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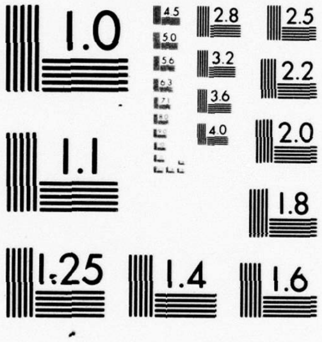

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Excitations and Metastability in Amorphous Semiconductors*

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ABSTRACT

The Anderson negative-U model for diamagnetic glasses is studied. The optical and thermodynamic excitations are evaluated for equilibriated and non-equilibriated systems. The model is generalized to include non-local phonons and these are shown to lead to new low energy processes which may be important for thermodynamic properties.

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I. Introduction

Most approaches (Mott, Davis and Street (1975), Street and Mott (1975), Kastner, Adler and Fritzsche (1976), Kastner and Fritzsche (1978)) employed in understanding the electronic properties of amorphous semiconductors focus on specific electronically active defects. The corresponding states are localized, lie in the gap, and are therefore supposed responsible for pinning the Fermi level, variable range hopping (when it is observed), and are likely recombination centers in photoconduction. These approaches require elucidation of the nature of the defect in each case and bypass the notion of an "ideal" or intrinsic noncrystalline semiconductor. The similarity of optical data for both amorphous and crystalline materials has led many theorists (Phillips (1971), Weaire (1971)) to suggest a small role for the underlying disorder. It is argued (Phillps (1971)), for example, that atomic relaxation during glass quenching acts to repel states from the region of the crystalline gap. Weaire (1971) has shown how real gaps can occur in a simple model without long-range order.

Anderson (1975) observed that the diamagnetic properties of many glasses can follow from considering a <u>statistical</u> distribution of two electron states or bonds. The distribution is in bond strength and within this model no defect states with unpaired spins exist. The electrons are paired due to the polaron energy gained through bond contraction (after occupation) which more than compensates their electronic repulsion.

In this paper we examine the properties of the simple negative-U model considered by Anderson (1975). The structure of the model follows from two major assumptions:

1) that disorder plays a major role in accounting for the elementary electronic processes in glasses, especially those with low coordination number.

2) that these materials are strongly coupled, i.e. that the lattice-electron interaction is presumed large.

Little justification is provided for the former assumption beyond the qualitative success of the model. In defect models it is usually presumed that the host material (without defects) is described by an electronic structure with a good gap (or pseudogap). The argument typically given compares the energy of a deep level ~1 eV (relative to a crystal) to the thermal energy available at the glass transition temperature ~.05 eV. Thus usual defect counting arguments can give densities as low as $10^{14}/\mathrm{cm}^3$. We take the point of view that the energy of formation of a gap state can be much smaller in a disordered system. By similar entropy considerations, a reduction by only a factor of two can produce 10^4 more states near the Fermi level.

As an example, we may consider a typical valence band in a random covalent semiconductor formed from the bonding states of the bonds. A 10% variation of the band width is typically enough to wipe out any gap which occurs at the top of the band. Since bonding energies are exponentially related to bond lengths, we are considering a small variation in bond lengths (consistent with X-ray analysis) to produce the effect.

Given our initial assumption, the second is required to produce the observed properties. It should be emphasized that virtually all the success of approaches which employ a quasi-crystalline defect model follows from our considerations.

In Section II we describe the elementary excitations within the negative-U model. We also examine the consequence of introducing severe site correlation between the coupling parameter and the local electronic energy. In Section III we consider the system in non-equilibriated configurations and study the question of metastability. Finally, the model is generalized in Section IV to include phonon size effects. It is shown that some observed thermodynamic properties follow from these simple considerations.

II. The Anderson Negative-U Model

For simplicity, we consider one site to illustrate the model. The Hamiltonian $\mathcal{H}$ is

$$\mathcal{H} = E(n_\sigma+n_{-\sigma}) + U\, n_\sigma n_{-\sigma} + \omega b^\dagger b + g(n_\sigma+n_{-\sigma})(b+b^\dagger) \tag{1}$$

where $n_\sigma = c_\sigma^\dagger c_\sigma$. The operator $c_\sigma^\dagger$ creates an electron in the center with spin σ and the $b, b^\dagger$ are phonon operators. The parameter E is the energy of an electron localized on the center, U is the Hubbard electronic repulsion which contributes when there is double occupancy, and ω is the (Einstein) frequency of the phonon. The last term describes the electron-phonon interaction where g is the coupling parameter. In order to diagonalize the phonon part, we rewrite the above Hamiltonian in two convenient forms appropriate to different occupations: For single occupation of the center, we write

$$\begin{aligned} \mathcal{H}_1 = {} & E(n_\sigma+n_{-\sigma}) + U\, n_\sigma n_{-\sigma} - \tfrac{1}{2} C + \omega \tilde{b}^\dagger \tilde{b} \\ & - g\, n_\sigma (b+b^\dagger) + g(1-n_{-\sigma})(b+b^\dagger) \end{aligned} \tag{2}$$

where $C \equiv \dfrac{2g^2}{\omega}$ and we define a displaced phonon operator $\tilde{b} \equiv b + g/\omega$. This form is diagonal for $n_\sigma = 1$, $n_{-\sigma} = 0$. For double occupancy,

$$\begin{aligned} \mathcal{H}_2 = {} & E(n_\sigma+n_{-\sigma}) + U\, n_\sigma n_{-\sigma} - 2C + \omega \tilde{\tilde{b}}^\dagger \tilde{\tilde{b}} \\ & - g(1-n_\sigma)(b+b^\dagger) - g(1-n_{-\sigma})(b+b^\dagger) \end{aligned} \tag{3}$$

where we have defined the doubly displaced phonon operator

$$\tilde{\tilde{b}} \equiv b + \frac{2g}{\omega} \quad .$$

$\mathcal{H}_2$ is diagonal for $n_\sigma = n_{-\sigma} = 1$ and the eigenvalue for this case, is given by inspection.

