PHYSICAL REVIEW B VOLUME 9, NUMBER 2 15 JANUARY 1974

Correlation effects in hopping conduction: A treatment in terms of multielectron transitions*

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(Received 30 March 1973)

The problem of impurity conduction at moderate compensation has been treated using the concept of multielectron single-phonon transitions. The problem was treated in the region of density, temperature, and compensation where two- (or many-) electron transitions begin to be important. A compensation of 0.5 is used with a temperature range of 1 to 5 K and an average majority impurity separation of 200 to 600 Å in germanium. The problem is treated by comparing the transition rates of one- and multielectron transitions of the localized electron system where the one-electron transition defines the critical impedance in a percolation path at low densities and high temperatures. It is found that two- and three-electron effects may account for the lowering of the "activation energy" seen experimentally as the density of impurities is raised. Comparison to currently available experimental data is made.

I. INTRODUCTION

This paper investigates the contribution of correlated many-electron excitations to the conductivity through localized states (hopping), and evaluates the conditions under which such a contribution is important. We restrict ourselves here primarily to the impurity conduction systems because these systems are well characterized and have been extensively studied. Especially useful for this work is the Fritzsche-Cuevas (FC) systematic study[1] of the dc conductivity of germanium doped by irradiation with thermal neutrons. The compensation in these samples is close to $\frac{1}{2}$ and this is where the correlation effects discussed here are most important.

The importance of carrier-carrier interactions on hopping conduction has been stressed before,[2] but the work[3,4] has been sketchy so far, and has been done from a less microscopic point of view than that taken here.[5]

The basic features of the problem we treat are shown in Fig. 1. Figure 1(a) shows the initial state, the transition to the final state, and the final state used in one-electron treatments for a transition from site a to site b. The details are given by Miller and Abrahams (MA).[6] The random energy difference between the sites, which is responsible for both the localization on individual sites and the energy needed for the transition, is assumed fixed. All other electrons are assumed frozen in space and all electron-electron correlation effects in the transition are thus ignored. When considering the electron-electron interaction, one must use a picture such as in Fig. 1(b). The transition of the charge from a to b is considered in conjunction with the correlated movement of some neighboring charge from c to d. The movement of the charge from c to d alters the energy difference between sites a and b. Under the proper conditions this correlated motion proceeds faster than the one-electron motion from a to b. It is found that the charges on a and c can move sequentially or simultaneously. In all cases the movement of charge from a to b is considered the current-carrying transition and the movement from c to d is considered an auxiliary transition which does not carry current but merely acts to enhance the transition rate from a to b. These correlation effects are found to become important as the temperature of the system is lowered and the density of localized states is raised.

In the following we briefly summarize the aspects of the MA theory which are relevant to the development of the present theory. MA began by calculating the wave functions of the two-site configuration

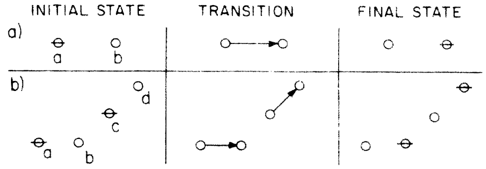

FIG. 1. Schematic representation of the hopping transitions. Occupation by an electron is indicated by a horizontal line. (a) One-electron transition, such as treated by MA. A two-site, one-electron configuration is sufficient to describe these processes. (b) Correlated two-electron hopping transition which relieves some of the Coulomb repulsion energy. A four-site two-electron system is needed to describe these processes.

in the tight binding approximation, assuming that the resonance energy W_{ab} is much less than the difference Δ_{ab} between the random potentials E_a and E_b. This assumption is also in line with Anderson's[7,8] criterion for the existence of localized states. The result is

$$\psi_{\text{initial}} = \phi_a + (W_{ab}/\,|\Delta_{ab}|)\phi_b = \psi_a, \tag{1}$$

$$\psi_{\text{final}} = \phi_b - (W_{ab}/|\Delta_{ab}|)\phi_a = \psi_b, \tag{2}$$

where ϕ_a and ϕ_b are the wave functions of isolated sites a and b. Next, MA calculate the phonon-induced transition rates between ψ_a and ψ_b, with the result

$$\begin{aligned} U_{ab} &= CW_{ab}^2|\Delta_{ab}|n(q_{ab}), & \Delta_{ab} > 0 \\ &= CW_{ab}^2|\Delta_{ab}|[(n(q_{ab})+1)], & \Delta_{ab} < 0. \end{aligned} \tag{3}$$

$n(q_{ab})$ is the phonon density for wave vector q_{ab} where $\hbar s q_{ab} = \Delta_{ab}$, and C depends on the electron-phonon coupling strength, the phonon density of states, and the elastic properties of the material.

