by scattering processes.

A. Stationary States in the Absence of Scattering. From the most general point of view, it may be argued that on the scale of length determined by the wavelength of typical electronic transitions, both liquids and solids display translational symmetry. Indeed, it is only for distances of the order of 5–50 Å that differences in the local geometries of liquids and solids are obvious. Thus, provided that the wavelength of an incident electromagnetic wave is large relative to the range of molecular ordering, localized excitations at two points in the liquid are related by the phase factor $\exp(i\mathbf{k}\cdot\mathbf{R})$, where $\mathbf{k}$ is the excitation propagation vector and $\mathbf{R}$ the vector separation of the two points. We shall see later that even in the absence of scattering, the disorder in the medium leads to damping, but this can be shown to be small in the limit that $|\mathbf{k}|$ is very small relative to the reciprocal of the near neighbor distance.

To describe the internal structure of a possible exciton state we utilize the deductions of section IIA, i.e., we assume that the wave function of a conduction electron in liquid Ar is adequately represented by a plane wave. It is also convenient, but not necessary, to assume that the hole (ion core) is stationary. Although the hole will have finite mobility, in general it moves much more slowly than does the electron. Now the simplest approximation to the dynamics of the hole–electron pair is the following. A wave packet describing the electron is constructed by superposing, with appropriate coefficients, the free-electron plane wave eigenfunctions. The Hamiltonian of the electron–hole pair is then represented as a sum of the free-electron Hamiltonian and the screened Coulomb interaction. It is then readily shown that[19]

$$\frac{\hbar^2 k^2}{2m_e} A(\mathbf{k}) + \sum_{\mathbf{k}'} \tilde{u}_{\mathbf{k}-\mathbf{k}'} A(\mathbf{k}') = EA(\mathbf{k}) \qquad (12)$$

where $A(\mathbf{k})$ is the coefficient of the plane wave $|\mathbf{k}\rangle$ in the electron wave packet, and $\tilde{u}_{\mathbf{k}-\mathbf{k}'}$ is the Fourier transform of the screened Coulomb potential. If u were a simple Coulomb potential, (12) would be the momentum representation of the hydrogenic Schroedinger equation for the amplitudes $A(\mathbf{k})$. In this limit, the manifold of levels is hydrogenic, and the amplitudes in the wave packet expansion satisfy a hydrogenic equation. The results of section IIA clearly show that u is not a Coulomb potential, and therefore the energy level structure deviates from the hydrogenic structure. Using the screened Coulomb interaction appropriate to
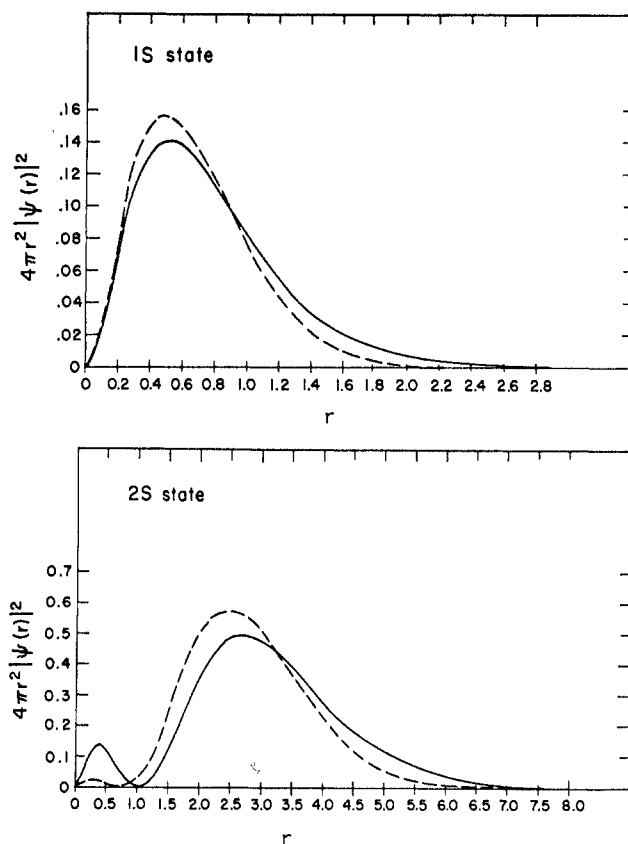
(19) S. A. Rice and J. Jortner, *J. Chem. Phys.*, **44**, 4470 (1966).

Figure 16. The charge density in s states of a quasi-hydrogen center in liquid Ar (——— constant dielectric constant, — — — correct shielding function).

liquid Ar, obtained by methods similar to those described earlier, the eigenstates of eq 12 having s symmetry have been determined.[20] The calculated charge densities for two states are shown in Figure 16 together with the corresponding hydrogenic charge densities. Clearly, the shifts in charge density are just those to be expected from the modified form of the Coulomb interaction.

