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# Do Exciton States Exist in the Liquid Phase?

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In this note we conjecture that a sufficient condition for the existence of Wannier exciton states in a dense liquid is that an excess electron be accurately describable as a plane wave. Scattering processes then lead to a broadening of the exciton level. A theory of electron scattering in simple liquids is used to estimate linewidths, and the predictions are consistent with the data available. A number of predictions resulting from, and implications of, the proposed mechanism are considered.

IN connection with a general experimental and theoretical study of the electronic structure of disordered systems, we have been led to enquire whether or not exciton states exist in the liquid phase. In this publication, we show that, when certain conditions are satisfied, exciton states do exist, but will be of short lifetime. An estimate of the line broadening is given which is in satisfactory agreement with the data obtained by Beaglehole in a study of the optical spectrum of liquid xenon.[1]

From the most general point of view, it may be argued that a liquid is a homogeneous phase with translational symmetry. Indeed, provided that the wave vector of an incident electromagnetic wave is very large relative to the range of molecular ordering (which is about three molecular diameters), localized excitations at two points in the liquid are related by the phase factor $\exp(i\mathbf{k}\cdot\mathbf{R})$, where $\mathbf{k}$ is the excitation propagation vector and $\mathbf{R}$ the vector separation between the points. The propagation vector is uncertain by an amount $\Delta\mathbf{k}$, which is of the order of the reciprocal of the range of order in the liquid. Because of this, localized excitations closer than $1/\Delta\mathbf{k}$ cannot be described as having the phase relationship cited. Nevertheless, the simple observation that the liquid has, on the macroscopic scale, translational symmetry, is sufficient to define an excitation propagation vector.

Consider now the internal structure of a possible exciton in a simple liquid. From the experimental studies of Schnyders, Meyer, and Rice,[2] we conclude that, to a reasonable first approximation, an excess electron in liquids Ar, Kr (and probably Xe) behaves as a quasi-free particle. We assume, therefore, that the excess electron wavefunction is of the form

$$|\,\mathbf{k}\rangle=(1/\Omega^{\frac{1}{2}})\exp(i\mathbf{k}\cdot\mathbf{X}), \tag{1}$$

where $\Omega$ is the volume of the liquid. Further, we now assume that the ion core (hole) is stationary. Although the hole will have finite mobility, in general it moves much more slowly than the electron because of self-trapping. A wave packet describing the electron is constructed as follows:

$$\Psi=\sum_{\mathbf{k}}A(\mathbf{k})\,|\,\mathbf{k}\rangle. \tag{2}$$

If the Hamiltonian for the cone-electron pair is written in the form

$$H=H_0+V, \tag{3}$$

$$H_0=-(\hbar^2/2m_e^*)\nabla_e^2, \tag{4}$$

then

$$H_0\,|\,\mathbf{k}\rangle=(\hbar^2k^2/2m_e^*)\,|\,k\rangle \tag{5}$$

and

$$(\hbar^2k^2/2m_e^*)A(\mathbf{k})+\sum_{\mathbf{k}'}V_{\mathbf{k}-\mathbf{k}'}A(\mathbf{k}')=EA(\mathbf{k}), \tag{6}$$

with $V_{\mathbf{k}-\mathbf{k}'}$ the Fourier transform of the interaction $V$ between the core and the electron. Note that the effective mass of the electron is $m_e^*$, and, if $V$ is the Coulomb potential, Eq. (6) becomes a hydrogenic wave equation in the momentum representation for the *amplitudes* $A(\mathbf{k})$ [compare Eq. (8.3) of Bethe and Salpeter[3]]. Thus, the manifold of energy levels is hydrogenic, and the amplitudes in the wave-packet expansion satisfy a hydrogenic wave equation.

The preceding argument is of great generality, relying only on the existence of plane-wave states such as assumed in Eq. (1). The bound states of the core–electron pair will be reasonably well defined if the mean free path of the electron is larger than the orbital circumference. Scattering of the electron by the atoms of the liquid causes a decrease in the lifetime of any given state, and, in the limit that the scattering is so frequent that an orbit cannot be closed, no bound state can exist. This limiting case is inconsistent with the assumption, embodied in Eq. (1), that the electron is almost free.

