

Excess electrons in condensed media. A model for migration in dilute molecular solutions

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A theoretical framework is developed for analyzing the migration of excess electrons in one-component molecular solids and liquids. The mean-square distance traveled by an electron as a function of time $\langle r^2 \rangle_t$ is shown to depend both upon the diffusion of the solvent molecules and the rate of hopping and tunneling of the electron from one molecule to another. By introducing several physically motivated approximations, the quantities appearing in the final expression for $\langle r^2 \rangle_t$ are expressed in terms of solvent structure information (distribution function) and the electron-solvent interaction potential. Planned extensions of this initial work are also discussed.

I. INTRODUCTION

The behavior of excess electrons in a wide variety of atomic and molecular liquids and solids has received a great deal of experimental and theoretical attention.¹ Two of the solution's physical characteristics which are frequently probed are the optical absorption spectra² and electron transport (mobility and diffusion) rates.³ Although theoretical models⁴ have been developed to treat the above properties for special cases (e.g., very polar solvents, nonpolar solvents, noble gas solvents, etc.), no one has yet achieved a unifying framework in terms of which each special class of solvent can be treated by making appropriate physical approximations. It is the purpose of this paper to put forth such a unifying theoretical framework for treating the mass transport of excess electrons in molecular solvents. In future publications, extensions will be made to the treatment of mixed solvents and to the optical spectra of the excess electrons. In the present work attention is limited to very dilute solutions (for which electron-electron interaction can be ignored) involving only one kind of solvent molecule. In Secs. II and III the combined electron-solvent Hamiltonian which is employed in this work is introduced and written in a form which makes the analysis to follow as straightforward as possible. Section IV contains the primary development of this paper in which the migration rate of the excess electron is related to solvent structure and electron-solvent interaction information. Section V provides an overview of the results and an indication of the directions in which this research project is progressing.

II. THE COMBINED ELECTRONIC AND MOLECULAR HAMILTONIAN

For describing a collection of N identical molecules, whose center-of-mass positions are $\{\mathbf{R}_i\}$ and whose orientations and internal geometries are $\{\Omega_i\}$ and $\{\mathbf{Q}_i\}$, respectively, the following Hamiltonian is appropriate:

$$H_N = \sum_{i=1}^N \left(\frac{P_i^2}{2M_i} + U(\mathbf{Q}_i) + \frac{1}{2} \sum_{j \neq i}^N V(\mathbf{X}_i, \mathbf{X}_j) \right) \quad (1)$$

Here $\{\mathbf{X}_i\}$ represents collectively $\{\mathbf{R}_i, \Omega_i, \mathbf{Q}_i\}$; \mathbf{P}_i is the

total (translational, rotational, vibrational) momentum of the i th molecule; $U(\mathbf{Q}_i)$ is the internal potential energy function (vibrational, torsional); and $V(\mathbf{X}_i, \mathbf{X}_j)$ is the intermolecular potential energy. The Hamiltonian describing the motion of a single excess electron in the presence of these N molecules is

$$H_e = -\frac{1}{2} \nabla_{\mathbf{r}}^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}_i) \quad (2)$$

where \mathbf{r} represents the position of the electron and $u(\mathbf{r}, \mathbf{X}_i)$ is the interaction potential between the electron and the i th molecule. It should be pointed out that by employing an energy-independent form for u one is indeed making an approximation. This approximation involves not explicitly treating all of the electrons belonging to the N solvent molecules in order to deal with a one-electron Schrödinger equation, as well as not using a non-local energy-dependent electron-molecule effective potential. Such a proper potential is well known⁵ as the optical potential or self-energy which is widely used in electronic structure⁶ and electron scattering⁷ investigations. This self-energy has a component, known as the static exchange potential, which is composed simply of the Coulomb and exchange terms in the Hartree-Fock electron-molecule interaction. Another contribution to the self-energy arises from the long-range interactions (charge-dipole, charged-induced dipole, etc.). In the present work, we assume that $u(\mathbf{r}, \mathbf{X}_i)$ contains proper short-range Coulomb, exchange, and nuclear attraction contributions as well as good approximations to the long-range electron-molecule interaction. However, all energy-dependent terms in u are ignored. The principal justification for making this approximation is the reasonably high success rate⁷ of electron-molecule collision studies which employ potentials including only static exchange and polarization effects.

In treating the combined electron-molecule Hamiltonian $H = H_N + H_e$, it is useful to expand the electron-coordinate dependence of H in terms of a (presumably complete) basis. For reasons which should become obvious shortly, this basis is chosen to consist of an orthonormal set of orbitals $\{\phi_\alpha(\mathbf{r}, \mathbf{X}_i)\}$ localized on the individual molecules plus a set of continuum orbitals $\phi_{\mathbf{k}}(\mathbf{r})$ which are orthogonalized to the $\{\phi_\alpha(\mathbf{r}, \mathbf{X}_i)\}$. The localized orbitals could, for example, be Wannier orbitals⁸ formed from a set (hence the index α) of unfilled molecular or-

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bitals on each of the N solvent molecules. The continuum orbitals might simply be plane waves which have been made orthogonal to the localized orbitals, or they could be Wannier-like combinations of such orthogonalized plane waves.⁹ In terms of this basis, the electronic Hamiltonian H_e is

$$H_e = \int \psi^*(\mathbf{r}) \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}_i) \right) \psi(\mathbf{r}) d\mathbf{r} \quad (3)$$

where the (second-quantized)¹⁰ field creation operator $\psi^*(\mathbf{r})$ is expressed as

$$\psi^*(\mathbf{r}) = \sum_{j,\alpha} \phi_{\alpha}^*(\mathbf{r}, \mathbf{X}_j) a_{j\alpha}^* + \int d\mathbf{k} \phi_{\mathbf{k}}^*(\mathbf{r}) a_{\mathbf{k}}^* \quad (4)$$

The $a_{j\alpha}^*$ and $a_{\mathbf{k}}^*$ are Fermion creation operators corresponding to creating an (excess) electron in the orbitals $\phi_{\alpha}(\mathbf{r}, \mathbf{X}_j)$ and $\phi_{\mathbf{k}}(\mathbf{r})$, respectively. For notational convenience the sets $\{a_{j\alpha}^*, a_{\mathbf{k}}^*\}$ and $\{\phi_{\alpha}(\mathbf{r}, \mathbf{X}_j), \phi_{\mathbf{k}}(\mathbf{r})\}$ will be denoted by $\{a_n^*\}$ and $\{\phi_n(\mathbf{r})\}$, respectively.

III. THE CANONICAL TRANSFORMATION

In describing the evolution of an electron which is initially created in the presence of N solvent molecules whose spatial locations, orientations, and momenta are distributed according to an equilibrium probability density, it is useful to introduce the concept of a dressed electron.¹¹ A dressed electron consists of an electron which has been created in an environment of solvent molecules whose coordinates $\{\mathbf{X}_i\}$ have already been adjusted to "feel" the presence of the nascent excess electron. To further develop this concept, let $\mathbf{X}_i(m)$ designate the

values of the coordinates of molecule i which yield the minimum potential energy ($U + V + u$) for the N -molecule system in the presence of a single excess electron which is spatially distributed according¹² to the charge density $|\phi_m(\mathbf{r})|^2$. Further, let $\{\mathbf{X}_i^0\}$ denote the minimum-potential-energy coordinates for the N solvent molecules in the absence of the excess electron. Then the canonical transformation of the Fermion operators

$$\exp(S) a_m^* \exp(-S) \equiv A_m^* \quad (5)$$

with

$$S \equiv \sum_n a_n^* a_n \sum_{i=1}^N [\mathbf{X}_i(n) - \mathbf{X}_i^0] \cdot \nabla_{\mathbf{X}_i} \quad (6)$$

can be shown to yield

$$A_m^* = a_m^* \exp \left(\sum_{i=1}^N (\mathbf{X}_i(m) - \mathbf{X}_i^0) \cdot \nabla_{\mathbf{X}_i} \right) \quad (7)$$

$$A_m = a_m \exp \left(- \sum_{i=1}^N (\mathbf{X}_i(m) - \mathbf{X}_i^0) \cdot \nabla_{\mathbf{X}_i} \right) \quad (7)$$

where

$$\mathbf{X}'_j(m) \equiv \mathbf{X}_j + \mathbf{X}_j(m) - \mathbf{X}_j^0 \quad (8)$$

are the coordinates of molecule j after the "dressing process." Clearly the effect of A_m^* is to both create an electron in orbital $\phi_m(\mathbf{r})$ and modify the coordinates and geometries of all solvent molecules to their new "dressed" values $\mathbf{X}'_i(m)$. The amount by which these coordinates deviate from the minimum potential energy coordinates $\mathbf{X}_i(m)$ is identical to the deviation $\mathbf{X}_i - \mathbf{X}_i^0$ which existed prior to the creation of the excess electron.