To illustrate the need for considering the correlated many-electron transitions, it is of interest to discuss briefly MA's results. The theory of MA gives activation energies which are in good agreement with experimental results throughout the compensation range. As explained in the following, this is unexpected because the density of states used by MA is, even approximately, only correct for small compensations. The error which this causes in the activation energy is compensated for by the correlated motion of carriers.

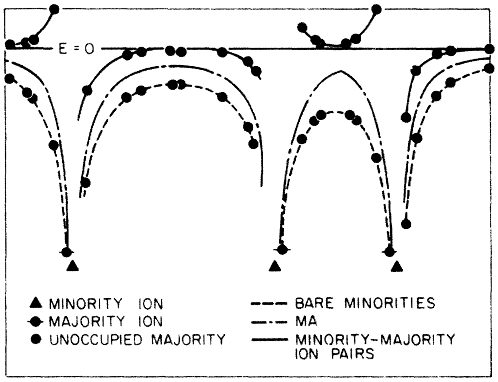

FIG. 2. One-dimensional representation of the potential surfaces for carrier appropriate for hopping conduction at low compensation. The carrier here is considered to be the majority ion, an electron in p-type, and a "hole" in n-type material. The dashed line is the potential derived from interactions with minority ions only. The dash-dotted line is the potential derived from nearest-neighbor minority ions only and corresponds to the MA density of states. The solid line is the potential derived from paired minority and majority ions.

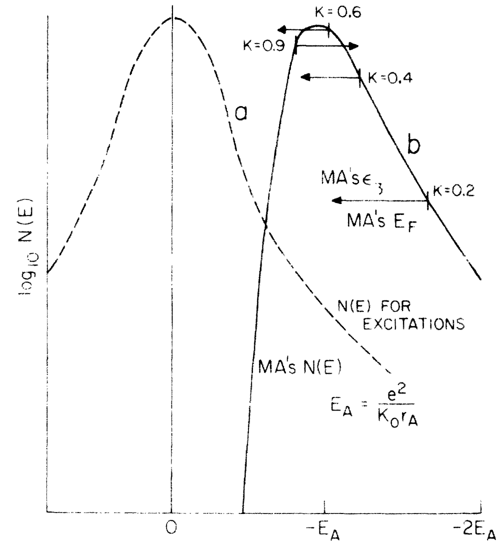

FIG. 3. Density of states for electrons trapped near a minority ion (solid line), and for conduction electrons moving among ion pairs (dashed line). The latter is only qualitatively correct. The bars and arrows on the solid plot indicate MA's Fermi energies, and activation energies, respectively, for various compensations K.

Miller and Abrahams assumed that the density of states was determined by the distribution of nearest-neighbor minority ions. the energy of a given site being determined by the Coulomb interaction with its nearest-neighbor minority. The potential energy surface used by MA is shown in the middle of Fig. 2 in a one-dimensional representation.[2,3] Shown in Fig. 3 is the corresponding one-particle density of states. This form can be seen to be nearly correct for determining E_F at low temperatures where each charged majority is paired with a charged minority. Thus, each majority ion sees a nearest-neighbor minority ion and an atmosphere of neutral minority-majority pairs, which leads to a density of states such as MA use. However, the use of this density of states is not correct when considering excitations that lead to dc conduction. This is because the interaction between electrons creates a gap at the Fermi energy.[2,9] Carriers that contribute to the dc conductivity must move in an atmosphere of neutral minority-majority ion pairs, so that the density of states for these conducting electrons must peak at $E = 0$. The potential energy for such conducting carriers is shown in the upper line of Fig. 2. The corresponding density of states is shown in Fig. 3. Miller and Abraham's $N(E)$ is peaked at $E = -e^2/K_0 r_{\min}$ where $r_{\min}$ is the average nearest-neighbor minority distance. Use of this density of states for both determinations of E_F and the activation energy ϵ_3 leads to a value of ϵ_3 clearly too low for a one-electron excitation. The value of ϵ_3 found by MA is seen in Fig. 3 to be approximately equal to the distance from their Fermi level to the peak in their density of states. Instead, it should be equal to the distance from E_F to a point near $E = 0$, the peak of the density of the conducting electrons in the uncorrelated picture, representable by the one-electron density of states of Figs. 2 and 3. Figure 2 represents the case of low compensation because in this situation it is easier to visualize the various energies discussed. The difference between the above activation energies becomes larger as the compensation increases to 0.5.

The fact that MA's theory, which ignores the need to go to the dashed curve of Fig. 3, gives good agreement to experiment at low densities means that the need for activation to $E \approx 0$ is somehow alleviated by a correlated motion of the carriers. This causes the carrier-carrier repulsion, which shifts MA's $N(E)$ to the neutral pair $N(E)$ in Fig. 3, to be partly relieved.