The preceding simple calculations in no way elucidate the dependence of the energy of the exciton on the propagation vector, called the dispersion relation. To study the dispersion relation we resort to a different set of considerations. Suppose some one molecule in the liquid is excited, and that there is a nonvanishing dipole matrix element between the excited state and the ground state of the molecule. Then, because all the molecules in the liquid are identical, and each of the excited states of the N molecules is N-fold degenerate, excitation energy may be transferred from molecule to molecule. This resonance transfer of energy may be described in terms of the coupling between the transition dipole moments of the molecules. Because of the long range of the dipole interaction, dipolar motion is organized into collective dipolar polarization waves. In turn, the polarization waves may be interpreted as the classical equivalent of an exciton field. It may be shown, for example, that the van der Waals energy of a medium of nonoverlapping molecules arises from

(20) These calculations were made by Mr. Leon Glass.

the shift in the spectrum of dipolar fluctuations under the influence of their mutual interactions.[21] In making this last statement we have emphasized that the molecules concerned must be such that there is vanishingly small overlap of the electronic wave functions in both the ground state and the excited states. If there is overlap between the molecules when one is excited, additional interactions not included (*e.g.*, charge transfer) must be of some importance in determining the cohesive energy and other properties of the system. In the following we confine attention to the case that overlap of electronic wave functions is vanishingly small.

To compute the exciton dispersion curve in a simple liquid Nicolis and Rice[22] make use of the analogy between the classical polarization field and an exciton field. They consider an assembly of N atoms (molecules) in a volume V, and represent each atom by a Drude atom, *i.e.*, each atom is assumed to have s bound electrons of charge $ef_n^{1/2}$ ($n = 1, 2, \ldots, s$). Furthermore, each of the electrons is assumed to undergo undamped harmonic oscillation about the nucleus with frequencies ω_n ($n = 1, 2, \ldots, s$). The connection between this classical model and the correct quantum mechanical description is established by requiring f_n to be the oscillator strength corresponding to the transition of interest. To complete the specification of the model system we must describe the nature of the interatomic interactions. Nicolis and Rice assume that the total potential energy of interaction consists of: (a) a dipole–dipole interaction between the instantaneous transition dipoles on each atom and (b) a superposition of pair interactions corresponding to short-range repulsions and whatever residual high-order multipolar interactions may exist in the system.

The system just described has two features of interest. First, the equations of motion for the amplitudes of individual atomic dipoles, including the coupling terms, are linear when represented in the complete phase space of the system. Second, the range of the transition dipole–transition dipole interaction is very large relative to the range of the other interactions between atoms, and this interaction is also weak relative to the strength of the other interactions. The first observation suggests that the dipole amplitudes oscillate harmonically. Indeed, if a_n is the amplitude of the nth dipole, and we set

$$a_n = b_n e^{i\omega(\mathbf{k})t} \tag{13}$$

it is found that the coupled equations of motion lead to the following equation for the frequencies of the polarization waves

$$[-\omega^2(\mathbf{k}) + \omega_n^2]b_n = -\frac{1}{N}\sum_{j=1}^{s} f_j^{1/2} b_j U_\mathrm{d} \tag{14}$$

where U_d is the sum over all transition dipole–transition

(21) W. L. Bade, *J. Chem. Phys.*, **27**, 1280 (1957); W. L. Bade and J. G. Kirkwood, *ibid.*, **27**, 1284 (1957).
(22) G. Nicolis and S. A. Rice, *ibid.*, **46**, 4445 (1967).

dipole interactions. The second observation enables us to evaluate the partition function for the system in terms of an expansion in which the parameter is the ratio of the ranges of the short- and long-range interactions. This parameter is very small for our case. It is found that the spectrum has transverse and longitudinal modes with the dispersion relations[22]

$$\omega_l^2(\mathbf{k})\alpha_l(\mathbf{k},0) = \sum_n e^2 f_n - \left(\frac{m}{2\pi k_B T}\right)^{s/2} \prod_j \omega_j \sum_n \frac{e^2 f_n^{3/2}}{\omega_{nl}^2(\mathbf{k})} \times$$
$$\frac{1}{2\rho M k_B T} \int_\sigma^\infty dR\, \frac{G_f(R)}{R} \left[\frac{24\pi}{(kR)^3}\sin(kR) - \frac{24\pi}{(kR)^2}\cos(kR) - \frac{8\pi}{kR}\sin(kR)\right]$$