In general, the wave function may be written $\psi = |n_e, n)$ where the electron occupation $n_e = 0,1,2$ and n is the phonon occupancy at the center. With the phonon system in its ground configuration, i.e. $n = 0$, the energy eigenvalues are given from eqs 1-3:

$$\begin{aligned} n_e &= 0 \qquad & E_0 &= 0 \\ n_e &= 1 \qquad & E_1 &= E - \frac{1}{2} C \\ n_e &= 2 \qquad & E_2 &= 2E + U - 2C \end{aligned} \tag{4}$$

Thus we see for soft enough phonons, i.e. $C > U$ the ground state requires $n_e = 0$ or 2 depending on the electronic energy E. In particular, for $E > C - \frac{U}{2}$ the ground state is empty and for $E < C - \frac{U}{2}$ the ground state is doubly occupied.

It is straightforward to evaluate the excitation energy using the Hamiltonian of equation (1) for the process of adding a particle to a center in its ground state. As discussed by Anderson (1975), the frequency of the process is important: for low frequencies ($<\omega$), the phonon occupation n remains approximately zero throughout the process and the slow excitation energies E^s are given directly from eq. (4):

$$E^s_{0\to 1} = E_1 - E_0 = E - \frac{1}{2} C \tag{5a}$$

$$E^s_{2\to 1} = E_1 - E_2 = -E - U + \frac{3}{2} C \quad . \tag{5b}$$

Eq. (5b) gives the energy to add a hole to a doubly-occupied center. Note that both these quantities are positive under the assumption $C > U$ with the center initially in its ground occupancy.

We also consider high frequency processes (Franck-Condon) in which the excited $n_e = 1$ contains a large number of phonons. In this case, the center does not relax to a configuration containing one electron but remains (during the period of the process) in the phonon state appropriate for $n_e = 0,2$. In the excited state $n_e = 1$, the coherent phonon system contains energy $\omega \simeq \frac{1}{2} C$ and so equation (2) gives the energy $E_{1,n}$ for the state $\psi = |1,n>$. Thus, the fast excitation energies E^f are given by

$$E^f_{0\to1} = E_{1,n} - E_0 = E \tag{6a}$$

$$E^f_{2\to1} = E_{1,n} - E_2 = -E - U + 2C \tag{6b}$$

which includes the additional energy C/2.

In a solid, the real process requires two centers in which an electron is promoted from a doubly occupied state to an empty one (particle-hole excitation). Assuming, for simplicity, that the process involves two identical centers, the energy for an optical excitation Δ^f is

$$\Delta^f = E^f_{0\to1} + E^f_{2\to1} = -U + 2C \tag{7}$$

using eq. 6. The analysis implies (Spear (1977)) an optical gap even in the case of weak diamagnetism $C \gtrsim U$.

The corresponding slow gap Δ^s given from eq. 5,

$$\Delta^s = E^s_{0\to1} + E^s_{2\to1} = -U + C \tag{8}$$

defines the true gap of the one-particle excitation spectrum.

A summary of these processes is illustrated in figure 1. The abcissa denotes electron occupation and the states corresponding to $n_e = 0,1,2$ are indicated. The vertical axis gives the energy of the configuration normalized to the electron energy E. In particular, we take $U/E = 0$, $C/E = 4/3$, in which $n_e = 2$ is the ground state. The curves describe the energy dependence of excited configurations for which the model of eq. (1) gives a quadratic dependence on occupation. Optical excitations are vertical transitions in the diagram (solid lines) and low frequency processes are indicated by the dashed lines. Other processes are described in the section III where the question of metastability is discussed.

Up to now, we have considered only one or two sites. To treat the solid, we introduce a spatial distribution of such centers which are each characterized by new site parameters $\tilde{E}_i \equiv E_i - C_i/2$ and $\tilde{U}_i \equiv C_i - U_i$ where i labels the site. The parameters E_i, C_i and U_i are those defined in equation (1) appropriate here for the site i. Anderson presumed that the renormalized quantities

$$\tilde{E}_i\,,\ \tilde{U}_i \geq 0$$

are random, taken each independently from some distribution. The system Hamiltonian may be written

$$H = \sum_{i,\sigma} \tilde{E}_i n_{i\sigma} - \sum_i \tilde{U}_i\, n_{i\sigma}\, n_{i-\sigma} + \sum_{i>j,\sigma} T_{ij} C_{i\sigma} C_{j\sigma} \qquad (9)$$

where we have now introduced a hopping term with a transfer matrix element T_{ij} which allows the electron to hop from site i to site j. The Hamiltonian equation (9) is equivalent to the Hubbard model with random negative correlation energy $\tilde{U}_i$, and with random site energies $\tilde{E}_i$. In the absence of electronic hopping, i.e. $T_{ij} = 0$, the model is solved exactly with eigenvalues given in equation (4) in terms of the unrenormalized parameters for each site.

One can define a two-electron spectrum which in the absence of hopping is a site-energy spectrum. It is convenient to adjust the occupation of the one-electron renormalized energies, $\tilde{E}_i$, so that only states (sites) with $\tilde{E}_i < 0$ are doubly-occupied in the ground state with $\tilde{U}_i = 0$ for all i. This places the chemical potential for adding two electrons at energy $\mu_2 = 2\tilde{E}_i - \tilde{U}_i < 0$ for $\tilde{U}_i$ positive for all i. Note that in this case not all sites will be in their ground state with respect to site occupation: some sites with $2\tilde{E}_i - \tilde{U}_i < 0$ will be unoccupied $(2\tilde{E}_i - \tilde{U}_i > \mu_2)$ and others will be occupied with $0 < 2\tilde{E}_i - \tilde{U}_i < \mu_2$.

