where $F_\beta'(k, 0)$ are the initial values for the hydrodynamic equations. The prime is used to distinguish these initial conditions from the physical conditions $F_\beta(k, 0)$, since in general they differ[14] [see Eq. (A.3)].

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[3] E. G. D. Cohen, in Statistical Mechanics of Equilibrium and Non-equilibrium, edited by J. Meixner (North Holland Publishing Co., Amsterdam, 1962), and references therein.

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[7] The ensemble considered here arises from an initial value problem. However, the nonlocal equations to be discussed are formally the same as those obtained in Ref. 2 for a system interacting at its boundaries. This is expected since the hydrodynamic equations are the same for both initial and boundary value problems.

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Study of Exciton Dynamics in a Simple Liquid

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A quantum-mechanical formulation of the theory of Frenkel excitons in a simple liquid is given with attention focused on the interaction of the exciton with the collective translational excitations of the liquid. Using a Born-Oppenheimer approximation to define a basis, the nonadiabatic term which describes the coupling of the exciton to the momentum density of the liquid is treated as a perturbation. It is shown, by use of Green's-function methods, that this coupling to the collective modes of the liquid is more important than is elastic scattering arising from the disorder in the system. The energy shift, damping, and the line shape of the Frenkel exciton are expressed in terms of the resonance interaction, the structure function, the translational kinetic energy of the liquid, and the lifetime of translational collective excitations.

I. INTRODUCTION

The description of the excited electronic states of a liquid is complicated by (a) the lack of long-range order in the liquid: (b) the short lifetime of small-wavelength collective motions of the atoms (molecules) constituting the liquid; and (c) lack of detailed knowledge of the dynamics of molecular motion and of the possible forms of coupling between nuclear motion and electronic motion in the liquid.

Consider, first, item (a). Nicolis and Rice[1] have shown that, when the coupling between electronic motion and nuclear motion is neglected, a liquid can support collective electronic excitations of the Frenkel type. The dispersion relation for these excitations was derived and shown to depend upon the structure of the liquid through the molecular pair distribution function. Moreover, Nicolis and Rice showed that the disorder in the liquid structure does lead to damping of the collective excitations, but that that damping is small relative to the damping arising from electron-atom interaction. At the other extreme of the conventional classification of electronic states, Rice and Jortner[2] have shown that Wannier type excitons can exist in a simple liquid if the electron-atom interaction is not too strong. The two studies cited clearly show, that in the absence of electron-atom scattering disorder in the liquid is not sufficient to destroy collective electronic excitations.

There has been less progress on problems related to items (b) and (c). From model calculations Rice and Jortner,[2] and also Rice, Nicolis, and Jortner,[3] give estimates of the effect of electron-atom scattering on the exciton spectrum. In these analyses the motion of the molecules of the liquid is described classically and by the use of simplified models, e.g., by the use of the small-step diffusion or linear trajectory approximations. The models used fail to describe collective translational motions in the liquid and do not provide a systematic description of the variation of electronic-nuclear motion coupling with exciton wave vector. However, the model calculations do provide predictions concerning the exciton line shape which may be tested against experiment, an achievement not exhibited by the more exact but formal analysis of Popielawski and Rice.[4]

Recent work by Rahman[5] and by Zwanzig[6, 7] provides us with the information necessary for a more incisive description of exciton damping in a simple liquid. Zwanzig has shown how, by the use of a variational principle and a simple relaxation time ansatz, a spectrum of collective translational excitations can be deduced for a simple liquid. These collective translational excitations are short-lived ($\sim 10^{-12}$–10^{-13} sec) when the wavelength is of the order of magnitude of the average intermolecular separation; they are long-lived when the wavelength is large relative to the average intermolecular separation. The revelant time scale on which long and short are defined is, in this case, the time scale defined by translational relaxation as in diffusion, i.e., 10^{-13} sec. Now, from an analysis of a computer experiment Rahman has deduced the spectrum and lifetimes of collective translational excitations for a pair potential model of liquid Ar. It is found that the predictions of the Zwanzig analysis are in excellent agreement with the results of the computer experiment. It may therefore be concluded that the Zwanzig formalism leads to a very good zero-order description of collective translational excitations in a simple liquid.

In this paper we undertake the following tasks: (i) A reformulation of the description of the excited states of a simple liquid in the Frenkel limit using quantum mechanics instead of classical mechanics; (ii) inclusion in the description of the system the coupling between collective electronic excitations and collective translational excitations; and (iii) explicit demonstration of the relationship between the collective translational excitations of the liquid, their lifetimes, and the transition line shape in the liquid.

In the analysis to follow we use a semi-classical representation of the translational spectrum of the liquid while retaining a full quantum-mechanical representation of the Frenkel exciton spectrum. The Hamiltonian operator contains terms corresponding to uncoupled electronic excitations, uncoupled translational excitations, and an interaction represented by the coupling of Born-Oppenheimer states. This approach has the advantage that the nonadiabatic term which describes the coupling can be written so as to display explicitly the collective coordinates of the liquid. The Hamiltonian used herein resembles the corresponding Hamiltonian describing the electronic states of a crystalline solid, except that in our case the Born-Oppenheimer states are approximate and because of the disorder in the system are not orthogonal. To actually determine the properties of the liquid described by the Hamiltonian mentioned, a closed equation for the Green's function of the system is developed by breaking the highest-order correlations between the exciton and the translational motion of the liquid in the heirarchy equation of motion for the Green's function. From this approximate Green's function are derived the spectral function and the damping and energy shift of the exciton spectrum.

II. THE HAMILTONIAN OF THE LIQUID

We begin our analysis by representing the Hamiltonian of the liquid in the form

$$H = H_e + H_f + H_{\text{int}} \,, \tag{1}$$

where H_e describes the internal degrees of freedom of the isolated molecules, H_f is the Hamiltonian describing translational motion of the fluid molecules, and H_{int} is the interaction term. Let us consider only one electronic excited state and the electronic ground state (two-state molecule). Then, if ${}^1a_n{}^\dagger$ and ${}^0a_n{}^\dagger$ create an electron in the excited and in the ground state, respectively, the corresponding wave functions read

$$\varphi_n{}^1 = {}^1a_n{}^\dagger \,|\Omega\rangle \,,$$

$$\text{and}\quad \varphi_n{}^0 = {}^0a_n{}^\dagger \,|\Omega\rangle \,, \tag{2}$$

where $|\Omega\rangle$ is the state vector of the vacuum corresponding to our system. Denoting the energy corresponding to $\varphi_n{}^1$ by E_1 (relative to the ground-state energy), the first term in (1) may be written in the form

$$H_{\mathrm{e}}=\frac{1}{N}\sum_{n=0}^{N}H_{\mathrm{e}}{}^{n}=\frac{1}{N}\sum_{n}E_{1}\,{}^{1}a_{n}{}^{\dagger}\,{}^{1}a_{n}\quad . \tag{3}$$

The second term in (1) has the form

$$H_{\mathrm{f}}=\frac{1}{N}\sum_{n}\frac{P_{n}{}^{2}}{2M}+\frac{1}{N}\sum_{n,m}V(n,m)\ . \tag{4}$$

when the interaction between molecules is adequately represented as a sum of pair potentials, $V(n,m)$. For all of the general part of the analysis we need not specify the form of $V(n,m)$. As usual, $\vec{P}_n$ and M are the linear momentum and mass of the n^{th} molecule.