It is also seen experimentally[1] that when the density is raised, ϵ_3 is even smaller than MA's prediction. Qualitatively, this can be understood as a situation approaching the bare minority potential distribution shown in Fig. 2. If the carrier-carrier repulsion is completely relieved, i.e., each carrier behaves as though locally there are no other carriers, then the bare minority potential is the correct one to use.

A less detailed treatment of the electron-electron interaction effects on intersite transitions has been reported by Pollak and Knotek[3] and Pollak[4] who treat the correlated motion of carriers in terms of a dielectric response of localized electrons to a current-carrying electron. Allen and Adkins[10] finds that a large dielectric contribution is necessary to explain their results and we feel therefore that the work of Allen and Adkins may be an experimental confirmation of the importance of the multielectron effect.

The connection between the microscopic elemental excitation and the macroscopic properties of the system is made using the impedance network representation of MA. Miller and Abrahams find the distribution function $f_i(T)$ by solving the Boltzmann equation for equilibrium using the intersite transition rate as a starting point. The solution is found to be a Fermi distribution and the Fermi level is solved for. Miller and Abrahams then find an effective impedance connecting sites i and j to be $(\mathcal{E}_i < \mathcal{E}_j)$

$$(Z_{ij})^{-1} = (e^2/kT)[f_i(1-f_j) + f_j(1-f_i)] \times C W_{ij}^2 \,|\Delta_{ij}|\, n(q_{ij})[n(q_{ij})+1] \tag{4}$$

$$\approx (e^2/kT) f_i(1-f_j) U_{ij} \, . \tag{5}$$

Clearly Z_{ij} includes both the phonon emission and absorption rates.

The complete system is then reduced to an interconnected impedance network, each site i connected to every other site j by the impedance Z_{ij}. Miller and Abrahams then solve for the resistivity of the bulk by constructing a path through the solid which presumably carries most of the current. Miller and Abraham's path has been since modified by the use of percolation theory.[11-14] We make use of the results of Ref. 13. It will be seen that the "critical impedance" which arises naturally in this percolation problem is an obvious point at which to include the effects of many-electron transitions.

The results of the one-electron treatment are

$$\rho \propto e^{n\alpha r_s + \epsilon_3/kT} , \tag{6}$$

where ρ is the bulk resistivity and $\alpha = 2/a$, $r_s = (3/4\pi N_s)^{1/3}$, with N_s being the concentration of localized states. $n \approx 1.3$,[13] and $\epsilon_3 \propto 1/r_s$.

The extrapolation to $T = \infty$ is seen to agree well with experimental results. As already mentioned, MA's ϵ_3 results are seen to agree at low densities, both as to form and magnitude, but we feel the agreement in magnitude is fortuitous. The form at low densities arises naturally from the fact that the energies involved are Coulombic and thus should scale with r_s, like r_s^{-1}. The high-density results are seen to depart from this form and it is the purpose of this paper to argue that the departure is due to correlated motion of electrons. We also will show qualitatively how the low value for the low-density activation energy may arise from another type of correlated motion, namely, the adiabatic transitions mentioned below.

Our steps for the four-site two-electron model follow MA's procedure for the two-site one-electron case. (i) We calculate the two-electron wave functions for the four-site system. We find that we can use Hartree wave functions because the exchange effects are small. (ii) We then derive the phonon-induced transition rates from any initial to any final state; these include two-electron transitions. Again, we find that exchange effects are unimportant. (ii) We modify MA's impedances to include two-electron transitions. This is done as follows: One of our two charges is a carrier and is termed the primary charge. Its initial and final sites are termed the primary pair. The other charge is the assistant or auxiliary and the pair of sites on which it moves is termed the auxiliary pair. The motion of an electron on the auxiliary pair, while not directly contributing to the current, modifies the impedance of the primary pair. Such an effect comes from simultaneous as well as sequential motion of the two electrons. We pay attention primarily to the simultaneous two-electron transitions.

It is found that there is a temperature-dependent critical density which must be exceeded before two-electron transitions can make a significant contribution to the transport. This critical density is given in Eqs. (91) and (92). Finally, the conductivity is calculated from a percolation theory using the modified impedances.