$$\omega_t^2(\mathbf{k})\alpha_t(\mathbf{k},0) = \sum_n e^2 f_n - \left(\frac{m}{2\pi k_B T}\right)^{s/2} \prod_j \omega_j \sum_n \frac{e^2 f_n^{3/2}}{\omega_{nt}^2(\mathbf{k})} \times$$
$$\frac{1}{2\rho M k_B T} \int_\sigma^\infty dR\, \frac{G_f(R)}{R} \left[\frac{-24\pi}{(kR)^3}\sin(kR) + \frac{24\pi}{(kR)^2}\cos(kR) + \frac{4\pi}{kR}\sin(kR)\right] \tag{15}$$

where α_l and α_t are the longitudinal and transverse components of the polarizability of the liquid. Transverse modes, in which the direction of propagation of the wave is perpendicular to the polarization, may be excited by light. Longitudinal modes, in which the direction of propagation of the wave is parallel to the polarization, are not excited by light, but are of importance in other phenomena. In eq 15 $G_f(R)$ is the excess pair correlation function, $g_f(R) - 1$, for a fluid with all components of the interaction except that arising from the transition dipole–transition dipole coupling. However, it is well known that the form of the pair correlation function is determined primarily by the repulsive interactions, so we may think of $G_f(R)$ as referring to the fully coupled fluid for all qualitative considerations. The lower limit of integration, σ, is taken to be a rigid core cut-off for simplicity.

Equation 15 has several interesting properties. These include: (a) The two transverse branches of the dispersion relation differ only through the difference between the unperturbed modes, ω_{nt_1}, ω_{nt_2}. (b) When the wave vector $\mathbf{k}$ is small, the change in spectrum introduced by the dipole–dipole coupling is parabolic in k. (c) There is a gap in the spectrum of transverse polarization waves at $\mathbf{k} = 0$, with the magnitude of the gap dependent on the magnitude of the dipole–dipole coupling. (d) In the limit $\pi/2 < k\sigma < \pi$, there is a change in sign of the frequency shift arising from dipole–dipole coupling and the frequency shifts of the longitudinal and transverse modes are of opposite sign. The change in sign results from a reversal of the orientation of the dipoles which are near neighbors to any selected dipole when $|\mathbf{k}|$ passes into the indicated range from larger to smaller values of $|\mathbf{k}|$. (e) Equation 15 suffices to determine the real part of the dielectric function. The imaginary part of the dielectric function may then be determined by use of a Kramers–

Kronig transform.[23]   An examination of the imaginary part of the dielectric function shows that the longitudinal polarization waves are damped, but that in the limit $\mathbf{k} \rightarrow 0$ the damping is small.   The damping arises from phase mixing which leads to instability of the collective polarization wave relative to the independent dipole oscillations, and is the analog of Landau damping in a plasma.[23]   Thus, in the absence of real scattering, we are justified in considering the polarization waves to be quasi-normal modes when $\mathbf{k} \rightarrow 0$, but because the Landau damping increases greatly as $|\mathbf{k}| \rightarrow \sigma^{-1}$ this interpretation would not be valid as $|\mathbf{k}| \rightarrow \sigma^{-1}$. Since optical excitation in the visible and ultraviolet regions corresponds to $|\mathbf{k}|\sigma \ll 1$, we conclude that in the absence of real scattering events in the liquid excitons can exist despite the disorder in the liquid phase.

The limitations and approximations of the theory of Nicolis and Rice resulting from the simple model used are, with one exception, of secondary importance. The one exception is the neglect of all scattering events. Although it has been shown that in the long-wavelength limit there exists a damping of the polarization waves arising from phase mixing, it is obvious that there must exist other more efficient damping mechanisms.   For the case of electronic excitation these will arise from the scattering of the excited electron by the fields of the surrounding atoms and are analogous to electron–phonon coupling in the crystalline solid. We therefore expect there to be a shift and broadening of the exciton spectrum calculated for the case of no scattering.   Before examining the limited experimental data we consider this problem.

B.   The Shift and Broadening of the Excitation Spectrum.   The simplest description of the effects of scattering is in terms of the hydrogenic model discussed at the beginning of section IIIA.   The argument leading to the conclusion that bound excited states exist is of considerable generality, relying only on the existence of plane wave states for the free electron.[24]   The bound states of the core-electron pair will be reasonably well defined if the mean free path of the electron is significantly larger than the orbital circumference. Scattering of the orbital electron by the atoms of the liquid causes a decrease in the lifetime of any given state and, in the limit that the scattering is so frequent that an orbit cannot be closed, no bound state can exist.   This limiting case is, of course, inconsistent

with the assumption that the free electron is in a plane wave state.