The third term in (1) contains all contributions which depend on both the molecular and the electronic coordinates. One example of such contributions is the resonance interaction. Now, again using the second quantisation representation, H_{int} assumes the form

$$H_{\mathrm{int}}=\frac{1}{N}\sum_{n,m}\ \sum_{\alpha,\alpha',\beta,\beta'}W(n,m)_{\alpha\alpha'\beta\beta'}$$

$$\times\,{}^{\alpha}a_{n}{}^{\dagger}\,{}^{\alpha'}a_{n}\,{}^{\beta}a_{m}{}^{\dagger}\,{}^{\beta'}a_{m}\ , \tag{5}$$

where $\alpha,\alpha',\beta,\beta'$ refer to the ground or the excited state of the molecule. The interaction energy $W(n,m)$ depends upon the distance between the pair of molecules n,m and on the specific electronic states in which the molecules exist.

When the overlap between molecules is very small in the electronic ground state and in the electronic excited state (Frenkel limit), the electronic ground-state wave function is, in first approximation,

$$\psi_{0}=\prod_{n}\varphi_{n}{}^{0}\equiv\prod_{n}{}^{0}a_{n}{}^{\dagger}\ \ \Omega\rangle\ , \tag{6}$$

and a nonstationary localized excited electronic state wave function is

$$\psi_{n}=\varphi_{n}{}^{1}\prod_{m\neq n}\varphi_{m}{}^{0}\equiv c_{n}{}^{\dagger}\ \ \Omega\rangle\ . \tag{7}$$

In the next approximation one would like to include molecular (and possibly electronic) correlation effects in the wave function. This can be done by use of a correction factor in (7) of the Jastrow type,[8] which factor includes in an approximate but accurate form the effects of the short-range repulsion between the molecules. However, inclusion of short-range correlations in the wave function forces us to use approximations which we wish to avoid at first. Our first goal is to stress the main features of the coupling between the electronic and the translational excitations of the liquid; the effects arising from short-range repulsions between the molecules are discussed in Appendix A. In (7), the operators $c_n{}^{\dagger}$ and c_n are of the Pauli type, i.e., they commute for $n\neq n'$ (Bose operators) and anticommute for $n=n'$ (Fermi operators):

$$[c_{n},c_{n'}{}^{\dagger}]=(1-2c_{n}{}^{\dagger}c_{n})\delta_{n,n'}\ . \tag{8}$$

The fact that the c_n have Fermi character for $n=n'$ reflects the observation that only one excitation is allowed at a given molecule at a given time. If we consider only weakly excited states of the liquid the occupation number $\langle c_n{}^{\dagger}c_n\rangle$ will be small compared to unity, and the system behaves as if it had pure Bose excitations. This limit will describe the system when $E_1\gg k_BT$. Corrections to the Bose approximation can expressed in terms of short-ranged dynamical interactions between the excitons (see Appendix B).

Now we shall assume that the set of the functions $\{\psi_n\}$ is complete, so that the true exciton wave function may be expressed in terms of the $\{\psi_n\}$. In this approximation, the Hamiltonian operator may be represented as

$$\begin{aligned}H_{T}&=N^{-1}\sum_{n,m}\langle\psi_{n}|H|\psi_{m}\rangle c_{n}{}^{\dagger}c_{m}\\&=N^{-1}\sum_{n}E_{1}c_{n}{}^{\dagger}c_{n}+N^{-1}\sum_{n}D(n)c_{n}{}^{\dagger}c_{n}\\&\quad+N^{-1}\sum_{n,m}F(n,m)c_{n}{}^{\dagger}c_{m}+H_{f}\end{aligned} \tag{9}$$

where the matrix elements $D(n)$ and $F(n,m)$ are

$$D(n)=N^{-1}\sum_{m}W(n,m)_{1100}-N^{-1}\sum_{m}W(n,m)_{0000}\ ,$$

$$F(n,m)=W(n,m)_{0110}\ . \tag{10}$$

The term $D(n)$ plays the same role in the liquid as does the term usually denoted D in the Frenkel-Davydov theory of the electronic states of molecular crystals.[9] This interaction leads to a shift of the entire electronic manifold relative to the spectrum of the free molecule. The term $F(n,m)$ describes excitation exchange between the molecules n and m.

In a liquid all molecules are equivalent, and therefore $D(n)$ does not depend on the molecule index n. Let the Fourier transform of the excitation exchange-interaction energy be defined by

$$\tilde{F}(\vec{k})=(2\pi)^{-\frac{3}{2}}\int d\vec{R}F(\vec{R})\,e^{-i\vec{k}\cdot\vec{R}} \tag{11}$$

with the inverse transform

$$F(n-m)=(2\pi)^{-\frac{3}{2}}\int d\vec{k}\tilde{F}(\vec{k})\,e^{i\vec{k}\cdot(\vec{R}_{n}-\vec{R}_{m})}\ . \tag{12}$$

Correspondingly, consider the new operators

$$\tilde{c}_{\vec{k}}{}^{\dagger}=N^{-\frac{1}{2}}\sum_{n}e^{i\vec{k}\cdot\vec{R}_{n}}c_{n}{}^{\dagger} \tag{13}$$

and $$\tilde{c}_{\vec{k}}=N^{-\frac{1}{2}}\sum_{n}e^{-i\vec{k}\cdot\vec{R}_{n}}c_{n}\ . \tag{14}$$

The operators defined by (13) and (14) satisfy the commutation relation

$$[\tilde{c}_{\vec{k}'},\tilde{c}_{\vec{k}}{}^{\dagger}]=N^{-1}\sum_{n}e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_{n}}\ . \tag{15}$$

It is now recognized that the right-hand side of (15) is the $(\vec{k}-\vec{k}')^{\text{th}}$ Fourier component of the density fluctuations in the liquid, i.e.,

$$\tilde{\rho}_{\vec{k}-\vec{k}'} = N^{-1}\sum_n e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_n} . \tag{16}$$

Using (13)–(15) the Hamiltonian displayed in (9) may be rewritten in the form

$$H_T = \mathcal{E}_0 \mathfrak{N} + (2\pi)^{-3/2}\int d\vec{k}\,\tilde{F}(\vec{k})\tilde{c}_{\vec{k}}^{\,\dagger}\tilde{c}_{\vec{k}} + H_f , \tag{17}$$

where $\mathfrak{N} = N^{-1}\sum_n c_n^{\,\dagger} c_n$ is the number operator and

$$\mathcal{E}_0 = E_1 + D . \tag{18}$$

Although the Hamiltonian operator (17) is diagonal in $\vec{k}$, the energy $\tilde{F}(\vec{k})$ cannot be interpreted as the energy of an elementary excitation because the operators $\tilde{c}_{\vec{k}}$ and $\tilde{c}_{\vec{k}}^{\,\dagger}$ are not canonical operators.