The model, as stated, does not prejudice the nature of the center, e.g. bonding, non-bonding, defect, etc., but it is clear that any reasonable energy distribution should require the density of states near the two-electron chemical potential, μ_2, to be depressed (pseudogap). Anderson has argued that the randomness is likely to be severe, with a reduction of only one or two orders of magnitude near μ_2. This would account for the strong Fermi-level pinning of most glassy semiconductors although recent work (Spear (1977)) on the doping characteristics of silicon-hydrogen alloys demonstrates that it can be much smaller.

It is important to realize that although the chemical potential may be pinned by the presence of a large number of two-particle states in the pseudogap, the one-electron or excitation spectrum may have a well-defined gap within this model. The absorption edge for particle-hole excitations occurs, for the process $i \to j$, at $\min(\tilde{E}_j - \tilde{E}_i + \tilde{U}_i)$: E_j satisfies $\tilde{E}_j > \mu_2/2 + \tilde{U}_j/2$ and $\tilde{E}_i < \mu_2/2 + \tilde{U}_i/2$. If $\tilde{E}_i$ and $\tilde{U}_i$ are uncorrelated, there are two possibilities for forming a gap in the particle-hole excitation spectrum. One can, as Anderson (1975) supposed, presume that at least for some materials there exist no sites with $\tilde{U}_i$ less than some min $\tilde{U}_i$. Alternatively, Licciardello (1978) argued that some correlation certainly exists and that states near μ_2 tend to have larger values of U_i . In addition to producing a gap , the absorption edge, in this case, may arise from states deep in the valence band, perhaps from below the mobility edge. This is a very likely explanation of the sharpness of the absorption edge: it results from absorption between mobile states. Anderson (1975) has also suggested that the mobility gap for extended states may fall below the gap implied by min $\tilde{U}_i$.

One may also examine the consequence of introducing severe correlation. One possibility is shown in Figure 2 where we assume a Gaussian-like relation between $\tilde{U}$ and $\tilde{E}$. In a covalently bonded semiconductor, one may regard the zero of energy in Figure 2 as corresponding to the atomic level out of which bonding occurs. Thus states $\tilde{E}_i < 0$ are typically bonding-like whereas states $\tilde{E}_i > 0$ are antibonding in character. Since states near zero are greatly perturbed from the simple bonding-antibonding configuration, they are likely to be more strongly coupled with the lattice. This occurs for two reasons: for broken bonds, i.e. defects, the local phonons are likely to be softer, and the electronic states can be more severely localized giving rise to a larger electron-phonon coupling, g (see eq. 1). Since $\tilde{U}_i \sim g^2/\omega_i$, $\tilde{U}_i$ can be much larger. Street and Mott (1975), in their model implicitly assumed that states in the gap were strongly lattice-coupled. A recent band calculation (Vanderbilt and Joannopoulos (1979)) for specific defect configurations in glassy Se has demonstrated severe localization near coordination defects. The sharp fall-off of $\tilde{U}$ for occupied states with large negative energy (i.e. deep in the valence band) and unoccupied states with large positive energy (conduction band states) is expected for extended two-particle wave functions. These states should be derivable from a one-electron calculation of the crystal (band structure) within perturbation theory.

Also indicated in Figure 2 is the two-electron chemical potential relation. There are several remarks about the ansatz of Figure 2 worth mentioning. One is that it predicts no true one-electron gap. That is, the min($\tilde{E}_j - \tilde{E}_i + \tilde{U}_i$) , which occurs at the point labeled (a), vanishes. Low energy excitations may occur at (b) and (c) but require the correlation energy $\tilde{U}_b$ and $\tilde{U}_c$. Secondly, if a site is considered electrically neutral if it is occupied when $\tilde{E} < 0$ and unoccupied when $\tilde{E} > 0$, then Figure 2 predicts strongly-coupled negative sites (part of curve where $\tilde{E} > 0$ and $2 E - U < \mu_2$) and weakly-coupled positive sites ($\tilde{E} < 0$ and $2 \tilde{E} - \tilde{U} < \mu_2$) . Detailed defect band calculations (Vanderbilt and Joannopoulos (1979)) have shown this in Se and we suggest here the pheonomenon may have very general validity.

III. Metastability

It is also possible to examine the question of stability with regard to nonequilibrated occupations. In the absence of a T_{ij} term, of course, stability is guaranteed for all configurations. Given a finite coupling, however, an excited center may be unstable with respect to the spontaneous addition of an electron or hole with a corresponding phonon emission (relaxation). We define metastable states as those which require the absorption of a phonon (or photon) in order to spontaneously relax to a state of lower energy with a different electronic occupation.

We consider excited 2-particle states with energy $E_2 > \mu_2$. We take $\mu_2 = 0$ for simplicity. The center will spontaneously emit one particle if

$$E_2 > E_1 + \frac{1}{2} C \tag{10a}$$

or both if

$$E_2 > E_0 + 2C \tag{10b}$$

From equation (4) we see the former criterion requires $E > 2C - U$ whereas the second is satisfied when $E > 2C - U/2$, larger by $U/2$. Thus the center is unstable with respect to emission of one electron, and metastable 2-particle states occur for

$$\mu_2 < E_2 < 2C - U + \mu_2 \quad . \tag{11a}$$

Similar considerations for empty states with energy smaller than μ_2 give metastability in the range

$$\mu_2 - (2C-U) < E_2 < \mu_2 \quad . \tag{11b}$$

We may also examine the stability of states occupied by one electron which may occur after photoexcitation and subsequent trapping. Such a configuration of energy E_1 is unstable with respect to the absorption of a second electron if $E_1 < E_2 + \frac{1}{2} C$ and unstable to emission if $E_1 < \frac{1}{2} C$. Thus, from equation (4), the band of two-particle energies metastable to single occupation occurs in the range

$$- U + \mu_2 < E_2 < U + \mu_2 \quad . \qquad (12)$$

Note that the bandwidth of these paramagnetic metastable states does not depend on the strength of the electron-phonon coupling but only on the Hubbard coulombic repulsion. Since we have presumed throughout this work that $U < C$ this leads to a narrow band near the Fermi level μ_2 .