Let us assume that the scattering of the electron is sufficiently weak that bound states do exist.   We propose to compute the line width by setting[19]

$$\Delta\nu = \frac{1}{\pi\tau} \tag{16}$$

where the relaxation time, τ, includes the effects of coherence between the scattering amplitudes from different centers.   Rice and Jortner[19] assume (16) to be valid, and use for τ the relaxation time for momentum transfer considered in section IIA.   When the scattering potential is represented in terms of the zero energy scattering length, a, they find

$$\frac{1}{\tau(\mathbf{k})} = \frac{\rho h^2 a^2 k}{m} S(\mathbf{k}) \tag{17}$$

Because the magnitude of the electron wave vector in a bound state is related to the orbital velocity by $|\mathbf{k}| = m|\mathbf{v}|/h$ we conclude that the scattering time is inversely proportional to the speed of the electron. Thus, the electron makes fewer collisions in the tightly bound states, and the lifetimes of the states should decrease as the principal quantum number increases.

An immediate test of (16) and (17) is possible using the reflection spectrum of liquid Xe measured by Beaglehole.[25]   From the available electron–atom cross sections we are led to the prediction that hydrogen-like levels will be broadened, in liquid Xe, by about 0.1 eV.   Since the spacing between levels is only about 0.2 eV,[26] the set of exciton levels will appear as an unresolved spectrum.   As seen in Figure 17 this is in agreement with what is observed—the total width of the exciton manifold is about the same in liquid and solid, but resolution of the level structure in the liquid is not possible.

Although the preceding arguments are informative they do not come to grips with the fundamental problems which arise in describing the influence of scattering events on the exciton spectrum.   These difficulties are of two kinds: (i) It is necessary to describe dynamical processes in a liquid, for which the simplifications provided by the binary collision approximation (valid in a dilute gas) or the simple exciton–phonon linear interaction (valid in a class of crystals) are not available. (ii) There is coupling between the resonant interactions and nonresonant interactions in the medium.

At present no fully satisfactory solution to these problems is available, but there do exist approximate calculations that suggest which physical phenomena are of importance.   Popielawski and Rice[27] have studied an approximation, based on the Fano theory of line broadening,[1] to describe the shift and broadening of impurity spectra in a liquid.   In the general theory of Fano, the line shape function, which is determined

(23) R. Balescu, "Statistical Mechanics of Charged Particles," Interscience Publishers, New York, N. Y., 1963.

(24) Can the electron-atom interaction be so strong that no bound excited state exists? Our studies of liquid He reveal that geometric reorganization of the liquid can occur. This might lead to broadening so great that no bound state is possible, or to a void around the excited atom minimizing electron–atom interaction and hence the level broadening.   But a bubble can form only if the atoms have time to move away from the electron. The velocity of a thermal electron in He is small enough that on the time scale of electron motion the state of lowest free energy is achieved. On the other hand, the orbital velocity of a bound electron is very large, and the atoms can move only a small distance in the time required to complete an orbit.   In this limit electron–atom scattering does not lead to void formation.   We guess that the excited states of He are broadened but remain bound.

(25) D. Beaglehole, *Phys. Rev. Letters*, **15**, 551 (1965).
(26) G. Baldini, *Phys. Rev.*, **128**, 1562 (1962).
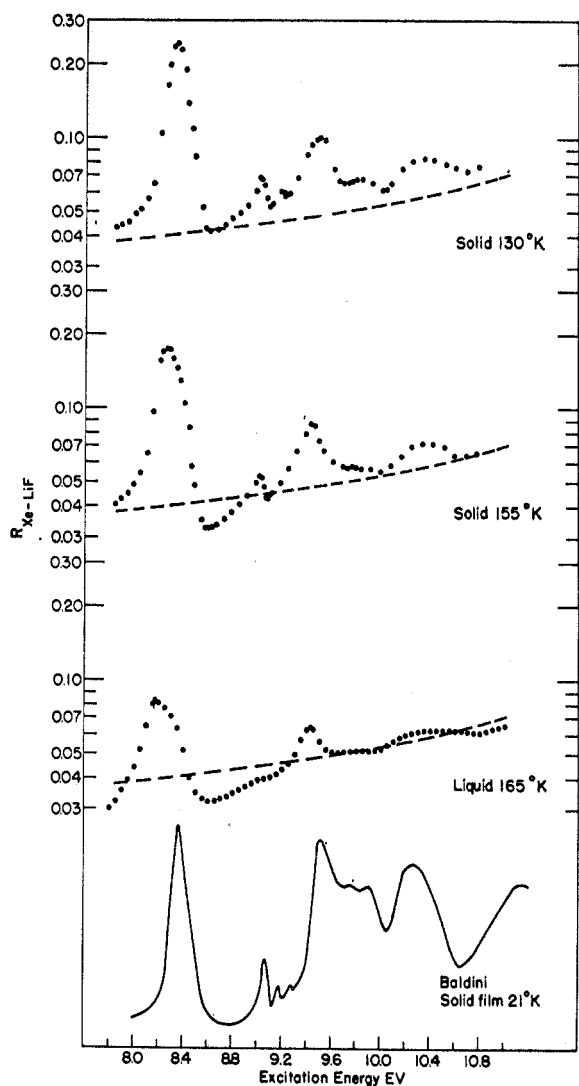(27) J. Popielawski and S. A. Rice, *J. Chem. Phys.*, **47**, 2292 (1967).