III. THE BORN-OPPENHEIMER APPROXIMATION

The operators defined by Eqs. (13) and (14) clearly depend upon the instantaneous positions of the molecules and do not commute with the translational kinetic-energy operator. We can use this property of $\tilde{c}_{\vec{k}}^{\,\dagger}$ and $\tilde{c}_{\vec{k}}$ to expand the right-hand side of (17) in a form suitable for the application of perturbation theory. For our purposes a convenient representation is obtained by use of the Born-Oppenheimer separation.[10] That is, we propose to fix the molecular positions and to determine the corresponding electronic eigenfunctions and eigenvalues, and then to couple the states so defined by the molecular translational kinetic-energy operator.

The first step in our analysis is the demonstration that the function

$$|\psi_{\vec{k}}\rangle = \tilde{c}_{\vec{k}}^{\,\dagger}|\Omega\rangle \tag{19}$$

is an approximate Born-Oppenheimer eigenfunction. Consider the equation

$$[\mathcal{E}_0\mathfrak{N} + (2\pi)^{-3/2}\int d\vec{k}'\tilde{F}(\vec{k}')\tilde{c}_{\vec{k}'}^{\,\dagger}\tilde{c}_{\vec{k}'}]\,|\psi_{\vec{k}}\rangle = \mathcal{E}(\vec{k})\,|\psi_{\vec{k}}\rangle . \tag{20}$$

Using (13)–(15) for the product of operators $\tilde{c}_{\vec{k}'}^{\,\dagger}\tilde{c}_{\vec{k}'}$ we now rewrite the left-hand side of (20) in the form [using (19) and (16)]

$$\begin{aligned}
&\mathcal{E}_0\mathfrak{N} + (2\pi)^{-3/2}\int d\vec{k}'\,\tilde{F}(\vec{k}')\tilde{c}_{\vec{k}'}^{\,\dagger}\,\tilde{c}_{\vec{k}'}\tilde{c}_{\vec{k}}^{\,\dagger}|\Omega\rangle = [\mathcal{E}_0\tilde{c}_{\vec{k}}^{\,\dagger} + (2\pi)^{-3/2}\int d\vec{k}'\tilde{F}(\vec{k}')\tilde{\rho}_{\vec{k}-\vec{k}'}\tilde{c}_{\vec{k}'}^{\,\dagger}]|\Omega\rangle \\
&= [\mathcal{E}_0 + (2\pi)^{-\frac{3}{2}}\int d\vec{k}'\tilde{F}(\vec{k}')\sum_{n-m} e^{i(\vec{k}-\vec{k}')\cdot(\vec{R}_n-\vec{R}_m)}]\,c_{\vec{k}}^{\,\dagger}|\Omega\rangle = [\mathcal{E}_0 + (2\pi)^{-\frac{3}{2}}\int d\vec{k}'\tilde{F}(\vec{k}')\,\mathrm{s}(\vec{k}-\vec{k}')]|\psi_{\vec{k}}\rangle .
\end{aligned} \tag{21}$$

The expectation value of $\mathrm{s}(\vec{k}-\vec{k}')$ is the structure function of the liquid. It then follows, using (20), that

$$\mathcal{E}(\vec{k}) = \mathcal{E}_0 + (2\pi)^{-3/2}\int d\vec{k}'\tilde{F}(\vec{k}')\,\mathrm{s}(\vec{k}-\vec{k}') \tag{22}$$

is the eigenvalue corresponding to the eigenfunction $\psi_{\vec{k}}$.

When the right-hand side of (17) is expanded using the Born-Oppenheimer separation, further analysis requires consideration of those operators that create or destroy excitons formed from the Born-Oppenheimer states. We denote these operators by $\tilde{b}_{\vec{k}}^{\,\dagger}$ and $\tilde{b}_{\vec{k}}$, respectively. Note that $\tilde{c}_{\vec{k}}^{\,\dagger}$ and $\tilde{c}_{\vec{k}}$ depend upon the instantaneous positions of the molecules and do not commute with the translational kinetic-energy operator, whereas $\tilde{b}_{\vec{k}}^{\,\dagger}$ and $\tilde{b}_{\vec{k}}$ do commute with the translational kinetic-energy operator. The difference in behavior arises because $\tilde{b}_{\vec{k}}^{\,\dagger}$ and $\tilde{b}_{\vec{k}}$ are defined to create or destroy exciton states on the Born-Oppenheimer basis, and in that basis the molecular coordinates are regarded as parameters.

In the Born-Oppenheimer basis the exciton part of the system Hamiltonian is, by definition,

$$H_{\text{exc.}}{}' = \mathcal{E}_0\mathfrak{N} + (2\pi)^{-3/2}\int d\vec{k}\tilde{F}(\vec{k})\tilde{b}_{\vec{k}}^{\,\dagger}\tilde{b}_{\vec{k}} , \tag{23}$$

whilst the interaction term is

$$H_{\text{int}}{}' = \frac{-1}{(2\pi)^3 N}\int d\vec{k}\int d\vec{k}'\sum_n \frac{1}{2M}\left\langle\psi_{\vec{k}}\left|\frac{\partial}{\partial\vec{R}_n}\right|\psi_{\vec{k}'}\right\rangle\frac{\partial}{\partial\vec{R}_n}\;\tilde{b}_{\vec{k}}^{\,\dagger}\tilde{b}_{\vec{k}'} - \frac{1}{(2\pi)^3 N}\int d\vec{k}\int d\vec{k}'\sum_n\frac{1}{2M}\left\langle\psi_{\vec{k}}\left|\frac{\partial^2}{\partial\vec{R}_n^{\,2}}\right|\psi_{\vec{k}'}\right\rangle\tilde{b}_{\vec{k}}^{\,\dagger}\tilde{b}_{\vec{k}'} . \tag{24}$$

Since we know the explicit form of the wave function we can evaluate the matrix elements easily;

$$\left\langle \psi_{\vec{k}} \left| \frac{\partial}{\partial \vec{R}_n} \right| \psi_{\vec{k}'} \right\rangle = i\vec{k}' e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_n} , \quad \left\langle \psi_{\vec{k}} \left| \frac{\partial^2}{\partial \vec{R}_n^{\,2}} \right| \psi_{\vec{k}'} \right\rangle = -k'^2 e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_n} \tag{25}$$

The substitution of (25) and the Fourier-transformed momentum density

$$\tilde{\vec{J}}_{\vec{q}} = N^{-1} \sum_n e^{i\vec{q}\cdot\vec{R}_n} (\partial/\partial\vec{R}_n)$$

into (24) leads to the following expression for the interaction contribution to the Hamiltonian in the Born-Oppenheimer basis:

$$H_{\text{int}}' = \frac{-i}{2M(2\pi)^3} \int d\vec{k} \int d\vec{q}\, \vec{q}\, \tilde{b}_{\vec{k}}^{\dagger} \tilde{b}_{\vec{k}+\vec{q}} \tilde{\vec{J}}_{\vec{q}} + \frac{1}{4M(2\pi)^3} \int d\vec{k} \int d\vec{k}' (k^2 + k'^2) \tilde{\rho}_{\vec{k}'-\vec{k}} \tilde{b}_{\vec{k}}^{\dagger} \tilde{b}_{\vec{k}'} . \tag{26}$$