To examine absorptive processes it is useful to consider the (fast) single particle excitation spectrum. We define this as the density of states available to add a single electron of energy ε or a single hole of energy $-\varepsilon$ to a system in the ground or metastable configuration.

In any configuration the energy required to add a single electron (without relaxations) to an empty state is (from eq. (6a)) $E^f_{0\to 1} = E$. The contribution of this process to the spectrum is determined by the availability of empty states. If the system is in the ground state, the minimum energy for an empty state is determined by $E_2 > \mu_2$ which from equation (4) requires $E^f_{0\to 1} > \frac{2C-U}{2} + \frac{\mu_2}{2}$. An excited system, however, may contain metastable empty states, as calculated above, with minimum energy $E_2 = \mu_2 - (2C-U)$ which requires only $E^f_{0\to 1} > \frac{\mu_2}{2}$.

In addition, a metastable configuration may contain singly occupied states as discussed above. Thus we consider the process $E^f_{1\to 2}$ which, using the analysis of Section II, requires an energy $E + U - C$. Using the range of energies (equation (12)) available to metastable $n_e = 1$ states and equation (4), we find $\frac{\mu_2}{2} < E^f_{1\to 2} < \frac{\mu_2}{2} + U$. Note that these excitations are bound from above as well as from below.

Using similar arguments we may evaluate the energy to add a hole to a doubly occupied state, $E^f_{2\to 1}$, or to a singly occupied one, $E^f_{1\to 0}$. We find:

Ground State $E^f_{2\to 1} > \frac{-\mu_2}{2} + \frac{2C-U}{2}$

Metastable $n_e = 2$ State $E^f_{2\to 1} > \frac{-\mu_2}{2}$

Metastable $n_e = 1$ State $-\frac{\mu_2}{2} < E^f_{1\to 0} < \frac{-\mu_2}{2} + U$

Denoting these energies as $-\varepsilon$, the full excitation spectrum is shown in Figure 3. The energy $\frac{\mu_2}{2}$ separates electron excitations from hole excitations and the figure represents a system in a metastable state. The band of paramagnetic states at $\frac{\mu_2}{2}$ is displayed assuming $U < (2C-U)/2$ which, of course, is more restrictive than requiring $U^{eff} < 0$. In addition, the density of paramagnetic states is presumed much larger than metastable two-particle states since the latter requires trapping of two electrons in the same state after photoexcitation.

Possible absorptive mechanisms for this spectra, which we label α_i, are as follows:

$$\alpha_1 : \; 2 \to 1 + 0 \to 1 \tag{13a}$$

$$\alpha_2 : \; 2 \to 1 + 1 \to 2 \tag{13b}$$

$$\alpha_3 : \; 1 \to 0 + 0 \to 1 \tag{13c}$$

$$\alpha_4 : \; 1 \to 0 + 1 \to 2 \tag{13d}$$

The energies for these processes are:

$$\alpha_1 = E_0 - E_2 + 2C - U$$

$$\alpha_2 = E_1 - E_2 + C$$

$$\alpha_3 = E_0 - E_1 + C$$

$$\alpha_4 = E_1 - E_1 + U$$

where the state energies E_{n_e} refer to the relaxed levels (ground or metastable) before photoexcitation. The absorption edge may be derived from the range of E_{n_e} given in equations 9,10, and 11. In particular, we find

$$\min \alpha_i = 0$$

for each process. Thus there is a complete collapse of the optical gap, i.e. photodarkening, in this case of extreme fatigue. This is also evident from inspection of Figure 3.

After moderate illumination, however, one expects very few two-particle states to be occupied out of equilibrium. Paramagnetic states will dominate the metastable populations and measurements of photoinduced ESR reveal (Bishop, Strom, and Taylor (1977)) about 10^{17} spins/cm^3. In this case, process 1 will give the ground state gap, 2C-U, and processes 2 and 3 yield half gap absorption at C-U/2. Process 4 is not expected to contribute for concentrations $\sim 10^{17}$ since it is proportional to matrix elements between paramagnetic levels. Thus the absorption spectra should behave as shown in Figure 4. Similar photoinduced absorption has been observed (Bishop, Strom, and Taylor (1975)) in the chalcogenide glass family. It should be noted that our model involves only distributions of two-particle states without reference to specific defects. Thus we predict half-gap photoinduced absorption in a model in which there are no a priori pseudogaps in the fundamental level structure. This is in sharp contrast to defect models (Street (1978), Phillips (1976)) of glasses.

IV. Phonon Sharing

The Anderson negative-U model we have been describing does not include an important contribution to the microscopic picture: pair interactions. These may be coulombic, in part, especially for the states near μ_2 which we have argued are charged. We introduce here a different mechanism for pair-pair interactions which gives rise to low energy electronic excitations. We show that these excitations may account qualitatively for the observed low-temperature thermodynamical behavior, attributed to atomic tunneling, observed generally in glasses.

The idea is simple - in the model of equation (9), there is associated with each site an independent oscillator system. Although the phonon variables have been suppressed, their main contribution is to renormalize the electronic energies $\tilde{E}_i$, $\tilde{U}_i$. In a real system, however, neighboring sites may "share" the same phonon coordinates since there is, in general, more than one covalent bond per atom. The effect may be to saturate the attractive interaction between two electrons at one site leaving no remaining displacement (coupling) between two electrons at the neighboring site.