Figure 17. The reflection spectrum of liquid Xe.

by the autocorrelation function of the transition moment, is represented in terms of an average involving the transition dipole moment, μ, the density matrix of the full system ϱ, and the time evolution operator of the system. The time evolution operator introduces the effects of molecular collisions. In their study of the impurity spectrum Popielawski and Rice assume that: (a) the internal states of the perturbing host molecules do not influence the internal states of the guest molecule, (b) the translational motion–internal state coupling may be represented as a sum of pair interactions, (c) the pair interaction may be meaningfully (even if formally) separated into a strong short-range component and a weak long-range component, (d) guest–guest interactions may be neglected, (e) in the initial state, the internal state of the guest is uncorrelated with host translational states; the initial state of the system may then be represented by the product of the density matrix for the internal state of a guest molecule and the density matrix for the translational states of all molecules in the liquid, $\varrho = \varrho_i{}^\sigma \varrho_e{}^{\sigma+h}$, (f) the strong short-ranged component of the intermolecular force leads to dynamical events which may be described by a modified t-matrix (binary col-

lision) expansion, (g) the weak long-ranged component of the intermolecular force leads to dynamical events which may be described by a weak coupling expansion. The analysis is designed to provide an approximate representation of the line shape function descriptive of transitions localized on an impurity molecule present in a simple liquid. The general physical picture which emerges from the analysis is the following: the internal states of an impurity molecule in a simple liquid are influenced by a mean field (and its fluctuations) arising from the superposed long-range components of the guest–host interactions of many molecules, and also by quasi-binary encounters arising from the near approach of one guest–host pair moving in the fluctuating force field of all the other molecules. In the quasi-binary encounters the important component of the interaction is short ranged. It is important to note that both the mean field effect and the quasi-binary encounters are defined so as to include the structure of the liquid in the local equilibrium approximation. The quasi-binary collision term contains the influence of all sequences of successive dynamically uncorrelated encounters.

What can be said about the list of assumptions used by Popielawski and Rice? Of the set of assumptions listed above (a) is not essential and could be removed, at least formally, though reduction of the final formulas to practical form is certainly complicated by the inclusion of internal state–internal state interactions. Also, (d) is unimportant, and is included so as to justify neglect of resonance interactions between the guest molecules. The important assumptions are (b), (c), (e), and (f) and (g).

Assumption (b), that the translational motion–internal state coupling may be represented as a sum of pair interactions, is valid if the following conditions are satisfied. Let the eigenstates of the complete system be represented as the product $\phi(t)\Lambda(t)$, where $\phi(t)$ represents the internal states of a guest molecule and $\Lambda(t)$ the translational states of all molecules in the system. Further, let $\mathcal{U}$ be the intermolecular interaction operator, and $\mathcal{V}$ the interaction operator coupling the internal states of a guest molecule to the translational motions of all molecules in the system. As defined, $\mathcal{U}$ is independent of the internal states of the guest molecules, while $\mathcal{V}$ is just that part of the interaction which depends on the actual state of the guest. The effective interaction potential is seen to be just the average of $\mathcal{U} + \mathcal{V}$ over all possible host molecule trajectories. If this interaction does not involve dipole–dipole coupling, or some other many-body force, then the decomposition of $\mathcal{V}$ into additive pair interactions is valid. Dipole–dipole coupling must be omitted because in a dense medium containing many dipoles one must consider the reaction field of a dipole, and this field arises from a many-body effect. Although there are many-body contributions to the van der Waals interaction, it is probably sufficiently accurate for our present purposes to neglect these terms.

When the product states described above are used,

and only internal transitions in the guest molecules considered, the average over translational coordinates is performed using (e). This assumption is equivalent to the statement that $\varrho_e{}^{g+h}$ ($\varrho \equiv \varrho_i{}^g \varrho_e{}^{g+h}$) is diagonal in all of the center of mass coordinates of all molecules in the system. If the mean interaction between the guest molecule internal states and the host molecules is small compared with the thermal energy, this approximation will be accurate.