The relative wave vector $\vec{q}$ is defined as $\vec{k}' - \vec{k}$. The first term in Eq. (26) corresponds to the exciton lattice coupling in a molecular crystal.[11] In Appendix C we show that the coupling constant has the same structure as the one derived by Davydov.[11] Our result, on the other hand, does not depend on the existence of a crystal lattice but only on the use of the Born-Oppenheimer separation. The second term is, essentially, the kinetic energy the exciton has in common with the molecules. Our final Hamiltonian now reads

$$H_T = \mathcal{E}_0 \mathfrak{N} + \frac{1}{(2\pi)^3} \int d\vec{k} \int d\vec{k}' \left(\tilde{F}(\vec{k})\, \delta_{\vec{k}\vec{k}'} + \frac{k^2 + k'^2}{4M} \rho_{\vec{k}'-\vec{k}} \right) \tilde{b}_{\vec{k}}^{\dagger} \tilde{b}_{\vec{k}'} - \frac{i}{2(2\pi)^3} \int d\vec{k} \int d\vec{q}\, \vec{q}\, \tilde{b}_{\vec{k}}^{\dagger} \tilde{b}_{\vec{k}+\vec{q}} \tilde{\vec{J}}_{\vec{q}} . \tag{27}$$

The appearance of $\tilde{\vec{J}}_{\vec{q}}$ in Eq. (27) is particularly significant, because Zwanzig[6] has shown how an ansatz relating to the time rate of change of $\tilde{\vec{J}}_{\vec{q}}$ may be used to generate an approximation to the spectrum of the collective translational excitations. Zwanzig assumes that the time rate of change of $\tilde{\vec{J}}_{\vec{q}}$ follows the equation of a damped harmonic oscillator

$$\frac{d^2}{dt^2} \tilde{\vec{J}}_{\vec{q}} = -\omega_{\vec{q}}^{\,2} \tilde{\vec{J}}_{\vec{q}} - \frac{1}{\tau} \frac{d}{dt} \tilde{\vec{J}}_{\vec{q}} \tag{28}$$

with the lifetime τ determined by the frequency-dependent shear and bulk viscosities (η, ϕ) and the infinite-frequency shear and bulk moduli (G_∞ and K_∞). In fact, Zwanzig shows that under the assumption that τ is independent of the wavenumber

$$\tau = (\tfrac{4}{3}\eta + \phi)/(\tfrac{4}{3}G_\infty + K_\infty) \tag{29}$$

while a variational ansatz leads to the spectrum

$$\omega_{q\lambda}^{\;2} = \frac{1}{Mk_B T} (1 + 2\hat{\epsilon}_{\vec{q}\lambda} \hat{\epsilon}_{\vec{q}3}) q^2 - \frac{\rho}{M} \int dR\, g(R) (\cos \vec{q}\cdot\vec{R} - 1) \left(\hat{\epsilon}_{\vec{q}\lambda} \frac{\partial}{\partial \vec{R}} \right)^2 V(\vec{R}) \tag{30}$$

with $g(R)$ the pair correlation function, and $\hat{\epsilon}_{\vec{q}\lambda}$, $\hat{\epsilon}_{\vec{q}3}$ orthogonal unit vectors, $\hat{\epsilon}_{\vec{q}3}$ lying along $\vec{q}$, i.e., $\hat{\epsilon}_{\vec{q}3} = \vec{q}/|q|$. The normal coordinates, whose time variation is described by the spectrum ω_q are just $\tilde{\vec{J}}_{\vec{q}} \pm (i/\omega_q)(d/dt)\tilde{\vec{J}}_{\vec{q}}$. As mentioned, the predictions of this simple analysis are in good agreement with the results of Rahman's computer experiments,[5] even for short wavelength collective excitations. The ansatz displayed in Eq. (28) seems accurate over a much larger range of excitation wavelength than might have been anticipated. (In a recent paper Zwanzig has justified the use of Eq. (28) from an analysis based on generalized hydrodynamic considerations.[7])

IV. THE EXCITON SPECTRUM

To determine the exciton spectrum including interactions between electronic and nuclear motion, we calculate the poles of the one exciton Green's function defined by

$$\langle\langle \tilde{b}_{\vec{k}}^{\dagger} ; \tilde{b}_{\vec{k}} \rangle\rangle = \frac{i}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} dt\, \Theta(t) \langle [\tilde{b}_{\vec{k}}^{\dagger}(t), \tilde{b}_{\vec{k}}] \rangle_T \, e^{i\epsilon t} \tag{31}$$

In Eq. (31) $\Theta(t)$ is the Heaviside unit step function, $\langle\cdots\rangle_T$ refers to an average over the canonical ensemble with full Hamiltonian H_T, and $\tilde{b}_{\vec{k}}^{\dagger}(t)$ is the Heisenberg operator corresponding to $\tilde{b}_{\vec{k}}^{\dagger}$:

$$\tilde{b}_{\vec{k}}^{\dagger}(t) = e^{iH_T t}\, \tilde{b}_{\vec{k}}^{\dagger}\, e^{-iH_T t} . \tag{32}$$

Consider the equation of motion of $\tilde{b}_{\vec{k}}^{\dagger}(t)$; this is

$$\frac{d}{dt}\tilde{b}_{\vec{k}}^{\dagger}(t)=\left[\mathcal{E}_0+\frac{1}{(2\pi)^{3/2}}\int d\vec{k}'\left(\tilde{F}(\vec{k}')+\frac{k'^2+k^2}{4M}\right)s(\vec{k}'-\vec{k})\right]\tilde{b}_{\vec{k}}^{\dagger}(t)-\frac{i}{2(2\pi)^{3/2}}\int d\vec{q}\,\vec{q}\,\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\tilde{\vec{J}}_{\vec{q}}\;. \tag{33}$$

In the kinetic-energy term, which results from the coupling to the molecular motion, we neglected nondiagonal elements which lead to unimportant elastic-scattering contributions. We now average both sides of (33) with respect to a canonical ensemble and take the Fourier transform of the resulting equation. It is found that

$$[\mathcal{E}_T(\vec{k})-\epsilon]\,\langle\langle\tilde{b}_{\vec{k}}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle=1+\frac{i}{2(2\pi)^{3/2}}\int d\vec{q}\,\vec{q}\,\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\tilde{\vec{J}}_{\vec{q}};\tilde{b}_{\vec{k}}\rangle\rangle \tag{34}$$

with $\mathcal{E}_T(\vec{k})=\langle\mathcal{E}(\vec{k})\rangle_T+\frac{1}{(2\pi)^{3/2}}\int d\vec{k}'\,\frac{k^2+k'^2}{4M}\,S(\vec{k}-\vec{k}')\,,$ (35)

where $S(\vec{k}-\vec{k}')$ is the structure function of the liquid. As a consequence of removing the expectation value of $s(\vec{k}-\vec{k}')$ from the integral we have neglected higher-order correlations in the liquid. Corrections to this factorization approximation result in elastic-scattering terms which are proportional to

$$\langle s^2(\vec{k}-\vec{k}')\rangle-S^2(\vec{k}-\vec{k}')$$

and which can be neglected. Clearly, Eq. (34) defines a hierarchy of equations, since there appears on the right-hand side of (34) a new Green's function. It is convenient to subdivide this new Green's function into two parts;

$$\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\tilde{\vec{J}}_{\vec{q}};\tilde{b}_{\vec{k}}\rangle\rangle=\tfrac{1}{2}\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\xi_{\vec{q}}^{+};\tilde{b}_{\vec{k}}\rangle\rangle+\tfrac{1}{2}\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\xi_{\vec{q}}^{-};\tilde{b}_{\vec{k}}\rangle\rangle\quad, \tag{36}$$