We propose that the linewidths of bound exciton

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states in a liquid can be accounted for in terms of scattering of the electron by the surrounding fluid atoms, the coherence between scattering amplitudes from different centers being taken into account in terms of the radial distribution function of the liquid. The situation under study has many features in common with the nature of the pressure broadening of the Rydberg states of the free (gaseous) alkali atoms[4] and also the broadening of impurity levels in semiconductors.[5] The linewidth of an exciton state in the liquid can be related to the mean lifetime of a phase coherent state. Thus, elastic electron scattering, involving phase changes of sufficient magnitude, will determine the lifetime of the exciton state. The present approach implies that the mean-free path of the free electron must exceed the length of the orbit pursued by the electron in the bound state.

Following Fermi[4] and Sampson and Margenau,[5] we now make the quantitative assumption that the scattering of the electron is insensitive to the radius of curvature, and therefore can be estimated from the relaxation time defining the mobility of the electron. In this case, the broadening of a level is simply

$$\Delta\nu = 1/\pi\tau, \tag{7}$$

with $\tau$ the relaxation time.

The relaxation time for the electron scattering may be represented in the form[2,6,7]

$$\frac{1}{\tau(k)} = \int (1-\cos\theta) Q(k,\theta)\, \sin\theta d\theta d\phi, \tag{8}$$

where the differential transition probability $Q(k,\theta)$ is given by second-order perturbation theory

$$Q(k,\theta) = (2\pi/\hbar)\, |\langle \mathbf{k}' | \sum_i v_i | \mathbf{k}\rangle|^2 N(E_k). \tag{9}$$

In Eq. (9), $\sum v_i$ is the scattering potential of the liquid atoms, and the density of states available for the electron in the energy range $dE_k$ about $E_k$ is given by

$$N(E_k) = \Omega m_e^* k / 2\pi^2\hbar^2. \tag{10}$$

The relaxation time can be separated into a structure factor $S(k)$ and an energy contribution

$$1/\tau(k) = (4Nm_e^* k\Omega/\hbar^3)\mu_k^2 S(k), \tag{11}$$

where $N$ is the number of the atoms in the liquid, while $\mu_k$, the Fourier transform of the scattering potential, can be related to the scattering length $a$ for low-energy electrons by the optical approximation

$$\mu_k = \Omega^{-1} \int \exp(i\mathbf{k}\cdot\mathbf{r}) v_i d^3\mathbf{r} = \frac{\hbar^2 a}{2m_e^*\Omega}, \tag{12}$$

and the structure factor can be expressed in terms of the radial distribution function

$$S(k) = 1 + \frac{N}{\Omega}\int [g_2(r)-1]\, \frac{\sin kr}{kr}\, 4\pi r^2 dr. \tag{13}$$

In the limit $k\rightarrow 0$, the structure factor is related to the isothermal compressibility $\mathcal{K}_L$ by the relation $S(k\rightarrow 0) = \rho_N \mathcal{K}_L k_B T$, where $\rho_N$ is the number density of the liquid ($\rho_N = N/\Omega$), and $k_B$ is the Boltzmann constant. The relaxation time, then, is

$$1/\tau(k) = (\rho_N \hbar a^2 k/m_e^*)\, S(k). \tag{14}$$

Now, the magnitude of the electron wave vector $\mathbf{k}$ is related to the velocity $\mathbf{v}$ of the electron in the excited Wannier orbital by the simple relation $\mathbf{k} = m_e^*\mathbf{v}/\hbar$. We thus conclude that the scattering time is inversely proportional to the speed of the electron. Hence the electron will make fewer collisions in the lowest excited state than in Wannier states characterized by large principal quantum numbers, and thereby the lifetimes of the higher states are expected to be shorter than that of the lowest excited state. We therefore are led to expect the line broadening to increase as the principal quantum number increases. In the study of electron mobility in liquid Ar,[2] the electron wavelength is sufficiently large that the asymptotic limit can be used to compute $S(0)$. On the other hand, the wavelength corresponding to a closed orbit is such that the $k$ dependence of the structure factor should be retained in the description of the scattering.