The same transformation, when applied to the remaining terms in H , yields

$$\tilde{H} = \exp(S) H \exp(-S) = \sum_p \left[(A_p^* A_p + 1 - n_e) \sum_{i=1}^N \left(\frac{P_i^2}{2M_i} + U(\mathbf{Q}'_i(p)) \right) + \frac{1}{2} \sum_{j \neq i} V(\mathbf{X}'_i(p), \mathbf{X}'_j(p)) \right] + A_p^* A_p \sum_{m,n} \langle \phi_m | -\frac{1}{2} \nabla^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}'_i(p)) | \phi_n \rangle_{\mathbf{X}'(p)} A_m^* A_n \quad (9)$$

where the orbital indices p , m , and n run over molecule j , α and continuum \mathbf{k} orbitals, and n_e is the total-number-of-excess-electrons operator ($n_e = \sum_p A_p^* A_p$). The expression given in Eq. (9) can be simplified to its final form by using the fact that no more than one excess electron is present (thus, $n_e = 0$, or 1):

$$\tilde{H} = \sum_p (A_p^* A_p + 1 - n_e) \sum_{i=1}^N \left(\frac{P_i^2}{2M_i} + U(\mathbf{Q}'_i(p)) \right) + \frac{1}{2} \sum_{j \neq i} V(\mathbf{X}'_i(p), \mathbf{X}'_j(p)) + \sum_{m,n} \langle \phi_m | -\frac{1}{2} \nabla^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}'_i(m)) | \phi_n \rangle_{\mathbf{X}'(m)} A_m^* A_n \equiv \tilde{H}_N + \tilde{H}_e \quad (10)$$

For notational ease, $-\frac{1}{2} \nabla^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}'_i(m))$ will be referred to as $h_e(\mathbf{X}'_i(m))$. The terms $U(\mathbf{Q}'_i(p))$ and $V(\mathbf{X}'_i(p), \mathbf{X}'_j(p))$ in \tilde{H}_N contain reference to the localization of the excess electron through $A_p^* A_p$. This means, for example, that the internal potential energy of the molecules and the intermolecular forces correspond to those of N solvent molecules with one electron in $\phi_p(\mathbf{r}, \mathbf{X}'_i)$. This introduces the solvent anion's vibrational frequencies and the anion-neutral potential energy into \tilde{H}_N . If \tilde{H}_N operates as a function containing no excess electron, then the coordinates in \tilde{H}_N are appropriate to N solvent molecules just as they were in Eq. (1) (i. e., $\tilde{H}_N = H_N$ if $n_e = 0$).

In the above expression for the transformed Hamil-

tonian \tilde{H} , both the molecular component \tilde{H}_N and the electronic component \tilde{H}_e have been expressed as matrix elements which are functions of the modified molecular coordinates $\mathbf{X}'_i(m)$. It is precisely this convenient form for \tilde{H} which facilitates the development of the next section, which deals with the migration of the excess electron.

IV. THE ELECTRON MIGRATION

To follow the average motion of a single excess electron, which is initially in the orbital¹³ $\phi_0(\mathbf{r}, 0)$ centered at the laboratory coordinate origin, it is convenient to compute¹⁴ the average electron density $\bar{n}(\mathbf{r}, t)$ at space-

time point \mathbf{r}, t . This quantity is given by

$$\bar{n}(\mathbf{r}, t) = \text{Tr} [\rho_{\text{eq}} a_0 \exp(iHt) \psi^*(\mathbf{r}) \psi(\mathbf{r}) \exp(-iHt) a_0^\dagger] \quad (11)$$

where the trace operation refers to averaging over the initial coordinates \mathbf{X}_i and momenta \mathbf{P}_i of the N solvent molecular according to the equilibrium distribution function ρ_{eq} ,

$$\text{Tr}(\rho_{\text{eq}} F) = Z^{-1} \int d\mathbf{X} d\mathbf{P} \langle 0 | \exp[-H(\mathbf{X}, \mathbf{P})/kT] F(\mathbf{X}) | 0 \rangle \quad (12)$$

with

$$Z = \int d\mathbf{X} d\mathbf{P} \exp[-H(\mathbf{X}, \mathbf{P})/kT] \quad (13)$$

In Eq. (12) and (13), $|0\rangle$ represents the ground electronic state of the N solvent molecules in the absence of the excess electron, which is a function of the coordinates $\{\mathbf{X}_i\}$, times the vacuum state for the excess electron (i. e., the state with no electron present).¹⁵ It is assumed that the excited states of the solvent are not thermally accessible at the temperature of interest; thus only the ground electronic state $|0\rangle$ occurs in the above equilibrium average.

If, on the left side of the trace operation appearing in Eq. (11), the identity $\exp(-S)\exp(S)$ is inserted with S given in Eq. (6), the above expression for $\bar{n}(\mathbf{r}, t)$ can be written in terms of dressed operators as follows:

$$\begin{aligned} \bar{n}(\mathbf{r}, t) = Z^{-1} \int d\mathbf{X} d\mathbf{P} \langle 0 | \exp[-H_N(\mathbf{X})/kT] A_0 \exp(i\tilde{H}t) \\ \times \tilde{\psi}^*(\mathbf{r}) \tilde{\psi}(\mathbf{r}) \exp(-i\tilde{H}t) A_0^\dagger | 0 \rangle \quad (14) \end{aligned}$$

The fact that only $H_N(\mathbf{X})$ appears in the equilibrium average is a consequence of the fact that $\langle 0 |$ is a zero-excess-electron state for which $S|0\rangle = 0$ and $H_e|0\rangle = 0$, so that

$$\langle 0 | \exp(S) \exp(-H/kT) \exp(-S) = \langle 0 | \exp(-H_N/kT) \quad (15)$$

The transformed field operators $\tilde{\psi}^*(\mathbf{r})$ appearing in Eq. (14) are expressed as

$$\tilde{\psi}^*(\mathbf{r}) = \sum_n \phi_n^*(\mathbf{r}, \mathbf{X}'_n(t)) A_n^\dagger \quad (16)$$

The primary motivation behind the introduction of dressed electron operators and matrix elements has to do with the fact that the time evolution of the nascent electron occurs on (at least) two different time scales. On a very short ($\approx 10^{-6}$ – 10^{-12} sec) time scale, the excess electron either migrates from its creation site to a nearby deep potential energy well or the solvent molecules quickly rearrange about the new electron to form such a deep well.¹⁶ This initial process does not result in a macroscopic displacement of the electron; in the short time involved in this process, the electron moves a distance of the order of (at most) the length of several solvent molecules. Once this initial fast process is completed, the dressed electron has been formed. Subsequent migration of this dressed species through the solvent occurs on a slower time scale and can result in a macroscopic displacement of the electron.¹⁷ It is important to distinguish between processes which result in macroscopic, in contrast to molecular, displacements because it is only the former which make any contribu-

tions to experimental observations which probe the appearance of excess electron density as a function of time and distance from the source of the newly created electrons. In developing a formal expression which relates $\bar{n}(\mathbf{r}, t)$ to the properties of the solvent (U, V, T) and the electron-solvent interaction energy (u), it is useful to exclude from consideration the short-time processes which do not affect $\bar{n}(\mathbf{r}, t)$ for large (macroscopic) \mathbf{r} and long time. By expressing $\bar{n}(\mathbf{r}, t)$ in terms of dressed-electron operators, as in Eq. (14), a first step in concentrating on the long-time behavior of $\bar{n}(\mathbf{r}, t)$ has been taken. This step facilitates the introduction of approximations to the time evolution operator $[\exp(-i\tilde{H}t)]$ appearing in Eq. (14) which are appropriate to the long-time dynamics of the system.