where $\xi_{\vec{q}}^{\pm}=\tilde{\vec{J}}_{\vec{q}}\pm(i/\omega_{\vec{q}})(d/dt)\tilde{\vec{J}}_{\vec{q}}$ (37)

is the normal coordinate related to the momentum density. The new Green's functions satisfy the following equations of motion

$$[\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon+\omega_q-\frac{i}{2\tau}]\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\vec{\xi}_{\vec{q}}^{+};\tilde{b}_{\vec{k}}\rangle\rangle$$

$$=\frac{i}{2M(2\pi)^{3/2}}\int d\vec{q}'\vec{q}'\langle\langle\vec{\xi}_{\vec{q}}^{+}\tilde{\vec{J}}_{\vec{q}'}\tilde{b}_{\vec{k}+\vec{q}+\vec{q}'}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle-\frac{i}{2\tau}\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\xi_{\vec{q}}^{-};\tilde{b}_{\vec{k}}\rangle\rangle \tag{38}$$

and $$[\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon-\omega_{\vec{q}}-\frac{i}{2\tau}]\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\vec{\xi}_{\vec{q}}^{-};\tilde{b}_{\vec{k}}\rangle\rangle$$

$$=\frac{i}{2M(2\pi)^{3/2}}\int d\vec{q}'\vec{q}''\langle\langle\vec{\xi}_{\vec{q}}^{-}\tilde{\vec{J}}_{\vec{q}'}\tilde{b}_{\vec{k}+\vec{q}+\vec{q}'}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle-\frac{i}{2\tau}\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\vec{\xi}_{\vec{q}}^{+};\tilde{b}_{\vec{k}}\rangle\rangle\;. \tag{39}$$

By combination of (38) and (39) we find for the Green's function appearing in (32) the equation

$$\left(\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon-\frac{\omega_{\vec{q}}^{2}}{\mathcal{E}_T(\vec{k}+\vec{q})-E-i/\tau}\right)\langle\langle\tilde{b}_{\vec{k}+\vec{q}}^{\dagger}\tilde{\vec{J}}_{\vec{q}};\;\tilde{b}_{\vec{k}}\rangle\rangle$$

$$=\frac{i}{2M(2\pi)^{3/2}}\int d\vec{q}'\vec{q}'\left[\langle\langle\tilde{\vec{J}}_{\vec{q}}\tilde{\vec{J}}_{\vec{q}'}\tilde{b}_{\vec{k}+\vec{q}+\vec{q}'};\;\tilde{b}_{\vec{k}}\rangle\rangle+\frac{\tau\omega_{\vec{q}}}{\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon-i/\tau}\;\langle\langle\frac{d}{dt}\tilde{\vec{J}}_{\vec{q}}\;\tilde{\vec{J}}_{\vec{q}'}\tilde{b}_{\vec{k}+\vec{q}+\vec{q}'}^{\dagger};\;\tilde{b}_{\vec{k}}\rangle\rangle\right] \tag{40}$$

Thus far we have used only the Born-Oppenheimer separation in our analysis. The use of the Born-Oppenheimer separation is not an approximation so long as the coupling terms are kept. Consider now the limiting case wherein the coupling between the collective electronic excitations and the collective translational excitations is not strong. In this limit we can reduce the Green's function on the right-hand side of (40) by breaking the higher-order correlations between the momentum density and the exciton. In formal terms, we now introduce the weak coupling limit with the approximations

$$\langle\langle\tilde{\vec{J}}_{\vec{q}}\tilde{\vec{J}}_{\vec{q}'}\tilde{b}_{\vec{k}+\vec{q}+\vec{q}'}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle=\langle\tilde{\vec{J}}_{\vec{q}}\tilde{\vec{J}}_{\vec{q}'}\rangle\langle\langle\tilde{b}_{\vec{k}+\vec{q}+\vec{q}'}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle=Mk_BT\,\delta_{\vec{q}+\vec{q}'}\langle\langle\tilde{b}_{\vec{k}}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle \tag{41}$$

and $$\left\langle\!\left\langle\left(\frac{d}{dt}\tilde{\vec{J}}_{\vec{q}}\right)\tilde{\vec{J}}_{\vec{q}'},\tilde{b}_{\vec{k}+\vec{q}+\vec{q}'}^{\dagger};\tilde{b}_{\vec{k}}\right\rangle\!\right\rangle=\left\langle\left(\frac{d}{dt}\tilde{\vec{J}}_{\vec{q}}\right)\vec{J}_{q}'\right\rangle\langle\langle\tilde{b}_{\vec{k}+\vec{q}+\vec{q}'}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle=0 \quad . \tag{42}$$

The use of (44)–(46) in (38) gives for the original Green's function of interest

$$\theta(\epsilon)\langle\langle\tilde{b}_{\vec{k}}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle=1 \,, \tag{43}$$

where $$\theta(\epsilon)=\mathcal{E}_T(\vec{k})-\epsilon+\frac{k_BT}{2M(2\pi)^{3/2}}\int d\vec{q}\,\vec{q}^{\,2}\left(\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon-\frac{\omega_q^{\,2}}{\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon-i/\tau}\right)^{-1} \quad . \tag{44}$$

The zeros of the function $\theta(\epsilon)$ determine the elementary excitations of the system. Also provided in $\theta(\epsilon)$ is information about the shift in excitation energy resulting from coupling of the excitons to the translational excitations, and about the line shapes of the transitions between the ground state and exciton states. In the weak coupling limit it is convenient to solve the equation $\theta(\epsilon)=0$ by iteration. The first-two orders of iteration yield

$$\epsilon^{(0)}(\vec{k})=\mathcal{E}_T(\vec{k}) \tag{45}$$

$$\epsilon^{(1)}(\vec{k})=\mathcal{E}_T(\vec{k})-\frac{k_BT}{2M(2\pi)^{3/2}}\int d\vec{q}\,q^2\frac{\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})-i/\tau}{[\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})][\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})-i/\tau]-\omega_q^{\,2}} \quad . \tag{46}$$

The damping is then given by the imaginary part of $\epsilon^{(1)}$:

$$\mathrm{Im}\,\epsilon^{(1)}(\vec{k})=\frac{k_BT\tau^{-1}}{2M(2\pi)^{3/2}}\int d\vec{q}\,q^2\frac{2[\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(k)]^2-\omega_q^{\,2}}{\{[(\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})]^2-\omega_q^{\,2}\}^2+[\mathcal{E}_T(\vec{k}+q)-\mathcal{E}_T(k)]^2\tau^{-2}} \tag{47}$$

while the energy shift results from the real part of $\epsilon^{(1)}$:

$$\mathrm{Re}\,\epsilon^{(1)}(\vec{k})=\mathcal{E}_T(\vec{k})-\frac{k_BT}{2M(2\pi)^{3/2}}\int d\vec{q}\,q^2\frac{[\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})]\{[\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})]^{-2}-\omega_q^{\,2}-\tau^{-2}\}}{\{[(\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})]^2-\omega_q^{\,2}\}^2+[\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})]\,\tau^{-2}} \tag{48}$$