From the preceding argument, using Eq. (14) for liquid Xe, we predict that the energy levels are broadened by about 0.1 eV. Since the spacing between the levels is only about 0.2 eV, the set of exciton levels will appear as an unresolved absorption. This is just the type of spectrum of liquid Xe obtained recently by Beaglehole,[1] who finds that the total width of the exciton absorption is about the same in the solid and liquid, but that the individual sublevel transitions are not resolved in the liquid.

What are the implications of the arguments presented herein?

(a) It appears clear the Wannier-like exciton states in the liquid phase will only be observed in those liquids in which the conduction electrons are in nearly plane-wave states. Of course, there will still be localized excitations, e.g., the $\pi\rightarrow\pi^*$ excitations of aromatic molecules, if the molecular overlap in the excited state is very small. However, such excitations are likely to propagate, if at all, only via diffusional hopping be-

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cause of the decrease in effective interaction arising from the orientational averaging in the liquid.

(b) When the scattering length for electron–atom scattering is small, the bound states should have longer lifetimes. We are, therefore, led to predict that observation of the exciton states of the liquids Ne (characterized by an atomic scattering length of 0.2 a.u. in the gas phase[8]) and Xe (scattering length of 6.5 a.u.[8]) will show that the transitions in Ne are much narrower than those in Xe.

(c) Because the relaxation time for scattering increases as the pressure increases, under the conditions we consider, we predict that the exciton transitions will narrow as the pressure is increased in liquids Ne, ···, Xe.

(d) Because of the existence of a Ramsauer minimum in the effective electron–atom scattering cross section, it is possible for different levels, corresponding to different orbital energies, to be broadened by very different amounts.

(e) The appreciable line broadening of the Wannier exciton states observed in unannealed solid xenon[9] can be properly accounted for in terms of the shortening of the lifetime of the state arising from electron scattering by the disordered solid in the region near the localized hole.

(f) From the remarks made, it appears likely that the only liquids in which even broadened exciton states can be observed are Ne, Ar, Kr, and Xe, and possibly $CH_4$.

(g) In crystals of organic compounds, where the conduction band is very far from free-electron like, it is unlikely that transitions to Wannier exciton states, or to molecular Rydberg states, can be observed. For, with an electron mobility of the order of 1 $cm^2/sec\cdot V$,[10] the broadening of the states is so large that only a broad continuum exists. This deduction is in agreement with the observation made by Pysh[11] of the spectrum of pure crystalline benzene in the vacuum-ultraviolet region.

(h) The identification of Rydberg states of molecules by correlating spectral shifts with the dielectric properties of a solvent is subject to ambiguities.

(i) Evan's observation[12] of the broadening of the Rydberg levels of the methyl halides and other compounds in the gas phase with ~100 atm of $N_2$ can be understood in terms of the scattering of the excited electron by the $N_2$ molecule. This broadening is analagous to the broadening of the excited levels of the alkali atoms by foreign gases.[4]

The general arguments presented herein are applicable to the description of those exciton states in disordered systems which arise from transitions lying below the threshold for interband transitions. In the case of metastable excitons, which are located in the continuum above the threshold for direct interband transitions, there is another important contribution to the linewidth which arises from the phase shift induced by a Fano-type interaction between discrete and continuum states.[13] It should be noted by the reader that we have attributed the line broadening solely to scattering processes, and additional contributions from core polarization[4] and thermal fluctuations in the dielectric functions of the liquids (i.e., in the electron–hold screening[5]) have not been included. These extra interaction contributions will be studied separately, and all that we wish to say herein, at present, we believe the contribution to exciton line broadening in a dense liquid from processes other than direct electron–atom scattering are small.

The condition we have used in this paper is clearly equivalent to the requirement cited for the existence of cyclotron resonance, namely $\omega\tau \gg 1$. If $\omega\tau < 1$, then an orbit cannot close, on the average, and cyclotron resonance cannot be observed. Similarly, if the scattering of the electron by the atoms of the liquid is such as to create a mean-free path less than one orbital circumference, a Wannier-type exciton state cannot exist.

Further implications of the arguments advanced herein and a quantitative theory of the line broadening and related phenomena will be the subject of a separate paper.

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