If the excess electron were to undergo a diffusional motion, then the second moment of $\bar{n}(\mathbf{r}, t)$

$$\langle r^2 \rangle_t = \int \bar{n}(\mathbf{r}, t) r^2 d\mathbf{r} \quad (17)$$

should reduce to $6Dt$, where D is the effective diffusion coefficient for the given solvent system. Of course, the conditions (if any) under which such diffusional motion is realized must be investigated; this is one of the long-term objectives of the present work. To further explore this question, the above expression for $\bar{n}(\mathbf{r}, t)$ can be used to write $\langle r^2 \rangle$ as follows:

$$\begin{aligned} \langle r^2 \rangle_t = \sum_{m,n} \int d\mathbf{X} d\mathbf{P} Z^{-1} \langle \phi_m | r^2 | \phi_n \rangle_t \langle 0 | \exp[-H_N(\mathbf{X})/kT] A_0 \\ \times \exp(i\tilde{H}t) A_m^\dagger A_n \exp(-i\tilde{H}t) A_0^\dagger | 0 \rangle \quad (18) \end{aligned}$$

The moment integrals $\langle \phi_m | r^2 | \phi_n \rangle_t$ can, using the fact that the $\{\phi_m\}$ are localized Wannier-like orbitals, be expressed as

$$\begin{aligned} \langle \phi_m(\mathbf{r}, \mathbf{X}'_m(m, t)) | r^2 | \phi_n(\mathbf{r}, \mathbf{X}'_n(m, t)) \rangle = \langle \phi_m | \phi_n \rangle [R'_m(t)]^2 \\ + \langle \phi_m | (\mathbf{r} - \mathbf{R}'_m(t))^2 | \phi_n \rangle + 2 \langle \phi_m | (\mathbf{r} - \mathbf{R}'_m(t)) | \phi_n \rangle \cdot \mathbf{R}'_m(t) \quad (19) \end{aligned}$$

where $\mathbf{R}'_m(t)$ is the center of expansion of the localized orbital $\phi_m(\mathbf{r}, \mathbf{X}'_m(t))$, whose coordinates at time t are $\mathbf{X}'_m(t)$. From this point on, it is assumed that even the continuum orbitals $\phi_x(r)$ have been chosen to be localized with centers at $\mathbf{R}'_m(t)$. Because the $\{\phi_n\}$ are Wannier-like, the second and third terms in Eq. (19) are limited in magnitude by the size $\langle (\phi_n | (\mathbf{r} - \mathbf{R}'_n)^2 | \phi_n) \rangle$ of these Wannier orbitals. On the other hand, the first term $\langle \phi_n | \phi_m \rangle \times [R'_m(t)]^2$ which is equal to $\delta_{mn} [R'_m(t)]^2$ can, if the orbital ϕ_m is centered a macroscopic distance from the origin at time t , be of macroscopic dimension. Therefore, in describing the movement of the excess electron over an experimentally measurable (macroscopic) distance, only the first term need be kept. It has been assumed that the size of the orbitals is no larger than several molecules, i. e., that the localized orbitals do not extend over more than 10–20 Å. This assumption restricts the development made here to those molecular solvents in which the excess electrons exist primarily in nonextended states.¹⁸

In the resulting expression for the moment integral,

$$\langle \phi_m | r^2 | \phi_n \rangle_t \cong \delta_{mn} [R'_m(t)]^2 \quad (20)$$

the time-dependent position of the orbital $\phi_m(\mathbf{r}, \mathbf{X}'_m(t))$ can be written in terms of the initial (dressed) position \mathbf{R}'_m and the displacement $\delta\mathbf{R}'_m(t) \equiv \mathbf{R}'_m(t) - \mathbf{R}'_m$. Upon inserting this expression for $\mathbf{R}'_m(t)$ into Eq. (18) and using the fact that the spatial average of $2\mathbf{R}'_m \cdot \delta\mathbf{R}'_m(t)$ is zero for an isotropic system, the following result obtains:

$$\langle r^2 \rangle_t = \sum_m \int d\mathbf{X} d\mathbf{P} Z^{-1} \{ (R'_m)^2 + [\delta R'_m(t)]^2 \} \langle 0 | \exp[-H_N(\mathbf{X})/kT] \times A_0 \exp(i\tilde{H}t) A_m^* A_m \exp(-i\tilde{H}t) A_0^* | 0 \rangle \quad (21)$$

Now, the first serious physical approximation is introduced. It is assumed that the time evolution of the position of the centers of the Wannier-like orbitals can be described by their average motion and that this average motion is diffusional [$(\delta R'_m(t))^2 = 6D_N t$], with the diffusion coefficient characteristic of that of a solvent anion.¹⁹ This does not mean that it is assumed that the excess electron can undergo only diffusional motion. As is pointed out by Huang and Kevan,²⁰ the temperature dependence of the migration rate (mobility or diffusion) of excess electrons in liquids is complicated. At temperatures higher than the Debye temperature, optical phonon modes which couple strongly with the excess electron are populated and thus take part in phonon assisted (incoherent) hopping. The associated diffusion coefficients correspond to mobilities which vary from 475 cm²/V·sec for argon to 0.1 cm²/V·sec for *n*-hexane. At low temperatures, it might be expected on the basis of Holstein's work (Ref. 4) on one-dimensional ordered systems, that the electron motion should become coherent ($\langle r^2 \rangle \sim t^2$). However, the coherent motion depends strongly on the degree of order in the system. Therefore, for liquids which are quite disordered below the Debye temperature, coherence may not appear; instead, one may observe diffusional motion which is not very temperature dependent (as Huang and Kevan see). For liquids which attain a high degree of order below the Debye temperature and for which the acoustical phonons do not strongly affect the excess electron, one most likely observes coherent migration. Funabashi and Maruyama have also observed²⁰ electron mobilities in 3-methylpentane which are temperature independent for low *T* (4.2–35 °K) and temperature activated for higher temperatures. These observations are consistent with the two possible mechanisms (*K*₁ and *K*₂) described here. There does not really exist a wealth of experimental data in which a sufficiently wide temperature range is studied to enable both the *K*₂ (high *T*) and *K*₁ (low *T*) migration of the electron to be probed. Most measurements of electron mobility and diffusion rate are carried out within the 100–400 °K range, which does not permit the low-temperature (*K*₁) component of the electron motion to be determined. It is hoped the number of experiments in the spirit of those by Kevan and by Funabashi discussed above will continue to increase so that data on *K*₁ and *K*₂ can be obtained for a wide range of solvents.

With this assumption and using the fact that $\sum_m A_m^* A_m \times \exp(-i\tilde{H}t) A_0^* | 0(\mathbf{X}) \rangle = \exp(-i\tilde{H}t) A_0^* | 0(\mathbf{X}) \rangle$ to express the second factor in Eq. (21) as $6D_N t$, the above expression for $\langle r^2 \rangle_t$ reduces to

$$\langle r^2 \rangle_t = 6D_N t + Z^{-1} \sum_m \int d\mathbf{X} d\mathbf{P} (R'_m)^2 \langle 0 | \exp[-H_N(\mathbf{X})/kT] \times A_0 \exp(i\tilde{H}t) A_m^* A_m \exp(-i\tilde{H}t) A_0^* | 0 \rangle \quad (22)$$

Again, the reasoning behind the statement that $[R'_m(t)]^2$ can be replaced by $6D_N t$ plus the time-independent initial position $(R'_m)^2$ is simply based in the assumption that the behavior of the time-dependent displacements $\delta\mathbf{R}'_m(t)$ can be adequately described by a diffusion result. This gives rise, as is always the case for two parallel pathways, to two separate contributions to $\langle r^2 \rangle_t$. One term has to do with movement (diffusion) of the molecules and holes; the second has to do with movement of the excess electron within a fixed solvent structure. Thus, the physical content of Eq. (22) is clear: the excess electron can diffuse through the solvent by "riding" a molecule or a hole [by being in $\phi_m(\mathbf{r}, \mathbf{X}'_m(t))$]; in addition, the excess electron can move from molecule to molecule by means of the dynamical processes described by the second term in Eq. (22). To gain some feel for the magnitudes of these two terms, recall that electron mobilities, which are related to "effective diffusion coefficients" by $D = \mu kT/e$, range²¹ from 10⁻⁴ to 10³ cm² V⁻¹·sec⁻¹, whereas molecular anion mobilities are rarely larger than 10⁻³ cm² V⁻¹·sec⁻¹. Thus, for many systems, both terms in Eq. (22) can be significant. It is toward the second contribution to the electron's migration that attention is now turned.