Finally we find for the line shape function, $\Gamma(\epsilon,\vec{k})$, as a function of the frequency ϵ,

$$\Gamma(\epsilon,\vec{k})=\frac{k_BT\tau^{-1}}{2M(2\pi)^{3/2}}\int d\vec{q}\,q^2\frac{2[\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon]^2-\omega_q^{\,2}}{\{[\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon]^2-\omega_q^{\,2}\}^2+[\mathcal{E}_T(\vec{k}+\vec{q})-\epsilon]^2\tau^{-2}} \quad . \tag{49}$$

If we introduce in analogy to the Debye frequency a frequency $\omega_D(\sim 10^{-13}\ \mathrm{sec}^{-1})$ and a mean frequency $\bar{\omega}$, and if we further replace the integrand by a square pulse function around $\vec{q}$ values such that $\mathcal{E}_T(\vec{k}+\vec{q})-\mathcal{E}_T(\vec{k})\approx\omega_q$, we arrive at the following simplified result for (47) and (48):

$$\mathrm{Im}\,\epsilon^{(1)}(\vec{k})\approx k_BT(k^2/2M)^2(\tau/\omega_D)(\omega_D\tau)^{-1/2} \tag{50}$$

$$\mathrm{Re}\,\epsilon^{(1)}(\vec{k})\approx\mathcal{E}_T(\vec{k})-k_BT(k^2/2M)^2(\tau/\omega_D)(\bar{\omega}\tau)^{-1}(\omega_D\tau)^{-1/2} \quad . \tag{51}$$

From (50) and (51) we find that the ratio of the energy shift to the dampimg is of order unity.

In an absorption experiment we measure, essentially, the imaginary part of the dielectric constant $\tilde{\kappa}(\vec{k},\epsilon)$, which can be expressed in terms of the one-particle Green's function

$$\tilde{\kappa}(\vec{k},\epsilon)=\tilde{\kappa}_0(\vec{k},\epsilon)-(4\pi f_{01}^{\,2}\mathcal{E}_0\rho_{\mathrm{ex}}/\omega k)\langle\langle\tilde{b}_{\vec{k}}^{\dagger};\tilde{b}_{\vec{k}}\rangle\rangle\,, \tag{52}$$

where f_{01} is the oscillator strength corresponding to the transition from the ground to the excited state singled out for study, and $\tilde{\kappa}_0(\vec{k},\epsilon)$ contains the contributions to $\tilde{\kappa}(\vec{k},\epsilon)$ from all other transitions. The imaginary part of $\tilde{\kappa}(\vec{k},\epsilon)$ is

$$\mathrm{Im}\,\tilde{\kappa}(\vec{k},\epsilon)=\mathrm{Im}\,\tilde{\kappa}_0(\vec{k},\epsilon)-(4\pi f_{01}^{\,2}\mathcal{E}_0\rho_{\mathrm{ex}}/\omega k)\Gamma(\vec{k},\epsilon)/\{[\mathcal{E}_T(\vec{k})-\epsilon]^2+\Gamma^2(\vec{k},\epsilon)\}\,. \tag{53}$$

The frequency dependence is of the Lorentzian type if $\Gamma(\vec{k}, \epsilon)$ is assumed to be constant. However $\Gamma(\vec{k}, \epsilon)$ as shown in (49) is itself a Lorentzian, so that we are dealing with a Lorentzian-modified Lorentzian. Deviations from a simple Lorentzian of similar nature have also been predicted by Rice, Nicolis and Jortner[3] in the Wannier limit.

V. DISCUSSION

In this paper we have developed a formalism capable of describing the interaction between collective electronic excitations of the Frenkel type and collective translational excitations in a simple liquid. The key element in our analysis is the use of Born-Oppenheimer states for an instantaneous configuration of molecular centers, together with the coupling between the Born-Oppenheimer states generated by the nuclear kinetic-energy operator. The interaction term, arising from the nuclear kinetic-energy operator, introduces in a natural way the translational momentum density of the liquid. In turn, using the spectrum of translational excitations derived by Zwanzig[6] for a simple model of the relaxation of the translational momentum density, the spectrum of coupled electronic-translational excitations, the shift, and the damping of an excitation are all described in terms of the liquid structure factor, the characteristic relaxation time of the translational excitations, etc. Detailed numerical calculations will require evaluation of electronic interaction matrix elements specific to a given system, and have not been considered in this paper. Our principle result is the generation of a formalism capable of describing the mutual interaction and influence of electronic resonance coupling between atoms and collective translational motion of the atoms.

As is shown in Appendix III, the same formalism, applied to the description of a molecular crystal, regenerates the Davydov theory of exciton-phonon coupling.[11] Our theory should be applicable if the exciton bandwidth given in the transition matrix element W_{0110} is large compared to the fluctuation of the band. We have neglected, for example, the deviation of the energy from its mean value, when we introduced the liquid structure function in (35). If the fluctuation is of the same order of magnitude as is the bandwidth the exciton will undergo incoherent diffusive motion instead of the coherent motion we considered. The diffusive limit has also been studied by Rice, Nicolis, and Jortner[3] where the final line shape is of the Gaussian type. In the other extreme, the Wannier limit corresponding to a large bandwith, scattering due to the disorder of the molecules is important. In our case, the Frenkel limit, the main effect of the disorder of the system is absorbed in the energy itself (Eq. 22) leaving the interaction with the collective transverse excitations of the liquid as a first-order effect.

We have, in all our considerations, neglected the interaction between the liquid and the radiation field. While such interaction does lead to level broadening, that broadening will be small relative to the interaction broadening we have studied. Moreover, because of the disorder in the liquid, and because of the allowed motion of the molecules, momentum conservation on photon absorption is easily accomplished and leads to no special features in this system. That is, for typical values of $|\vec{k}| \sim 10^{-3}(V/N)^{1/3}$, the momentum of the translational excitations is so much larger than $\hbar\vec{k}$ that line broadening corresponding to momentum conservation may be neglected. It is clearly of interest to carry through a complete quantum-mechanical description of the liquid and the coupled radiation field. We hope to return to this problem in a future publication. Finally, we merely comment that reduction of Eq. (49) to numerical form depends upon knowledge of the electronic interaction matrix elements and of the dispersion relation for the translational excitations of the liquid. At present very little is known concerning the line shapes of exciton transitions in a liquid, or about the lifetimes and spectrum of translational excitations. Since the elastic scattering arising from the disorder in the liquid system is negligible in the Frenkel limit, we may, by inversion, use experimental information about the line shape to determine the spectrum of the translational modes. An interplay of theory and experiment is necessary at this stage of development, since the theory cannot be pushed much further without knowledge of which interactions are important and in what directions the N-body problem may be simplified.