Assumption (c), referring to the possibility of representing the pair interaction as a superposition of a short-ranged and a long-ranged interaction, plays a crucial role in the considerations of Popielawski and Rice. Clearly, this will only be valid if the region in which strong rapidly changing interactions occur is restricted to pair separations which are small relative to the spacing between molecules. Long-range strong or weak interactions which involve many molecules can be described by the mean field term and fluctuations about the mean field. However, insofar as there is meaning to quasi-binary encounters, there must be a region of pair separation wherein the pair interaction is much larger than the interaction arising from the superposed fields of the other surrounding molecules. The effect of many strong, short-ranged repulsions is then synthesized by considering successive uncorrelated quasi-binary encounters. The kinetic theory of liquids developed by Rice and Allnatt utilizes the same subdivision of the intermolecular potential.[28] Studies of the kinetic equation for a simple liquid lead to the conclusion that the frequent superposed weak interactions which influence the molecular trajectory between strongly repulsive encounters suffice to destroy the correlation between successive binary encounters. The success of the Rice–Allnatt theory in the computation of zero frequency transport coefficients argues strongly for the accuracy of the subdivision of the interaction potential when dealing with ground-state interactions. In the absence of extensive overlap it seems likely that the same subdivision is useful when the interaction between a ground state and an excited state system is considered. Once adopted, the subdivision of the interaction leads us to considerations analogous to those introduced in the impact approximation.[5] In the impact approximation, the impurity molecule suffers, on the average, only a weak perturbation. Perturbations of the impurity by strong collisions are well-separated in time, and the duration of a strong collision is supposed small relative to the time between such collisions. In the Popielawski–Rice theory, during the intervals between strong collisions the impurity is influenced by the mean field, which leads to a static broadening of the spectrum. It has been assumed that the mean field is weak, hence the states between quasi-binary encounters serve as a basis to define the states which are strongly mixed by the quasi-binary encounter. This deduction

is valid if the relevant portion of the spectrum is still resolved, even after inclusion of the effects of strong collisions.

The kinetic theory of liquids, previously referred to, provides evidence that in a liquid such as Ar quasi-binary encounters are well-separated on the time scale which defines relaxation in the weak, long-ranged, molecular field. Provided that the interaction between an excited impurity molecule and a ground-state host molecule is similar in character to the ground state–ground state interaction, the results of the kinetic theory support assumption (c) and its implications.

For assumption (e) to be valid, it is necessary that the effect of the internal states of the impurity molecule on the host molecules is quickly dissipated, and is insignificant during a quasi-binary encounter. Finally, provided that assumptions (f) and (g) are valid, (e) will also be valid, to first order, in the description of the static field broadening.

Although the preceding arguments lead to a simple description of the relationship between the line shape function and the intermolecular interactions for the case of impurity spectra, they are not readily extended to the case where resonant interactions are important, i.e., the pure liquid. Even in the absence of overlap of the electronic wave functions of neighboring molecules, the mixing of effects arising from resonant and nonresonant interactions leads to complicated coupling phenomena. Considerable insight into the general structure of the theory can be obtained from an examination of a simple model. Even though the properties of the model considered depart in detail from the properties of real systems, the most important consequences of the mixing of resonant and nonresonant interactions can be elucidated and the complications attendant to a complete (but as yet unavailable) analysis avoided.

Using a kinetic equation approach, Nicolis and Rice[29] have extended the previously described analysis of the spectrum of polarization waves in a liquid of Drude molecules. As in the Popielawski–Rice treatment,[27] the interactions between the molecules are separated into components, in this case a short-ranged repulsive interaction, a resonance interaction represented as a sum of transition dipole–transition dipole couplings, and a residual soft (multipolar) interaction. In the case of an impurity spectrum the derived kinetic equation displays the effects of scattering from the short-ranged repulsions in a modified Enskog kernel and from the residual soft potential in a Fokker-Planck-like term.[28] It is found that even when the short-ranged repulsions are represented as hard core interactions, there is both a shift and a broadening of the spectrum. The average soft field contributes only a shift in the oscillator frequency, and fluctuations about the mean field lead, again, to both a shift and broadening of the spectrum. These deductions are in agreement with those of Popielawski and Rice.

Of most interest, however, is the influence of

(28) For a summary of the kinetic theory of liquids see: S. A. Rice and P. Gray, "The Statistical Mechanics of Simple Liquids," John Wiley and Sons, New York, N. Y., 1965.