In the second physically motivated approximation, the initial (*t*=0) positions of the centers $\{\mathbf{R}'_m\}$ of the localized orbitals, which occur in Eq. (22), are replaced by average solvent-structure information. In particular the following replacement is made in Eq. (22):

$$\sum_m \int d\mathbf{X} d\mathbf{P} (R'_m)^2 F(\mathbf{R}'_m) \cong \int d\mathbf{R} \rho_s(\mathbf{R}, 0) R^2 \int d\mathbf{X} d\mathbf{P} F(\mathbf{R}) + \int d\mathbf{R} \rho_h(\mathbf{R}, 0) R^2 \int d\mathbf{X} d\mathbf{P} F(\mathbf{R}) \quad (23)$$

where $F(\mathbf{R}'_m)$ represents the remainder of the second term of Eq. (22) and $\rho_s(\mathbf{R}, 0)[\rho_h(\mathbf{R}, 0)]$ gives the number of solvent molecule (hole) centers (i. e., \mathbf{R}'_m 's) per unit volume at point \mathbf{R} , given that there is a molecule or hole at the origin¹³ (where the excess electron initiated). This approximation, in which the "actual" initial positions \mathbf{R}'_m are replaced by the average solvent structural information [through $\rho_{s,h}(\mathbf{R}, 0)$], permits $\langle r^2 \rangle_t$ to be recast as

$$\langle r^2 \rangle_t = 6D_N t + \sum_{I=h,s} \int d\mathbf{R} \rho_I(\mathbf{R}, 0) R^2 Z^{-1} \int d\mathbf{X} d\mathbf{P} \langle 0 | \exp[-H_N(\mathbf{X})/kT] A_0^* \exp(i\tilde{H}t) A_{\mathbf{R}I}^* A_{\mathbf{R}I} \exp(-i\tilde{H}t) A_0^* | 0 \rangle \quad (24)$$

where $A_{\mathbf{R}I}^*$ creates an electron at \mathbf{R} in either a molecular orbital [$\phi_\alpha(\mathbf{r}, \mathbf{X}'_m)$] or a Wannier continuum orbital [$\phi_\alpha(\mathbf{r})$], depending on *I*. In the product $A_{\mathbf{R}I}^* A_{\mathbf{R}I}$, a sum over the orbital-number index α [e. g., in $\phi_\alpha(\mathbf{r}, \mathbf{R}_I)$] is implied. Thus, this product is really $\sum_\alpha A_{\mathbf{R}I\alpha}^* A_{\mathbf{R}I\alpha}$.

To make further progress in obtaining a more tractable form for $\langle r^2 \rangle$, the Hamiltonian \tilde{H} is decomposed into a zeroth order part consisting of \tilde{H}_N plus the equilibrium average of the diagonal part of \tilde{H}_e ,

$$\tilde{H}^0 \equiv \tilde{H}_N + \tilde{H}_e^0 = \tilde{H}_N + Z^{-1} \int d\mathbf{X} d\mathbf{P} \exp[-H_N(\mathbf{X})/kT] \sum_m \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_m \rangle_{\mathbf{X}'_i(m)} A_m^* A_m \equiv \tilde{H}_N + \sum_m \langle \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_m \rangle \rangle_N A_m^* A_m, \tag{25}$$

and a "perturbation" \tilde{V} consisting of the off-diagonal component of \tilde{H}_e plus the deviation of the diagonal components away from the equilibrium average

$$\tilde{V} = \sum_{m \neq n} \langle \phi_m | -\frac{1}{2} \nabla^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}'_i(m)) | \phi_n \rangle_{\mathbf{X}'_i(m)} A_m^* A_n + \sum_m \{ \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_m \rangle - \langle \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_m \rangle \rangle_N \} A_m^* A_m. \tag{26}$$

The off-diagonal terms appearing in \tilde{V} will be referred to as electron transfer integrals and operators ($A_m^* A_n$) because they involve the transfer of the dressed excess electron from orbital ϕ_n to orbital ϕ_m . The time-dependent operator appearing in Eq. (24) is then approximated by a (truncated) cumulant²² expansion as follows:

$$Z^{-1} \int d\mathbf{X} d\mathbf{P} \langle 0 | \exp[-H_N(\mathbf{X})/kT] \exp(i\tilde{H}t) A_{\mathbf{R}_I}^* A_{\mathbf{R}_I} \exp(-i\tilde{H}t) | 0 \rangle = \left[\exp\left(\sum_{i=1}^{\infty} K_i(t)/i! \right) A_{\mathbf{R}_I}^* A_{\mathbf{R}_I} \right] \cong \{ \exp[K_1(t) + \frac{1}{2}K_2(t)] A_{\mathbf{R}_I}^* A_{\mathbf{R}_I} \}, \tag{27}$$

where

$$K_1(t) = i \int_0^t d\tau \langle \tilde{V}^x(\tau) \rangle_N \tag{28}$$

and

$$K_2(t) = - \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 T \langle \delta \tilde{V}^x(\tau_1) \delta \tilde{V}^x(\tau_2) \rangle_N. \tag{29}$$

In these definitions of the cumulant operators K_1 and K_2 , T is the time-ordering operator, $\langle \rangle_N$ represents an average over the solvent molecules' positions and momenta

$$\langle F \rangle_N \equiv Z^{-1} \int d\mathbf{X} d\mathbf{P} \exp[-H_N(\mathbf{X})/kT] F(\mathbf{X}, \mathbf{P}), \tag{30}$$

and the commutator operators (denoted by the x superscript) are

$$\tilde{V}^x(\tau) = [\exp(i\tilde{H}_e^0 \tau) \tilde{V}(\mathbf{X}'_i(\tau)) \exp(-i\tilde{H}_e^0 \tau)], \tag{31}$$

and

$$\delta \tilde{V}^x(\tau) = \tilde{V}^x(\tau) - \langle \tilde{V}^x(\tau) \rangle_N. \tag{32}$$

The time dependence of $\tilde{V}(\mathbf{X}'_i(\tau))$ arises from the time evolution of the coordinates $\{\mathbf{X}'_i\}$ appearing in \tilde{V} under the influence of \tilde{H}_N , i. e., $\tilde{V}(\mathbf{X}'_i(\tau)) = \exp(i\tilde{H}_N \tau) \tilde{V}(\mathbf{X}'_i) \times \exp(-i\tilde{H}_N \tau)$. The additional $\exp(\pm i\tilde{H}_e^0 \tau)$ factors appearing in Eq. (31) then add the average effects of the excess electron to the time dependence of $\tilde{V}(\mathbf{X}'_i)$.