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APPENDIX A

For the ground state and the first excited state of the exciton we have used, in the main text, a simple Hartree product wave function. We can include the most important part of the molecular correlation in the wave function if we introduce a Jastrow-type wave function[8]:

$$\bar{\psi}_0 = \prod_n \bar{\varphi}_n{}^0 , \quad \bar{\psi}_n = \bar{\varphi}_n{}^1 \prod_{m \neq n} \bar{\varphi}_m{}^0 \tag{A-1}$$

where $\bar{\varphi}_n{}^\alpha = \psi_n{}^\alpha \exp[\sum_j \omega(n,j)] / \langle \exp[\sum_j \omega(n,j)] \rangle$, $(\alpha = 0, 1)$. (A-2)

Now $\omega(R)$ is approximately given in terms of the radial distribution function $g(R)$ through the hypernetted-chain relation[12]

$$\omega(\vec{R}) = \ln g(R) - g(R) + \rho_\infty (2\pi)^{-\frac{3}{2}} \int d\vec{k}\,[1 - S(\vec{k})]^{-1} e^{i\vec{k}\cdot\vec{R}} \ . \tag{A-3}$$

The explicit dependence of $\omega(n,j)$ on the molecular coordinates leads to the following interaction:

$$\begin{aligned} H_{\text{int}}{}' &= \frac{1}{2M(2\pi)^3} \sum_n \int d\vec{k} \int d\vec{k}' \left\langle \psi_{\vec{k}} \right| \frac{\partial}{\partial \vec{R}_n} \left| \psi_{\vec{k}'} \right\rangle \frac{\partial}{\partial \vec{R}_n} \tilde{b}_{\vec{k}}{}^\dagger \tilde{b}_{\vec{k}'} \\ &+ \frac{1}{2M(2\pi)^3} \sum_n \int d\vec{k} \int d\vec{k}' \left\langle \psi_{\vec{k}} \right| \frac{\partial^2}{\partial R_n{}^2} \left| \psi_{\vec{k}'} \right\rangle \tilde{b}_{\vec{k}}{}^\dagger \tilde{b}_{\vec{k}'} \\ &= \frac{1}{2M(2\pi)^3} \int d\vec{k} \int d\vec{q} \left\{ \tilde{\vec{J}}_{\vec{q}} \left[i\vec{q} + \sum_{m-j} \frac{\partial \omega(m-j)}{\partial \vec{R}_m} \left(1 - e^{i\vec{q}\cdot(\vec{R}_m - \vec{R}_j)} \right) \right] \right. \\ &\left. + \tilde{\rho}_{\vec{q}} \sum_{m-j} \left[\frac{\partial^2 \omega(m-j)}{\partial^2 R_m} + \left(\frac{\partial \omega(m-j)}{\partial \vec{R}_m} \right)^2 \right] \right\} \tilde{b}_{\vec{k}}{}^\dagger \tilde{b}_{\vec{k}+\vec{q}} \ . \end{aligned} \tag{A-4}$$

The structure of our final expression is of the same type as the one used in Eq. (26) when (A-1) and (A-2) are used in place of the Hartree product, we need merely replace the coupling constant $i\vec{q}$ by

$$i\vec{q} + \sum_{m-j} \frac{\partial \omega(m-j)}{\partial \vec{R}_m} \left(1 - e^{i\vec{q}\cdot(\vec{R}_m - \vec{R}_j)}\right)$$

and the energy $(k'^2 + k^2)/4M$ by

$$\frac{k'^2 + k^2}{4M} + \frac{\rho_{\vec{q}}}{2M} \sum_{m-j} \left[\frac{\partial^2 \omega(m-j)}{\partial R_m{}^2} + \left(\frac{\partial \omega(m-j)}{\partial \vec{R}_m} \right)^2 \right] .$$

APPENDIX B

The operators $c_n{}^\dagger$ and c_n defined in Eq. (7) are Pauli operators. An exact transformation to Bose operators $b_n{}^\dagger$ and b_n can be found, for example, in the paper by Agronovitch,[13] who writes

$$c_n = \left(\textstyle\sum_\nu a_\nu b_n{}^{\nu\dagger} b_n{}^\nu\right)^{\frac{1}{2}} b_n, \quad c_n{}^\dagger = b_n{}^\dagger \left(\textstyle\sum_\nu a_\nu b_n{}^{\nu\dagger} b_n{}^\nu\right)^{\frac{1}{2}} \tag{B-1}$$

with $a_0 = 1$; $a_\nu = -2a_{\nu-1}/(1+\nu)$. If we expand these expressions in a power series of the Bose operators

and introduce the result in the Hamiltonian, Eq. (9), we find terms which describe the repulsion between excitons on the same molecule. Since it may be assumed that the transition matrix element $\tilde{F}(\vec{k})$ is small compared to the local energy $\mathcal{E}_0$ we need consider only those interactions which arise from this local energy term. We then write the two-particle interaction as

$$H_2 = N^{-1} \sum_{n,m} \mathfrak{u}(n-m) d_n d_m \ , \tag{B-2}$$

where d_n is the number operator at the position $\vec{R}_n$

$$d_n = b_n{}^\dagger b_n \ . \tag{B-3}$$

We again introduce a Fourier transformation

$$d_{\vec{k}} = N^{-\frac{1}{2}} \textstyle\sum_n e^{-i\vec{k}\cdot\vec{R}_n} d_n \ , \tag{B-4}$$

and find for H_2

$$H_2 = (2\pi)^{-3/2} \int d\vec{k}\, \tilde{\mathfrak{u}}(\vec{k}) \tilde{d}_{\vec{k}}{}^\dagger \tilde{d}_{\vec{k}} \tag{B-5}$$

with $\tilde{\mathfrak{u}}(\vec{k}) = (2\pi)^{-3/2} \int d\vec{R}\, e^{i\vec{k}\cdot\vec{R}} \mathfrak{u}(\vec{R})$. (B-6)

The interaction energy can be approximated by

$$\mathcal{U}(R) = \mathcal{E}_0 \text{ for } |\vec{R}| < r_0, \quad \mathcal{U}(R) = 0 \text{ for } |\vec{R}| > r_0 \; . \tag{B-7}$$

with r_0 a molecular radius. The commutation relations between the operators $\tilde{d}_{\vec{k}}$, $\tilde{d}_{\vec{k}}^{\dagger}$ and $\tilde{b}_{\vec{k}'}^{\dagger}$, $\tilde{b}_{\vec{k}'}$ are

$$[\tilde{d}_{\vec{k}}, \tilde{b}_{\vec{k}'}] = N^{-1/2} \tilde{b}_{\vec{k}+\vec{k}'} \; , \quad [\tilde{d}_{\vec{k}}, \tilde{b}_{\vec{k}'}^{\dagger}] = -N^{-1/2} \tilde{b}_{\vec{k}'-\vec{k}}^{\dagger} , \quad \text{and} \quad d_{\vec{k}}^{\dagger} = -d_{-\vec{k}} . \tag{B-8}$$

We can now easily calculate the contribution of this interaction term to the exciton scattering. If we neglect the effect of the dynamical interaction between excitons in the interaction with the translational excitations of the liquid we need only know the commutators

$$[H_2, \tilde{b}_{\vec{k}}^{\dagger}] = 2N^{-1/2} (2\pi)^{-3/2} \int d\vec{q}\, \tilde{\mathcal{U}}(\vec{q}) \tilde{d}_{\vec{q}} \tilde{b}_{\vec{k}+\vec{q}}^{\dagger} \tag{B-9}$$

and $$[H_2, \tilde{d}_{\vec{q}} \tilde{b}_{\vec{k}+\vec{q}}^{\dagger}] = 2N^{-1/2} (2\pi)^{-3/2} \int d\vec{q}\,' \tilde{\mathcal{U}}(\vec{q}\,') \tilde{d}_{\vec{q}\,'} \tilde{d}_{\vec{q}} \tilde{b}_{\vec{k}+\vec{q}+\vec{q}\,'}^{\dagger} \; .$$