The mechanism is illustrated in Figure 5. We imagine two sites (states) coupled by a common spring. In case (a), the state on the left is occupied by two electrons (labeled by spin up ↑ and spin down ↓). The effective negative interaction between the particles is mediated by atomic motions schematically indicated by a compression in the spring (b). No further interaction (compression) remains, however, for providing an interaction for a pair of electrons additionally placed in the state on the right. Alternatively, we could have placed the pair on the right initially (c), again reducing the negative attractive interaction available for occupation of the left site. The effect of this is to introduce an effective <u>positive</u>

interaction between <u>pairs</u> at neighboring sites. The range of the interaction may be longer than is suggested here, but the nature of the mechanism suggests that it will at least be short-ranged.

This leads us to reconstruct the negative-U Hamiltonian. We define the coupled system shown in Figure 5 as one site, say i, which consists of two orbitals, say α and β. Thus, in this representation, the repulsive interaction is an intra-site term denoted by $V_i^{\alpha\beta}$. It is convenient to introduce pair creation and destruction operators, which we denote by $d^+_{i,\alpha}$, $d_{i,\alpha}$, respectively. Introducing further a pair counting operator $m_{i,\alpha} = d^+_{i,\alpha} d_{i,\alpha}$, we may write the Hamiltonian

$$H = \sum_i (\epsilon_{i,\alpha} m_{i,\alpha} + \epsilon_{i,\beta} m_{i,\beta}) + \sum_i V_i^{\alpha\beta} m_{i,\alpha} m_{i,\beta} \qquad (14)$$

where the energies $\epsilon_{i,\substack{\alpha\\\beta}} \equiv 2\tilde{E}_{i,\substack{\alpha\\\beta}} - \tilde{U}_{i,\substack{\alpha\\\beta}}$. The Hamiltonian (14) is only convenient insofar as we do not consider single particle excitations. For the moment, we have also neglected any coupling between the pair states (see below).

In order to develop an intuitive feel for the model, it is useful to invoke a molecular bond interpretation of the states α and β. In general covalently bonded atoms do, of course, involve two levels per bond - the bonding (σ) and antibonding (σ*) states. In Anderson's negative-U model, no description is made of the nature of the state locally. There is only one state per site. Generally, σ*-like states would tend to occur with energies larger than μ_2 and σ states would tend to be occupied but no attempt is made to associate an empty and occupied state spatially.

The model of equation (14) specifically attempts to provide this association. In general, the parameters $\epsilon_{i\alpha}, \epsilon_{i\beta}, V_i^{\alpha\beta}$ are site random and no gaps are expected in general. At typical sites, however, $\varepsilon_\alpha = \varepsilon_\sigma < \mu_2$ and $\varepsilon_\beta = \varepsilon_{\sigma*} > \mu_2$; to a good approximation these parameters are distributed randomly about their probable values as depicted in Figure 6. The chemical potential μ_2 is pinned by the CFO overlap. It is less useful to think of the states near μ_2 as having σ and $\sigma*$ character.

The model may be viewed as a collection of centers whose properties depend on the values of the local parameters $\varepsilon_{i\alpha}$, $\varepsilon_{i\beta}$, $V^{\alpha\beta}$ which we describe as follows.

1) typical center: $\varepsilon_\alpha < \mu_2$, $\varepsilon_\beta > \mu_2$
which implies $m_\alpha = 1$, $m_\beta = 0$. These represent the familiar picture of states in the valence and condution bands - bonding orbitals are filled, antibonding orbitals are empty.

2) defect center: $\varepsilon_\alpha < \mu_2$, $\varepsilon_\beta < \mu_2$ and $\varepsilon_\alpha + \varepsilon_\beta + V^{\alpha\beta} < \mu_2$
which gives $m_\alpha = m_\beta = 1$. These states reside in the gap, are charged, and deviate from the normal coordination of the molecular structure, presumably as in the pictures of MDS and KAF.

3) tunneling center: $\varepsilon_\alpha = \varepsilon_\beta < \mu_2$ but $\varepsilon_\alpha + \varepsilon_\beta + V^{\alpha\beta} > \mu_2$
here we have $m_\alpha = 1, m_\beta = 0$ or $m_\alpha = 0, m_\beta = 1$ with equal probability.

The model has, by construction, a two-level center at every site. A much smaller number are at low energies $\varepsilon_\alpha \simeq \varepsilon_\beta$: these may be properly called tunneling centers and can contribute to a low temperature thermodynamic properties.

It should be pointed out that low-energy two-electron excitations already exist in Anderson's original Hamiltonian (eq. (9)). These consist of two-electron excitations at μ_2 where, of course, there is no gap. However, Phillips (1976) has pointed out that the assoiciated matrix elements may be large for these processes and therefore may not contribute to short-time thermodynamic measurements. The arguments presented in Sections II and III support this point of view since these states tend to be strongly localized (near μ_2).

The generalized model allows another possibility, however: the excitation of a pair from $\alpha \rightarrow \beta$ at the site i where both ε_α and ε_β are far from μ_2. These excitations may be properly called biexcitons since they involve two electrons excited to an empty state in which a relaxation "binds" the pair. The binding energy can take on a range of values because $\varepsilon_\alpha - \varepsilon_\beta$ is site random. In particular, it may take the value zero (i.e. case 3)) and it is expected that a condensate of biexcitons exists in the ground state. Evidence for their existence has been discussed by Street (1978) and they have been described as "intimate valence alternation pairs" by Kastner et al. (1976, 1978) within the framework of a defect model. We point out here that they are readily predicted from the continuous microscopic model described by equation (15).

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Figure Captions

Fig. 1. The energy eigenvalue of the Hamiltonian (1) (normalized to the electronic energy level E) as a function of electron occupation n_e for $U = 0$ and $C/E = 4/3$. The minima of each of the three curves corresponds to the eigenvalue for the relaxed center with $n_e = 0$, 1 and 2. The curves describe the energy of the level resulting from displacing the nuclear coordinates to positions corresponding to electronic occupations different from the minima value. The solid arrows describe optical transitions which result in a charge of electronic occupation by one carrier. The dashed arrows depict slow transitions.