The cumulant operator K_1 , which contains the equilibrium average effects of the electron transfer terms, can be expressed more explicitly in terms of the dressed electron operators as follows:

$$K_1(t) = i \int_0^t d\tau \sum_{m \neq n} \langle \langle \phi_m | -\frac{1}{2} \nabla^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}'_i(\tau)) | \phi_n \rangle_{\mathbf{X}'_i(\tau)} \rangle_N \times \exp[i(E_m^0 - E_n^0)\tau] [A_m^* A_n], \tag{33}$$

the terms arising from the diagonal components of V vanish in $K_1(t)$. In Eq. (33), the energy E_m^0 is equal to

$\langle \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_m \rangle_{\mathbf{X}'_i(m)} \rangle_N$, and represents the average energy of an excess electron residing in orbital ϕ_m . Because the equilibrium average $\langle \rangle_N$ is defined with $Z^{-1} \exp[-H_N(\mathbf{X})/kT]$ as its probability density and because

$$\langle \phi_m | h_e(\mathbf{X}'_i(\tau)) | \phi_n \rangle_{\mathbf{X}'_i(\tau)} = \exp(i\tilde{H}_N \tau) \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_n \rangle_{\mathbf{X}'_i(m)} \exp(-i\tilde{H}_N \tau),$$

it follows from the time invariance of equilibrium averages that $\langle \langle \phi_m | h_e(\mathbf{X}'_i(\tau)) | \phi_n \rangle_{\mathbf{X}'_i(\tau)} \rangle_N$ is independent of τ . Therefore, $K_1(t)$ can be expressed in its most explicit form as

$$K_1(t) = \sum_{m \neq n} \langle \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_n \rangle_{\mathbf{X}'_i(m)} \rangle_N \Delta_{mn}(t) [A_m^* A_n], \tag{34}$$

where

$$\Delta_{mn}(t) = \lim_{\delta \rightarrow 0} \{ \exp[i(E_m^0 - E_n^0 + \delta)t - 1] / (E_m^0 - E_n^0 + \delta) \}. \tag{35}$$

It is clear that $K_1(t)$ contains terms which allow the excess electron to be transferred from site to site with the transfer probability being determined both by the equilibrium averages of the transfer integrals $\langle \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_n \rangle_{\mathbf{X}'_i(m)} \rangle_N$ and by the zeroth order energy difference $E_m^0 - E_n^0$ between the two sites. These quantities will be determined by the depth of the electron-molecule and electron-hole potential wells (E_m^0) and the overlap of one localized orbital with neighboring localized orbitals.

The second cumulant operator $K_2(t)$ involves changes in $\tilde{V}^x(\tau)$ about its equilibrium value. At low temperatures the fluctuations in the coordinates $\mathbf{X}'_i(\tau)$, which give rise to the fluctuations in $\tilde{V}^x(\tau)$, are sufficiently small to permit $K_2(t)$ [and the higher $K_n(t)$, $n \geq 3$] to be neglected in comparison with $K_1(t)$. As the temperature reaches a level at which thermal excitations of the modes (vibrational, torsional, etc.) which affect $\delta \tilde{V}^x(\tau)$ take place, then $K_2(t)$ is not negligible in comparison with $K_1(t)$. As Grover and Silbey¹⁴ have shown for exciton migration within a one-dimensional nearest-neighbor

model, K_1 gives rise to coherent ($\langle r^2 \rangle \sim t^2$) motion of the electron whereas K_2 allows the electron to diffuse ($\langle r^2 \rangle \sim t$). At temperatures for which both K_1 and K_2 contribute, a mixture of coherent and diffusional motion is expected.

To express $K_2(t)$ in an explicit fashion, which is analogous to Eq. (34) for $K_1(t)$, Eqs. (25), (26), (30), and (31) can be employed in Eq. (29) to give

$$K_2(t) = -2 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \sum_{\substack{m,n \\ p,q}} \{ \langle [h_{mn}(\tau_1) - \hat{h}_{mn}] [h_{pq}(\tau_2) - \hat{h}_{pq}] \rangle_N$$

$$\times \exp[i(E_m^0 - E_n^0)\tau_1 + i(E_p^0 - E_q^0)\tau_2] [A_m^* A_n, [A_p^* A_q,] \} , \tag{36}$$

where

$$h_{mn}(\tau) \equiv \langle \phi_m | h_{\sigma}(\mathbf{X}'_i(\tau)) | \phi_n \rangle_{\mathbf{X}'_i(\tau)} , \tag{37}$$

and

$$\hat{h}_{mn} \equiv \langle h_{mn}(\tau) \rangle_N . \tag{38}$$

Again, because of the time invariance of equilibrium averages, $\langle (h_{mn}(\tau_1) - \hat{h}_{mn})(h_{pq}(\tau_2) - \hat{h}_{pq}) \rangle_N$ is really only a function of the time interval $\tau_1 - \tau_2$. Therefore, by replacing the integration τ_2 by $x \equiv \tau_1 - \tau_2$, $K_2(t)$ can be reduced to

$$K_2(t) = -2 \sum_{\substack{m,n \\ p,q}} \int_0^t d\tau_1 \exp[i(E_m^0 - E_n^0 + E_p^0 - E_q^0)\tau_1] \int_0^{\tau_1} dx \exp[-i(E_p^0 - E_q^0)x] \langle [h_{mn}(x) - \hat{h}_{mn}] [h_{pq}(0) - \hat{h}_{pq}] \rangle_N [A_m^* A_n, [A_p^* A_q,] . \tag{39}$$

Further simplification of $K_2(t)$ can be achieved once a specific model or approximation has been made for the time dependence of the equilibrium averaged terms appearing in Eq. (39). Although a satisfactory solution to this problem is not yet available, this topic is discussed briefly in the following section, which deals with planned applications and extensions of the theoretical framework developed here as well as suggestions of physically reasonable models to be employed when implementing the theory.

At this stage in the development, the average of the square of the distance moved by the excess electron has been expressed as follows¹⁵:

$$\langle r^2 \rangle = 6D_N t + \sum_{I=h,s} \int d\mathbf{R} \rho_I(\mathbf{R}, 0) R^2 \langle \text{vac} | A_0 \{ \exp[K_1 + \frac{1}{2}K_2] A_{\mathbf{R}_I}^* A_{\mathbf{R}_I} \} A_0^* | \text{vac} \rangle , \tag{40}$$

With K_1 and K_2 given as in Eqs. (34) and (39). The primary justification for terminating the cumulant expansion at K_2 is simply the presumption that the equilibrium average dynamics will be the dominant contributor to $\langle r^2 \rangle_t$ with (small) fluctuations²³ about the average being the next most important factor. Clearly this line of reasoning leads to the (probably correct) conclusion that the truncated cumulant expansion breaks down near critical points or phase transitions. Assuming that adequate structural data (ρ_s and ρ_h) and transport data (D_N) are available for the solvent, only two problems remain. First, the expressions for K_1 and K_2 must be made more tractable and, secondly, a mechanism for expressing $\exp[K_1 + \frac{1}{2}K_2]$ in a computationally useful form must be found. It is to these two subjects that attention is now focused.

In both K_1 and K_2 , the integrals $h_{mn}(\tau)$ appear; in particular, K_1 contains $\langle h_{mn} \rangle_N$ and K_2 involves $\langle h_{mn}(x) h_{pq} \rangle_N - \langle h_{mn} \rangle_N \langle h_{pq} \rangle_N$. The equilibrium average $\langle h_{mn} \rangle_N$ can be expressed as

$$\langle h_{mn} \rangle_N = Z^{-1} \int d\mathbf{X} d\mathbf{P} \exp[-H_N/kT] \langle \phi_m(\mathbf{r}, \mathbf{X}'_m(m)) | -\frac{1}{2}\nabla_r^2 + u(\mathbf{r}, \mathbf{X}'_m(m)) + u(\mathbf{r}, \mathbf{X}'_n(m)) + \sum_{\substack{i=1 \\ i \neq m,n}} u(\mathbf{r}, \mathbf{X}'_i(m)) | \phi_n(\mathbf{r}, \mathbf{X}'_n(m)) \rangle , \tag{41}$$

which can be written in terms of the two- and three-body distribution functions²⁴ ($f(\mathbf{R}_1, \mathbf{R}_2), f(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$) of the solvent as follows:

$$\langle h_{mn} \rangle_N = \int f(\mathbf{R}_m, \mathbf{R}_n) \langle \phi_m | -\frac{1}{2}\nabla^2 + u(\mathbf{r}, \mathbf{X}'_m(m)) + u(\mathbf{r}, \mathbf{X}'_n(m)) | \phi_n \rangle d\mathbf{R}_m d\mathbf{R}_n + N \int f(\mathbf{R}_m, \mathbf{R}_n, \mathbf{R}_1) \langle \phi_m | u(\mathbf{r}, \mathbf{X}'_1(m)) | \phi_n \rangle d\mathbf{R}_1 d\mathbf{R}_m d\mathbf{R}_n . \tag{42}$$