We again break the correlation, in the Born approximation, to find

$$\langle\langle \tilde{d}_{\vec{q}} \tilde{d}_{\vec{q}\,'} b_{\vec{k}+\vec{q}+\vec{q}\,'}^{\dagger}; \tilde{b}_0 \rangle\rangle \approx \langle \tilde{d}_{\vec{q}} \tilde{d}_{\vec{q}\,'} \rangle \langle\langle \tilde{b}_{\vec{k}+\vec{q}+\vec{q}\,'}^{\dagger}; \tilde{b}_0 \rangle\rangle \approx NS(\vec{q}) \rho_{\text{ex}}^2 \langle\langle \tilde{b}_{\vec{k}}^{\dagger}; \tilde{b}_0 \rangle\rangle \; . \tag{B-10}$$

If the density of excitons $\rho_{\text{ex}} \sim e^{-\beta \mathcal{E}_0}$ is small, the term displayed in (B-10) can be neglected. The final contribution, $\theta_2(\epsilon)$, to the denominator of the one particle Green's function $\theta(\epsilon)$ is then

$$\theta_2(\epsilon) = 4(2\pi)^{-3/2} \int d\vec{q}\, |\tilde{\mathcal{U}}(\vec{q})|^2 S(\vec{q}) \rho_{\text{ex}}^2 / [\mathcal{E}(\vec{k}+\vec{q}) - \epsilon] \; , \tag{B-11}$$

while the contribution to the damping is

$$\text{Im}\,\epsilon_2^{(1)} = (2/\pi)^{1/2} \int d\vec{q}\, |\tilde{\mathcal{U}}(\vec{q})|^2 S(\vec{q}) \rho_{\text{ex}}^2 \, \delta[\mathcal{E}(\vec{k}+\vec{q}) - \mathcal{E}(\vec{k})] \; , \tag{B-12}$$

and the contribution to the energy shift is

$$\text{Re}\,\epsilon_2^{(1)} = 4(2\pi)^{-3/2} P \int d\vec{q}\, |\tilde{\mathcal{U}}(q)|^2 S(\vec{q}) \rho_{\text{ex}}^2 / [\mathcal{E}(\vec{k}+\vec{q}) - \mathcal{E}(\vec{k})] \; . \tag{B-13}$$

APPENDIX C

In this Appendix we demonstrate the relation between our interaction Hamiltonian

$$H_{\text{int}}' = \frac{N^{-1}}{2M(2\pi)^3} \int d\vec{k} \int d\vec{k}' \sum_n \left\langle \psi_{\vec{k}} \left| \frac{\partial}{\partial \vec{R}_n} \right| \psi_{\vec{k}'} \right\rangle \frac{\partial}{\partial \vec{R}_n} \tilde{b}_{\vec{k}}^{\dagger} \tilde{b}_{\vec{k}'} \; , \tag{C-1}$$

and the exciton-phonon interaction Hamiltonian as used by Davydov[11]

$$H_{\text{int}}^{(D)} = \frac{N^{-1}}{(2\pi)^3} \int d\vec{k} \int d\vec{q} \sum_{m-j} \sum_n \frac{\partial F(m-j)}{\partial \vec{R}_m} e^{i\vec{k} \cdot (\vec{R}_m{}^0 - \vec{R}_j{}^0)} (1 - e^{i\vec{q} \cdot (\vec{R}_m{}^0 - \vec{R}_j{}^0)}) \Delta \vec{R}_n \tilde{b}_{\vec{k}}^{\dagger} \tilde{b}_{\vec{k}+\vec{q}} \; . \tag{C-2}$$

As interaction we use the resonance from

$$H_{\text{int}} = N^{-1} \sum_{n-m} F(n-m) c_n^{\dagger} c_m \; . \tag{C-3}$$

First we express the matrix element in Eq. (C-1) in terms of the interaction (C-3)

$$\langle \psi_{\vec{k}} | \partial / \partial \vec{R}_n | \psi_{\vec{k}'} \rangle = \langle \psi_{\vec{k}} | \partial H_{\text{int}} / \partial \vec{R}_n | \psi_{\vec{k}'} \rangle / [\mathcal{E}(\vec{k}\,') - \mathcal{E}(\vec{k})] \; , \tag{C-4}$$

and evaluate the matrix element

$$\left\langle \psi_{\vec{k}} \left| \frac{\partial H_{\text{int}}}{\partial \vec{R}_n} \right| \psi_{\vec{k}'} \right\rangle = \frac{1}{N} \sum_{m-m'} e^{-i\vec{k} \cdot \vec{R}_m + i\vec{k} \cdot \vec{R}_{m'}} \frac{\partial F(m-m')}{\partial \vec{R}_m} [\delta(\vec{R}_n - \vec{R}_m) - \delta(\vec{R}_n - \vec{R}_{m'})] \; . \tag{C-5}$$

We then introduce this result together with (C-4) in (C-1) and arrive at

$$H_{\text{int}}' = \frac{N^{-1}}{(2\pi)^3} \int d\vec{k} \int d\vec{q} \sum_{n-m} \sum_n e^{i\vec{k} \cdot (R_m - R_n)}$$

$$\times\left(1-e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}_m-\vec{\mathrm{R}}_n)}\right)\frac{1}{[\mathcal{E}(\vec{\mathrm{k}})-\mathcal{E}(\vec{\mathrm{k}}+\vec{\mathrm{q}})]}\,\frac{\partial F(n-m)}{\partial\vec{\mathrm{R}}_n}e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{R}}_n}\frac{\partial}{\partial\vec{\mathrm{R}}_n}\,\tilde{b}_{\vec{\mathrm{k}}}^{\dagger}\,\tilde{b}_{\vec{\mathrm{k}}+\vec{\mathrm{q}}}\,. \qquad \text{(C-6)}$$

If we now consider only first-order phonon processes the energy difference $\mathcal{E}(\vec{\mathrm{k}})-\mathcal{E}(\vec{\mathrm{k}}+\vec{\mathrm{q}})$ may be replaced by the phonon frequency $\omega_{\vec{\mathrm{q}}}$. The final result is then in agreement with the Davydov expression (C-2) for the solid. On the other hand, we can start from (C-6) and develop the expression for the coupling constant given in Eq. (26) by use of partial integration and by introducing the expectation value

$$\frac{1}{N}\left\langle\sum_{n-m}e^{i\vec{\mathrm{k}}\cdot(\vec{\mathrm{R}}_m-\vec{\mathrm{R}}_n)}\left(1-e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}_m-\vec{\mathrm{R}}_n)}\right)F(n-m)\right\rangle=(2\pi)^{-3/2}\int d\vec{\mathrm{k}}'\tilde{F}(\vec{\mathrm{k}}')[S(\vec{\mathrm{k}}-\vec{\mathrm{k}}')-S(\vec{\mathrm{k}}+\vec{\mathrm{q}}-\vec{\mathrm{k}}')]$$

$$=\mathcal{E}(\vec{\mathrm{k}})-\mathcal{E}(\vec{\mathrm{k}}+\vec{\mathrm{q}}). \qquad \text{(C-7)}$$

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