Fig. 2. Conjectural correlation between the effective (negative) $\tilde{U}$ and the effective site energy $\tilde{E}$ in a typical diamagnetic glass. $\tilde{E} = 0$ is roughly where a non-bonded orbital would occur. States corresponding to the part of the curve in the shaded region are occupied by pairs of electrons.

Fig. 3. Excitation spectrum for model described in text. Here μ_2 is taken to be zero for simplicity. Metastable two-electron states appear to the right of the Fermi level and metastable zero-electron states to the left. The narrow band at center consists of one-electron states.

Fig. 4. Photoinduced absorption spectrum.
Absorption begins at an energy equal to half the gap

(processes α_2 and α_3) and increases at full gap, when process α_1 begins to contribute.

Fig. 5. Schematic of neighboring two-electron states sharing a common spring system (bond). Double occupation of both states is energetically unfavorable (see text).

Fig. 6. Probability distribution of site energies α and β for tunneling model presented in Section IV.

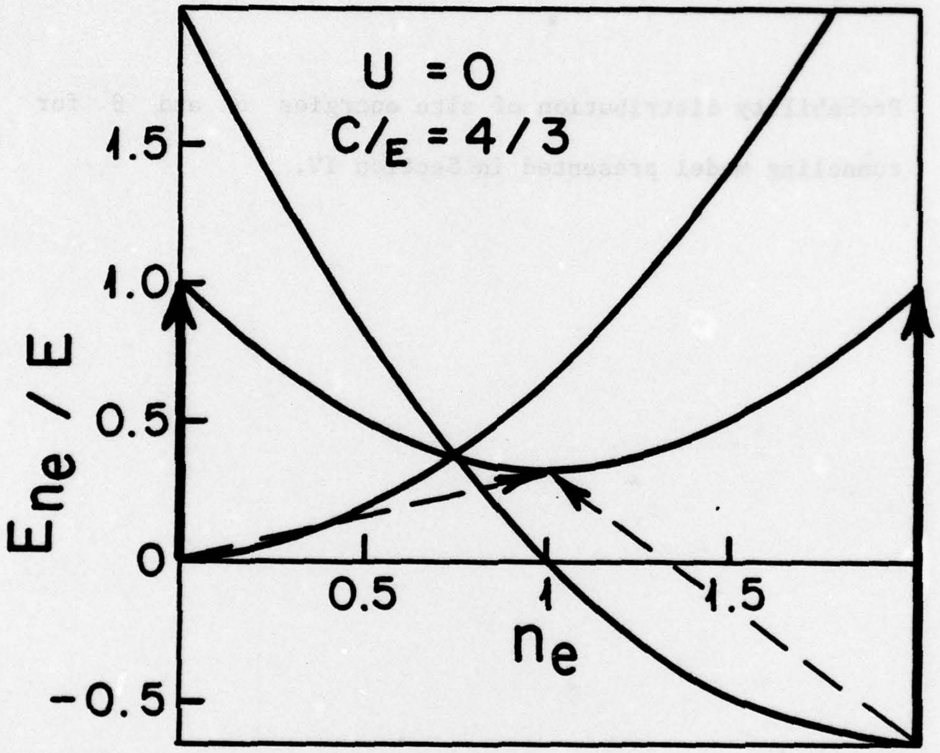

Fig. 1

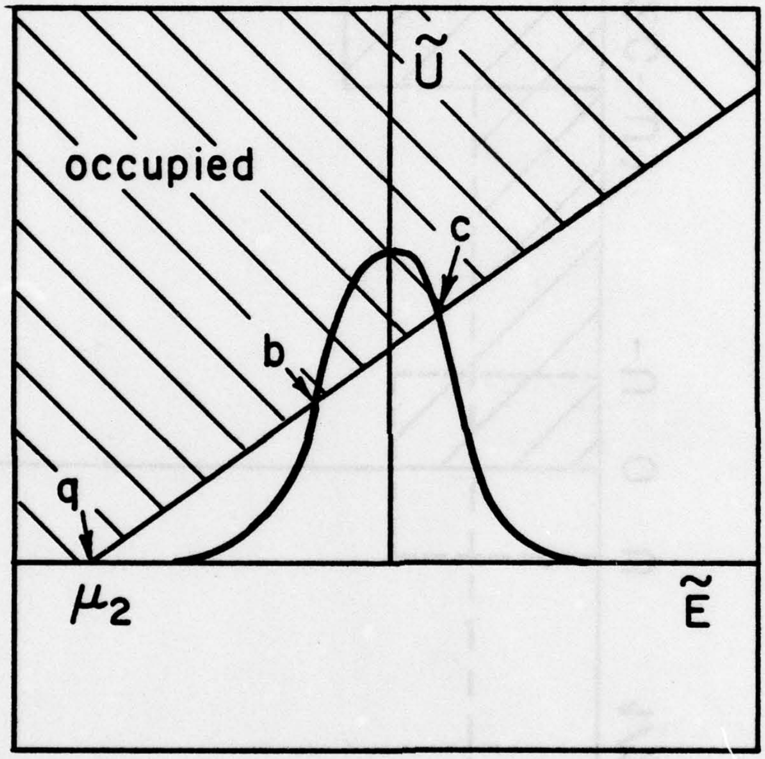

Fig. 2

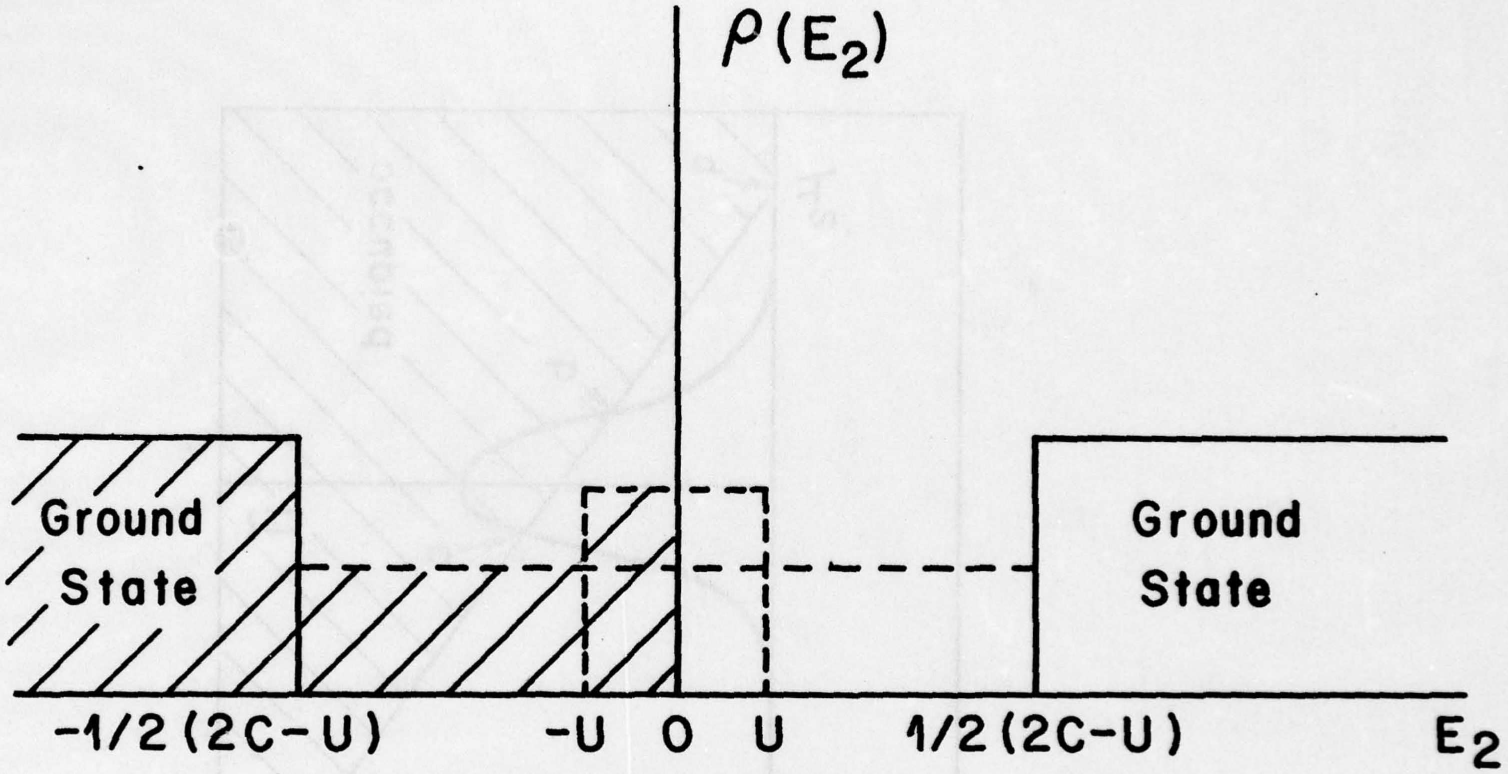

Fig. 3

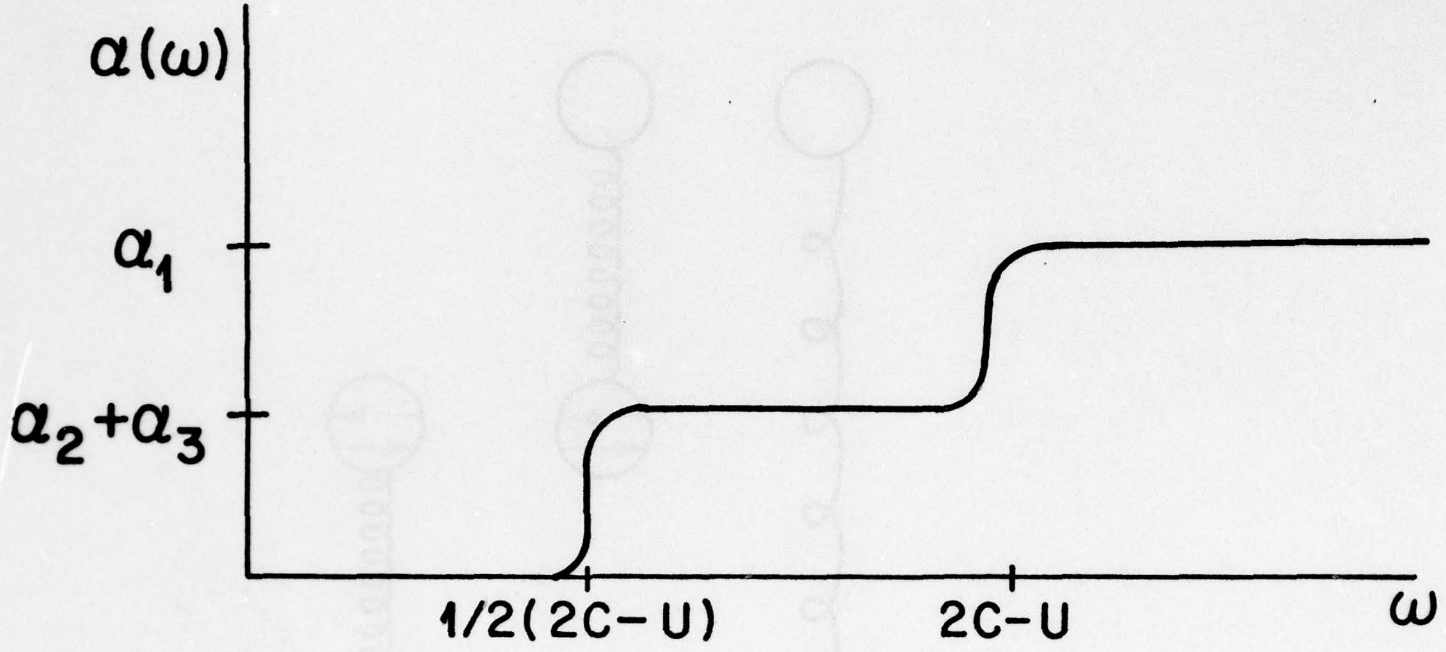

Fig. 4

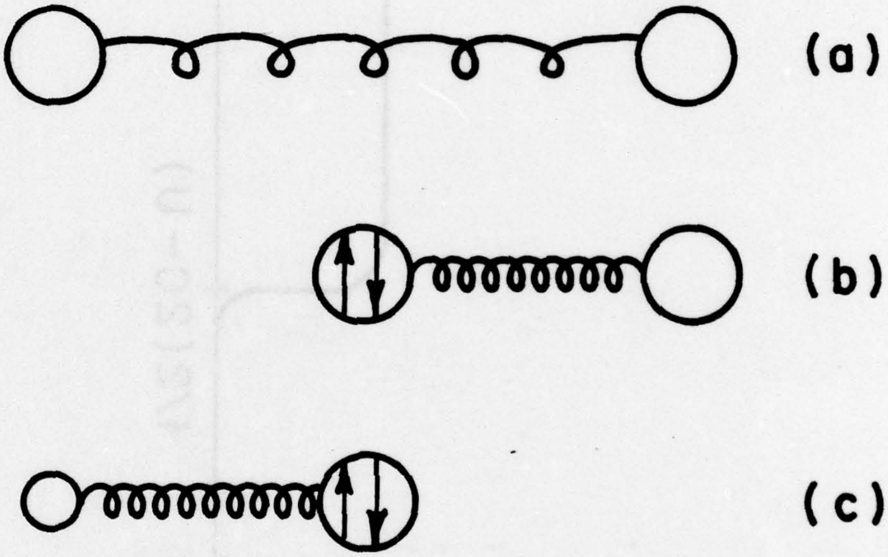

Fig. 5

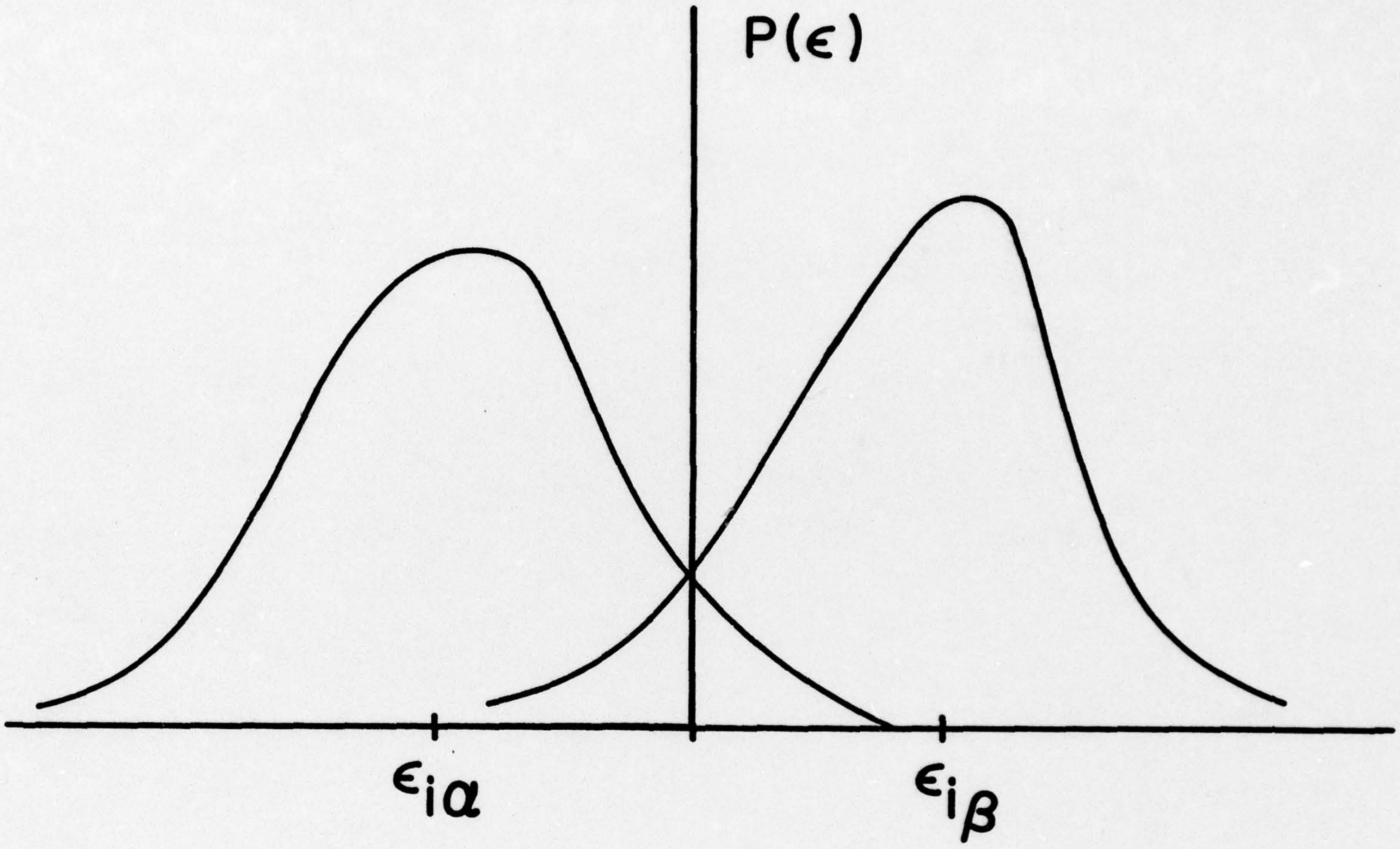

Fig. 6