Similarly, the average $\langle h_{mn}(x) h_{pq} \rangle_N$ can be written in terms of the two- through six-body distribution functions of the solvent. For example, the "diagonal" term is

$$\begin{aligned} \langle h_{mn}(x) h_{mn} \rangle_N = & \int f(\mathbf{R}_m, \mathbf{R}_n) \{ \langle \phi_m | -\frac{1}{2}\nabla^2 + u(\mathbf{r}, \mathbf{X}'_m(m)) + u(\mathbf{r}, \mathbf{X}'_n(m)) | \phi_n \rangle \langle \phi_m | -\frac{1}{2}\nabla^2 + u(\mathbf{r}, \mathbf{X}'_m(m)) + u(\mathbf{r}, \mathbf{X}'_n(m)) | \phi_n \rangle_{\mathbf{X}'_i(x)} \} d\mathbf{R}_m d\mathbf{R}_n \\ & + N \int f(\mathbf{R}_m, \mathbf{R}_n, \mathbf{R}_1) \{ \langle \phi_m | u(\mathbf{r}, \mathbf{X}'_1(m)) | \phi_n \rangle \langle \phi_m | u(\mathbf{r}, \mathbf{X}'_1(m)) | \phi_n \rangle_{\mathbf{X}'_i(x)} + \langle \phi_m | -\frac{1}{2}\nabla^2 + u(\mathbf{r}, \mathbf{X}'_m(m)) + u(\mathbf{r}, \mathbf{X}'_n(m)) | \phi_n \rangle \\ & \times \langle \phi_m | u(\mathbf{r}, \mathbf{X}'_1(m)) | \phi_n \rangle_{\mathbf{X}'_i(x)} + \langle \phi_m | u(\mathbf{r}, \mathbf{X}'_1(m)) | \phi_n \rangle \langle \phi_m | -\frac{1}{2}\nabla^2 + u(\mathbf{r}, \mathbf{X}'_m(m)) + u(\mathbf{r}, \mathbf{X}'_n(m)) | \phi_n \rangle_{\mathbf{X}'_i(x)} \} d\mathbf{R}_m d\mathbf{R}_n d\mathbf{R}_1 \\ & + N^2 \int f(\mathbf{R}_m, \mathbf{R}_n, \mathbf{R}_1, \mathbf{R}_2) \langle \phi_m | u(\mathbf{r}, \mathbf{X}'_1(m)) | \phi_n \rangle \langle \phi_m | u(\mathbf{r}, \mathbf{X}'_2(m)) | \phi_n \rangle_{\mathbf{X}'_i(x)} d\mathbf{R}_n d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_m . \tag{43} \end{aligned}$$

Analogous expressions can easily be written for the "off-diagonal" terms. If ϕ_m and/or ϕ_n is a hole Wannier orbital, these expressions remain valid if the distribution functions (f) are generalized to pertain to the distribution of both molecules and holes and if $u(\mathbf{r}, \mathbf{X}'_m(m))$ and/or $u(\mathbf{r}, \mathbf{X}'_n(m))$ are defined as zero for holes.

Although these results appear to be rather complicated, they do represent an important contribution toward the stated objective of expressing K_1 and K_2 in terms of solvent structure information (the distribution functions) and electron-solvent interactions (the u potential). Because only pair distribution function information is known for most liquids, implementation of the expressions given in Eqs. (42) and (43) would require that the three- and higher-body distribution functions be approximated in terms of the two-body function. This could be accomplished, for example, through a Kirkwood superposition approximation.²⁵ Because this step introduces a set of further approximations within the general theoretical framework developed in this initial paper, discussion of such topics will be deferred to subsequent publications; Eqs. (42) and (43) will be preserved as is, for now.

The expression obtained for $\exp(K_1 + \frac{1}{2}K_2)A_{\mathbf{R}_I}^* A_{\mathbf{R}_J}$ by expanding the exponential and truncating at some small (say, 10) power is simply not of use in evaluating the contribution of this term to $\langle \rho^2 \rangle$. Because K_1 and K_2 contain single and double commutators ($[A_m^* A_n]$ and $[A_p^* A_q, [A_m^* A_n]]$), respectively, a typical term $(K_1 + \frac{1}{2}K_2)^l /$

$l!$ arising in the expansion of the above exponential contains, at most, $2l$ such commutators. Suppose that, as is most probably the case for molecular solids and liquids, the electron transfer integrals h_{mn} , which combine with $[A_m^* A_n]$ in K_1 and K_2 , are significant only for molecules m and n which are first or second nearest neighbors. Then the effect of $(K_1 + \frac{1}{2}K_2)^l / l!$ on $A_{\mathbf{R}_I}^* A_{\mathbf{R}_J}$ would, at most, be to move the excess electron from \mathbf{R}_I to a position which is of the order of $2l$ molecular dimensions away from \mathbf{R}_I . Thus, unless l is chosen to be large enough (say, 10^6) so that $2l$ times the "range" of h_{mn} is of a macroscopic (experimentally measurable) dimension, the truncated power series expansion of $\exp(K_1 + \frac{1}{2}K_2)$ can not give rise to a movement of the electron over a macroscopic distance. Clearly, to carry the exponential series to such a high power is technically impossible.

An alternative approach to the problem of expressing $\exp(K_1 + \frac{1}{2}K_2)A_{\mathbf{R}_I}^* A_{\mathbf{R}_J}$ in a more useful form is to find an equation which this quantity obeys and to solve this equation as accurately as is possible. To further explore this possibility, it is useful to define¹⁴ a quantity $g(\mathbf{R}_I, \mathbf{R}_J)$,

$$g(\mathbf{R}_I, \mathbf{R}_J) \equiv \{ \exp[K_1 + \frac{1}{2}K_2] A_{\mathbf{R}_I}^* A_{\mathbf{R}_J} \}. \tag{44}$$

By taking the time derivative of g and using Eq. (33) and (36) to express dK_1/dt and dK_2/dt , it is straightforward to demonstrate that g obeys the following differential equation:

$$\begin{aligned} \frac{dg(I, J, t)}{dt} = & i \sum_m \{ \exp[i(E_m^0 - E_I^0)t] \hat{h}_{mI} g(m, J, t) - \exp[i(E_J^0 - E_m^0)t] \hat{h}_{Jm} g(I, m, t) \} \\ & - \int_0^t d\tau \sum_{m,p} \{ \exp[i(E_p^0 - E_m^0)t + i(E_m^0 - E_I^0)\tau] \langle \delta h_{pm}(t - \tau) \delta h_{mI} \rangle_N g(p, J, t) \\ & + \exp[i(E_m^0 - E_p^0)t + i(E_J^0 - E_m^0)\tau] \langle \delta h_{mp}(t - \tau) \delta h_{Jm} \rangle_N g(I, p, t) - \exp[i(E_J^0 - E_p^0)t + i(E_m^0 - E_I^0)\tau] \\ & \times \langle \delta h_{Jp}(t - \tau) \delta h_{mI} \rangle_N g(m, p, t) - \exp[i(E_p^0 - E_I^0)t + i(E_J^0 - E_m^0)\tau] \langle \delta h_{pI}(t - \tau) \delta h_{Jm} \rangle_N g(p, m, t) \} , \end{aligned} \tag{45}$$

where the coordinates \mathbf{R}_I and \mathbf{R}_J have been denoted by I and J for notational ease. The indices m and p label the N solvent molecules' and holes' orbitals $\{\phi_m(\mathbf{r})\}$ and operators $\{A_m^*\}$ as discussed earlier, and $\delta h_{mn}(t - \tau) \equiv h_{mn}(t - \tau) - \langle h_{mn} \rangle_N$. The initial condition on $g(I, J, t)$ is $\langle \text{vac} | A_0 g(I, J, 0) A_0^* | \text{vac} \rangle = \delta_{IJ,0}$, which merely states that the electron is at the origin at $t = 0$.