(29) G. Nicolis and S. A. Rice, in preparation.

the resonance coupling in the pure liquid, which was not treated by Popielawski and Rice. It is found that the dipole–dipole coupling of a pair of molecules is shielded by the presence in the liquid of other molecules which are also coupled to the pair by dipolar interactions. The shielding depends on both the dipolar interactions and the short-range order in the liquid, as well as the internal state of the molecules. Further, the kinetic equation contains a term which plays the role of a friction coefficient. The evolution of the internal states of a molecule is now described by an operator which includes: (a) all dynamical events corresponding to interactions in the continuum states lying above the bound states that take part in energy transfer, (b) the scattering of molecules in excited bound states, in general with excitation transfer, and (c) the formation of new bound states. The events described by (a), wherein all bound states remain unchanged and there is a modification of the continuum states arising from scattering, correspond to the limit in which the internal degrees of freedom of the molecule are organized into Frenkel-type excitation waves, i.e., although collective states of the liquid exist they have one to one parentage in the states of the free molecule. In contrast, (c) describes the formation of Wannier excitons, and (b) an intermediate case.[30] Although the theory, in principle, permits passage from the tight binding Frenkel limit to the weak binding Wannier limit, the neglect of overlap and exchange effects limits the accuracy of the description of the transition. For this reason, Nicolis and Rice confine attention to the Frenkel limit. In this limit, it is shown that the resonance interaction leads again to both a shift and broadening of the spectrum of polarization waves. The dispersion relation still displays both longitudinal and transverse branches, and a preliminary estimate of the efficiency of resonance coupling vs. the internal state–translational motion coupling suggests that the friction associated with the resonance coupling is smaller than the friction associated with internal state–translational motion coupling. The theory described is too general and involves too many approximations to make any but simple deductions of the type described.

A simplified treatment of the shift and damping of polarization waves has been presented by Rice, Nicolis, and Jortner.[31] Because the electron in a bound state moves very rapidly only small displacements of the atoms are possible during the time between electron–atom interactions. This observation can be used to simplify the description of the excited atom–ground-state atom dynamics. For the case of an impurity in the liquid, the spectrum is predicted to be different in the limits of weak electron–atom coupling and strong electron–atom coupling. In the strong coupling limit the excitation spectrum consists of a superposition of Gaussian lines. In the weak coupling limit the excita-

tion spectrum consists of lines with a Lorentzian modulated Lorentzian shape. For the case of the pure liquid it is found that the line shapes in the weak coupling limit are the same as in the impurity spectrum in the weak coupling limit. Thus, the frequency dependence of the line shape is different from the familiar Lorentzian encountered in the theory of exciton damping in crystalline solids. As noted, what is found in the weak coupling limit is an inverse fourth power dependence on the frequency ω, in the form of the product of two Lorentzians. The first of these describes the frequency dependence of the electron–atom interaction for a given initial configuration while the second, which modulates the first, takes into account the "random" motion of the atoms in the fluid. That the line shape of a transition in a dense medium should depart considerably from a Lorentzian is also predicted by the Berne–Frisch treatment of the relaxation of a diatomic molecule in a host liquid.[32] Finally, numerical estimates by Rice, Nicolis, and Jortner lead to the conclusion that the lifetimes of typical electronic excitations in a liquid are of the order of magnitude of ten times shorter than the lifetime of typical thermal excitations in the liquid. Insofar as the theory is reliable, this suggests that even in the presence of scattering excitons can exist in certain liquids.

The experimental data available are inadequate to test even the limited theory described. As previously mentioned, Beaglehole has studied the reflection spectrum of liquid Xe and compared this with the spectrum of solid Xe. There is evidence for a collective excitation in the liquid corresponding to the known Wannier-like excitations of the solid (see Figure 17) and the inferred level broadening is about that predicted by the simple theory. More recently, Jortner and co-workers[33] have studied the absorption spectrum of Xe in Ar and have also shown that the broadening of the impurity spectrum is in agreement with the predictions of the simple theory.

Given that exciton states do exist in a liquid, i.e., that molecular scattering events do not so shorten the lifetime of collective excitations that these cease to be meaningful in the description of the liquid, it is to be expected that energy can be transferred over long distances. There exist, at present, no detailed studies of energy transfer in simple liquids. Meyer, Jortner, Rice, and Wilson[34] have studied the consequences of exciting liquid He, Ne, Ar, Kr, and Xe with α particles. The emission spectra of all the liquids are red shifted (from 2 eV to 6 eV) and, by comparison with known gas spectra, the emitting species is identified in each case as the excimer Ne_2^*, Ar_2^*,.... (see Figure 18). The binding energy of the He_2^* is 2.6 eV,[35] and of the other excimers presumably less, but enough to promote a change in local liquid structure resulting in trapping of the excitation energy. If the lifetime of

(30) S. A. Rice and J. Jortner, "Physics and Chemistry of The Organic Solid State," Vol. III, John Wiley and Sons, New York, N. Y., 1967, p 201.
(31) S. A. Rice, G. Nicolis, and J. Jortner, J. Chem. Phys., in press.