If it were possible to replace the functions $g(p, J, t)$ and $g(p, m, t)$ ($\equiv \exp[K_1 + \frac{1}{2}K_2] A_p^* A_m$), which depend upon the discrete indices m and p , by the function $g(\mathbf{R}_I, \mathbf{R}_J, t)$ of the continuous variables \mathbf{R}_I and \mathbf{R}_J , then Eq. (45) would become a closed equation for the desired function $g(I, J)$. This replacement can be accomplished by making an approximation analogous to that introduced in Eq. (23). In particular, the sums over m and p appearing in Eq. (45) are approximated as follows:

$$\sum_{m,p} F_{pm, mI}(t - \tau) g(p, J, t) \cong \sum_{K, L=hs} \int d\mathbf{R}_K d\mathbf{R}_L \rho_{KI}(K, I) \rho_{LK}(L, K) F(L, K, K, I, t - \tau) g(L, J, t) , \tag{46}$$

where

$$F(L, K, K, I, t - \tau) \equiv \exp[i(E_{\mathbf{R}_L}^0 - E_{\mathbf{R}_K}^0)t + i(E_{\mathbf{R}_K}^0 - E_{\mathbf{R}_I}^0)\tau] \langle \delta h_{\mathbf{R}_L \mathbf{R}_K}(t - \tau) \delta h_{\mathbf{R}_K \mathbf{R}_I} \rangle_N , \tag{47}$$

and $\rho_{KL}(\mathbf{R}_K, \mathbf{R}_L)$ is the average density of either (depending on K) holes or solvent molecules at \mathbf{R}_K given that there is a hole or molecule (depending on L) at \mathbf{R}_L . The integral equation for $g(\mathbf{R}_I, \mathbf{R}_J, t)$ which results from carrying out this approximation is

$$\begin{aligned} \frac{d}{dt}g(I, J, t) = & i \sum_{K=h, S} \int d\mathbf{R}_K \{ \rho(K, I) \bar{h}(K, I, t) g(K, J, t) - \rho(J, K) \bar{h}(J, K, t) g(I, K, t) \} \\ & - \sum_{K, L=h, S} \int d\mathbf{R}_K d\mathbf{R}_L \int_0^t \{ \rho(K, L) \rho(L, I) F(K, L, L, I, t - \tau) g(K, J, t) + \rho(L, K) \rho(J, L) F(L, K, J, L, t - \tau) g(I, K, t) \\ & - \rho(J, K) \rho(L, I) F(J, K, L, I, t - \tau) g(L, K, t) - \rho(K, I) \rho(J, L) F(K, I, J, L, t - \tau) g(K, L, t) \} d\tau, \end{aligned} \quad (48)$$

where

$$\bar{h}(K, I, t) \equiv \exp[i(E_{\mathbf{R}_K}^0 - E_{\mathbf{R}_I}^0)t] \hat{h}_{\mathbf{R}_K \mathbf{R}_I}.$$

The indices I, J, K, L have been used to represent $\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K$, and \mathbf{R}_L , and $\rho(K, L) \equiv \rho_{KL}(\mathbf{R}_K, \mathbf{R}_L)$ and $F(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K, \mathbf{R}_L, t - \tau)$ have been defined earlier. If information were available about the structure of the solvent (through the ρ_{KL} and distribution functions f), Eq. (48) could be used to determine $g(\mathbf{R}_I, \mathbf{R}_J, t)$ which gives $\langle r^2 \rangle$ by Eq. (40). Thus, the results expressed in Eq. (40) for $\langle r^2 \rangle$, Eqs. (42) and (43) for thermal averages and fluctuations of $h_{mn}(\tau)$, and Eq. (48) for $g(\mathbf{R}_I, \mathbf{R}_J, t)$ constitute a theoretical framework for analyzing the motion of excess electrons in condensed media. This result is the principal achievement of the research presented in this manuscript.

Grover and Silbey have solved Eq. (48) under one-dimensional nearest-neighbor approximation and under the assumption that $K_1 \gg K_2$ at low T and $K_2 \gg K_1$ at high T . Using their result simply as the crudest approximation to the solution of our Eq. (48), we obtain

$$\begin{aligned} \langle r^2 \rangle = & 6D_N t + a^2 [(2F + 4\bar{h}^2/3F)t \\ & + (4\bar{h}^2/9F^2)(\exp(-3Ft) - 1)], \end{aligned} \quad (49)$$

where F and \bar{h} are the values of $F(I, J, K, L)$ and $\bar{h}(I, J)$ evaluated at the nearest-neighbor geometry with intermolecular distance equal to a . For short times, it is clear that $\langle r^2 \rangle$ reduces to $6D_N t + (2Ft + 2\bar{h}^2 t^2) a^2$, i. e., to a mixture of coherent and diffusional behavior. For long times, $\langle r^2 \rangle$ reduces to $(2F + \frac{4}{3}\bar{h}^2/F)ta^2 + 6D_N t$, to purely diffusional motion. Of course, such a simplified one-dimensional model in no way addresses the question of the possible breakdown of coherent motion caused solely by breakdown in the order of the solvent. It does, however provide a potentially useful first step toward generating useful equations which relate experimentally determined $\langle r^2 \rangle_t$ values to the properties of the solvent [D_N in Eq. (49)] and electron-solvent interactions such as those contained in the average (\bar{h}) and fluctuation (F) interaction terms of Eq. (49). Low temperature measurements of $\langle r^2 \rangle$ yield information on \bar{h} , whereas high-temperature results allow F to be probed.

Of course, Eq. (48) must be solved for $g(\mathbf{R}_I, \mathbf{R}_J, t)$ using more realistic models than those discussed above before Eq. (40) can be used either to predict $\langle r^2 \rangle$ for a given system or to extract quantitative information about the electron-solvent interaction (E_m^0 and h_{mn}) from the experimentally observed temperature dependence of $\langle r^2 \rangle_t$. Such a solution of Eq. (48) requires that some model or approximation be introduced for the temporal and spatial dependence of $\hat{h}_{\mathbf{R}_I \mathbf{R}_J}$ and $\langle \delta h_{\mathbf{R}_I \mathbf{R}_J}(t - \tau) \times \delta h_{\mathbf{R}_K \mathbf{R}_L} \rangle_N$. For example, it is probably quite reason-

able to approximate the spatial behavior of the electron transfer integrals $\langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_n \rangle$ in terms of an exponentially decreasing function of the distance between the centers of the two orbitals,

$$\begin{aligned} \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_n \rangle \cong & \langle \phi_m | h_e(\mathbf{X}'_i(m)) | \phi_n \rangle_{|\mathbf{R}_m - \mathbf{R}_n| = \sigma} \\ & \times \exp[[-(\mathbf{R}'_m(m) - \mathbf{R}'_n(m))^2 + \sigma^2]/L^2], \end{aligned} \quad (50)$$

where σ is the nearest-neighbor distance in the solvent and L is characteristic of the "falloff" of this integral as the distance between the orbitals increases. The investigation of this and other models for the terms occurring in Eq. (48) will be treated in a subsequent publication, as will the techniques to be used in achieving a solution of the above integral equation for $g(I, J, t)$. To bring the present paper to a close now that the stated objective has been reached, attention is turned toward a summary and analysis both of that which has been accomplished and that which remains for the future.

V. SUMMARY

The fundamental result of this paper is contained in Eq. (40), in which the mean square distance $\langle r^2 \rangle_t$ moved by the excess electron is expressed as a sum of two contributions. The first component arises from the electron "riding" a solvent molecule which then diffuses as an anion through the solution. The second contribution contains the effects of both tunneling and hopping of the electron from one site to another. By performing a cumulant approximation to the time evolution operator appearing in this part of $\langle r^2 \rangle_t$ and introducing approximations related to the distribution of molecules and holes in the solvent, it was possible to express the dynamics of the electron migration in terms of solvent structure information (distribution functions) and properties of the electron-solvent interaction (the potential well depths E_m^0 , and the electron transfer integrals $\langle \phi_m | h_e | \phi_n \rangle$). The cumulant approximation allows the equilibrium average of the electron-solvent perturbation to be identified as the dominant influence at low temperatures for which fluctuations in molecular geometries are small. At higher temperatures, the effects of geometrical fluctuations on the electron-solvent interaction (through $\langle \delta h_{mn}(\tau) \delta h_{pq}(N) \rangle$) are given by the second term in the cumulant expansion.

The theoretical framework obtained in this paper is meant to provide a starting point for the further development of reasonable physical models for the behavior of excess electrons in condensed media (molecular solids and liquids). The basic result of Eq. (40) gives a closed theory only in the following sense: if information were available on the solvent's molecule and hole distribution

functions, and if reasonable models are introduced for the spatial and temporal behavior of the integral kernels (\bar{h} and F), then Eq. (48) could be solved for $g(I, J, t)$. Knowing $g(I, J, t)$ then makes it possible to employ experimental data on $\langle r^2 \rangle_t$ at various temperatures (and perhaps for a series of solvents) and Eq. (40) to extract information about well depths (E_m^0), electron transfer rates (\hat{h}_{mn}), and the effects of fluctuations on the transfer rates ($\langle \delta h_{mn}(t) \delta h_{pq}(t) \rangle_N$). It should be clear from the content of this paper that much work remains to be done before a situation in which the present theory is used to analyze experimental data is realized. At this point it would be instructive to review those specific areas in which further development of the theory is needed as well as the directions which at present seem to be most promising.

The most important unsolved problem which arises in attempting to implement this theory is concerned with the solution of Eq. (48) for $g(\mathbf{R}_I, \mathbf{R}_J, t)$; Grover and Silbey¹⁴ solved an equation of this form, which arose in their investigation of exciton migration in molecular solids, by invoking a one-dimensional nearest-neighbor treatment. Such a solution is of substantial merit in that it gives insight into the limiting coherent (low T) and diffusional (high T) behavior of the system. However, in a program whose ultimate goal is to provide a quantitatively accurate understanding of the migration of excess electrons in molecular solution, progress must be made beyond the nearest-neighbor model. In particular, physically reasonable models must be found for the spatial dependence of the electron transfer integrals $\langle \phi_m | h_e \times (\mathbf{X}_i'(m) | \phi_n \rangle$. One possibility for such a model was discussed in the preceding section. Clearly, any successful model should express these integrals (and the E_m^0) in terms of the "electron affinity" of the orbitals $\{\phi_m\}$, the size (spatial extent) of these orbitals, and the electron-molecule interaction potential $u(\mathbf{r}, \mathbf{X}_i(m))$. For specific solvent systems of interest, these quantities can then be probed by using Eq. (40) to extract information from experimental data on $\langle r^2 \rangle_t$.

The solution of Eq. (48) also requires that a reasonable approximation be made for the time dependence of the fluctuations $F(I, J, K, L, t - \tau)$. It is probably most reasonable to employ, as Grover and Silbey explored¹⁴ for the exciton migration problem, a model for the frequency dispersion of those vibrational, rotational, and torsional modes which couple most strongly to the electron transfer probability. Either Lorentzian or Gaussian frequency distributions yield exponentially decreasing time dependences²⁶ for the above fluctuation terms. The characteristic decay time of the resulting expression for $F(I, J, K, L, t - \tau)$ is determined by the decay time of the fluctuations in the dominant vibrational, rotational, and torsional modes. Because such a decay time is much faster than the time scale over which electron migration occurs, it is quite likely that a reasonably simple model for the time dependence of $F(I, J, K, L, t - \tau)$ will be adequate for describing the contributions to $\langle r^2 \rangle_t$ made by fluctuations. The development of good models for the spatial and time dependence of $F(I, J, K, L, t - \tau)$ and \bar{h}_{mn} are essential next steps in the implementation of the present theory. Munn and Siebrand in Ref. 4 pro-

vide a good deal of physical insight into these spatial and temporal quantities. They also give approximate values for the time scales and spatial ranges involved for molecular crystals. As was mentioned earlier, it is also important to devise a reliable scheme for approximating the three- and higher-body distribution functions appearing in \bar{h}_{mn} and $F(I, J, K, L, t - \tau)$ in terms of the two-body distribution. These higher distribution functions are simply unavailable for most systems.

The extension of the basic result of Eq. (40) to the case of a dilute solution of excess electrons in a mixed solvent is currently underway in this laboratory. This development will also provide a starting point for obtaining a reasonable framework in terms of which to examine the effects of electron scavengers, as well as the cases in which the electron undergoes chemical reactions with the solvent. Work is also underway on the specialization of Eq. (40) to the case of pure and mixed molecular solids for which translational symmetry can be used to simplify the spatial dependence both of the solvent's distribution functions and of the \bar{h}_{mn} and $F(I, J, K, L, t - \tau)$. The incorporation of electron-electron repulsion effects is also an important step to take in order to generate a theory which is not limited to dilute solutions of electrons. Likewise, the treatment of the motion of the electron in the presence of an applied external electric field is important for studying mobility.

In addition to the research directed at probing the migration of excess electrons by monitoring $\langle r^2 \rangle_t$, research is in progress whose goal is a quantitative but physically clear understanding of the spectral behavior of excess electrons in pure and mixed solvents. This work involves the calculation of the correlation function $\langle\langle 0 | a_0 F(t) F a_0^\dagger | 0 \rangle\rangle_N$, where F is the electric dipole operator

$$F(t) = \exp(iHt) \int \psi^*(\mathbf{r}) \boldsymbol{\epsilon} \cdot \mathbf{r} \psi(\mathbf{r}) d\mathbf{r} \exp(-iHt), \quad (51)$$

and $\boldsymbol{\epsilon}$ is the electric vector of the incident photon. The Fourier transform of this correlation function gives the frequency spectrum of the electron-solvent system. By expressing the field operator $\psi^*(\mathbf{r})$ in terms of the molecule and hole orbitals $\{\phi_m\}$ and operators, and performing a cumulant approximation to the time evolution operator, it will be possible to express the above correlation function in terms of the solvent structure information and the electron-solvent interaction potential. The dynamics of the motion of the solvent molecules will affect the frequency dependence of the excess electron's optical absorption spectrum.

As is clear from the above discussion, much important and challenging research remains to be done before this initial contribution can be brought to the stage where the theory is applied, in a straightforward manner, to the problems of excess electrons in molecular solids and liquids. It is hoped that the research presented here will stimulate new and innovative contributions to this exciting area of science.

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- ¹¹J. Jortner, *J. Chem. Phys.* **30**, 839 (1959) applied Landau's [L. Landau, *Z. Phys.*, *Z. Soviet Union* **3**, 664 (1933)] polaron model to electrons in liquids. In a sense, a dressed electron is similar to such a polaron.
- ¹²This does not imply that $\phi_m(\mathbf{r})$ is assumed to be an exact stationary state of the electronic Hamiltonian.
- ¹³This orbital could be either a molecular orbital $\phi_\alpha(\mathbf{r}, X_m)$ or a localized continuum orbital, depending upon where the electron is created. For some solvents it is more likely that the electron is formed in an interstitial region, whereas for other solvents the electron is more likely to form in a molecular region. For the rest of this paper, the orbital labeled $\phi_0(\mathbf{r}, 0)$ is, therefore, either a molecular or localized continuum orbital.
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- ¹⁵Later, this state will be written more explicitly as $|0(X)\rangle |vac\rangle$.
- ¹⁶N. R. Kestner, Ref. 1(b), Chap. 1, p. 2.
- ¹⁷Of course, other events can also occur. For example, the electron can react chemically with the solvent, as in the case of H₂O, or a scavenger molecule. In the present work, it is assumed that no such reaction is taking place.
- ¹⁸Thus, the present theory is not intended to be employed to investigate, for example, the migration of electrons in either solid or liquid metals.
- ¹⁹If the electron "rides" in the localized interstitial orbitals, then the diffusion coefficient should be that of the interstices (holes). However, the holes diffuse by way of the molecules diffusing, therefore their diffusion coefficient is identical to that of the solvent.
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- ²²The cumulant expansion was used by Grover and Silbey in their elegant treatment of exciton migration (see Ref. 14). The advantage of this device is that it permits the dynamics of the system to be approximated in terms of the equilibrium averaged dynamics plus terms involving instantaneous fluctuations away from equilibrium. For an excellent treatment of the cumulant method, see R. Kubo, *J. Phys. Soc. Jpn.* **17**, 1100 (1962).
- ²³Of course, in the neighborhood of phase transitions and critical points, these fluctuations may not be small. Therefore, it is assumed that the system is not in such a transition situation.
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- ²⁵J. G. Kirkwood and E. M. Boggs, *J. Chem. Phys.* **10**, 394 (1942).
- ²⁶ $\exp(-\Gamma t)$ for the Lorentzian and $\exp(-\Gamma^2 t^2)$ for the Gaussian.