(32) B. J. Berne and H. L. Frisch, Phys. Rev., 160, 202 (1967).
(33) Private communication from Professor J. Jortner.
(34) L. Meyer, J. Jortner, S. A. Rice, and E. G. Wilson, J. Chem. Phys., 42, 4250 (1965).
(35) M. L. Ginter, ibid., 42, 561 (1965)

Figure 19. The emission spectrum of liquid He doped with O_2 and N_2, excited by α-particle bombardment of He.
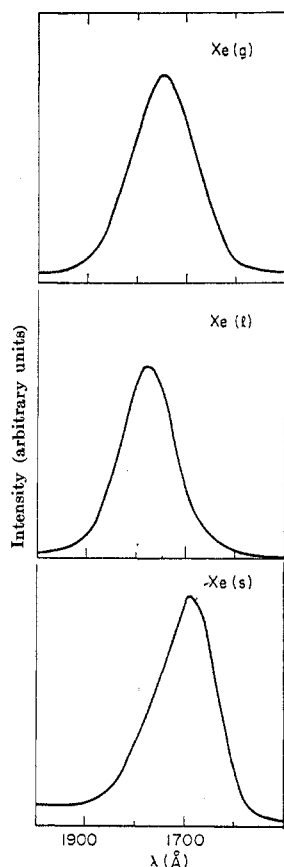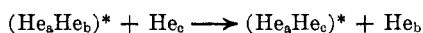

Figure 18. The emission spectrum of Xe.

the molecular excited state is long relative to the time required for molecular displacement, and if an excimer can be formed, it seems likely that excitation energy can be self-trapped with high efficiency. Clearly, the situation in which self-trapping is generated by exciton–fluid coupling is analogous to the electron self-trapping in liquid He. Just as the excess electron states of He and Ar are fundamentally different, corresponding to trapped and free electrons, we must expect to find liquids in which energy transfer does occur with ease. Each case must be examined separately.

Of course, if the excimer species is long lived, it can serve as the carrier of energy. Indeed, a phenomenon attributable to energy transfer *via* intermediacy of He_2^* was discovered by Meyer, Jortner, Wilson, and Rice.[36] When liquid He is doped with N_2 and O_2 (present as small solid particles) the emission spectrum of the α-particle irradiated liquid arises from the transitions $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ and $C^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ of N_2 and O_2, respectively (see Figure 19). These are the transitions that would be excited by triplet He_2^*, and since the lowest triplet state of He has a very long lifetime (many seconds) it is reasonable to suppose that diffusion of He_2^* can serve to transfer electronic excitation energy over long distances in liquid He. It should be noted that although we consider it unlikely we cannot, at present, rule out atom interchange–energy exchange

$$(He_aHe_b)^* + He_c \longrightarrow (He_aHe_c)^* + He_b$$

or other mechanisms of energy transfer. Much more experimental work will be required before energy transfer in liquids can even be outlined for detailed study, let alone interpreted completely.

It is clear that there remain many problems in the description of the exciton states of a liquid. These include: (a) development of a formalism that allows the treatment of overlap and charge-transfer phenomena, (b) development of an understanding of the relationship between scattering processes and excimer formation, (c) accumulation of a body of experimental data with which to test the ideas thus far put forward and to guide the development of an improved theory, (d) development of an understanding of the relationship between the transition from localized to delocalized excitation states and the nature of energy transfer in the liquid, (e) development of a more realistic theory in which the simplifications of the Drude model of the molecule and other approximations are removed.

It is my opinion that we are at the threshold of a vast expansion of our understanding of the electronic properties of liquids and other disordered systems. So little is known, either from experiment or theory, that almost any effort is likely to be rewarded with unexpected results. This field, unlike others, requires more than anything else new concepts and constructs, and novel ways of interpreting strongly coupled phenomena. For some time it is likely that only qualitative interpretations of data will be possible, but with the steady accumulation of information and the creation of new interpretations, we may look forward to the development of a quantitative theory encompassing in its scope the description of the properties of both ordered and disordered systems. Given that many systems of interest, including essentially all biological systems, are disordered to some extent, the importance of a deeper, broader, and more comprehensive description of the electronic properties of disordered systems cannot be overestimated.

(36) L. Meyer, J. Jortner, S. A. Rice, and E. G. Wilson, *Phys. Rev. Letters*, **12**, 415 (1964).