II. WAVE FUNCTIONS OF TWO-ELECTRON SYSTEM

The elemental unit of this treatment is four potential wells located at random in space and situated in some random potential suitable for the system under study. Into this system we introduce two electrons and include their Coulomb interaction into the Hamiltonian. As in MA, we will expect that the one-electron states of the system, for suitable values of the random potential, will correspond to an electron being confined to a single site and have only minor components of its wave function on other sites. If we consider two sites occupied by two electrons, we must work with a two-electron antisymmetrized space-spin wave function. If we assume a strictly covalent orbital, we are neglecting the ionic terms of the wave function. These correspond to a component of the wave function which has doubly occupied sites. Thus,

$$\psi_{\text{cov}} = (1/\sqrt{2})(\phi_a(1)\phi_c(2) \pm \phi_c(1)\phi_a(2)), \tag{7}$$

$$\psi_{\text{ion}} = (1/\sqrt{2})(\phi_a(1)\phi_a(2) \pm \phi_c(1)\phi_c(2)). \tag{8}$$

Coulson and Fischer[15] in treating H_2 have shown that if we write

$$\psi = \psi_{\text{cov}} + \lambda\psi_{\text{ion}} \tag{9}$$

and solve for λ variationally, we find that λ is very small when the internuclear separation is larger than 1.6 times the Bohr radius of a hydrogenlike wave function. The two occupied wells we consider are very similar to two hydrogen atoms at large separation. Equation (7) is therefore a good zero-order wave function for constructing two-electron four-well wave functions. The presence of the two added wells is treated as a perturbation.

We now consider the importance of exchange effects on the size of the minor components of the wave function. These are the important quantities in the transition matrix elements. First, we define the system and establish indices and labels. We label the wells a, b, c, and d and the electrons 1 and 2. We assume that in the ground state the main amplitudes of the two electrons are on sites a and c. The ground-state single-site wave function for site i is ϕ_i. Thus, the zero-order wave function is

$$\Psi^0 = (1/\sqrt{2})[\phi_a(1)\phi_c(2) \pm \phi_c(1)\phi_a(2)], \tag{10}$$

$$\phi_i = \sum_{p=1}^{n} \alpha_p F_p(\vec{r})\chi_p(\vec{r}). \tag{11}$$

The notation in Eq. (11) is that of MA.

We assume first-order corrections to the single-site one-electron wave functions, i.e.,

$$\psi_a^{(ac)} = \phi_a + \lambda\delta_{ab}^{(ac)}\phi_b + \lambda\delta_{ad}^{(ac)}\phi_d, \tag{12}$$

$$\psi_c^{(ac)} = \phi_c + \lambda\delta_{cb}^{(ac)}\phi_b + \lambda\delta_{cd}^{(ac)}\phi_d. \tag{13}$$

If now

$$\Psi = \psi_a^{(ac)}(1)\psi_c^{(ac)}(2) \pm \psi_c^{(ac)}(1)\psi_a^{(ac)}(2), \tag{14}$$

then to first-order in the perturbation parameter λ,

$$\Psi = \Psi^0 + \lambda\Psi^1, \tag{15}$$

where

$$\begin{aligned}\Psi^1 = {} & \delta_{ab}^{(ac)}[\phi_b(1)\phi_c(2) \pm \phi_c(1)\phi_b(2)] \\ & + \delta_{ad}^{(ac)}[\phi_d(1)\phi_c(2) \pm \phi_c(1)\phi_d(2)] \\ & + \delta_{cb}^{(ac)}[\phi_a(1)\phi_b(2) \pm \phi_b(1)\phi_a(2)] \\ & + \delta_{cd}^{(ac)}[\phi_a(1)\phi_d(2) \pm \phi_d(1)\phi_a(2)]\end{aligned} \tag{16}$$

Some care must be exercised in the choice of the zero- and first-order Hamiltonians. Consider for simplicity only sites a, b, and c and consider b as a perturbation on site a. The zero-order Hamiltonian for the ac pair consists of the effective-mass kinetic energy operator $T_1 + T_2$; the potential from sites a and c, $(e^2/K_0)[1/r_{1a} + 1/r_{1c} + 1/r_{2a} + 1/r_{2c}]$; the electron-electron interaction $e^2/K_0 r_{12}$; and the random potential $V(\vec{r}_1) + V(\vec{r}_2)$. The first-order correction to this is then the potential from site b, $(e^2/K_0)(1/r_{1b} + 1/r_{2b})$. The zero-order Hamiltonian for the cb pair is identical except that the Coulomb potential from site a is replaced by that from b. The first-order correction to the bc zero-order Hamiltonian is the Coulomb term from site a. Thus,

$$\begin{aligned}H_{ac}^0 = {} & T_1 + T_2 - \sum_{i=1}^{2} \frac{e^2}{K_0}\left(\frac{1}{r_{ia}} + \frac{1}{r_{ic}}\right) \\ & + \frac{e^2}{K_0 r_{12}} + V(r_1) + V(r_2),\end{aligned} \tag{17}$$

$$H_{ac}^1 = -(e^2/K_0)(1/r_{1b} + 1/r_{2b}), \tag{18}$$

$$\begin{aligned}H_{bc}^0 = {} & T_1 + T_2 - \sum_{i=1}^{2} \frac{e^2}{K_0}\left(\frac{1}{r_{ib}} + \frac{1}{r_{ic}}\right) \\ & + \frac{e^2}{K_0 r_{12}} + V(r_1) + V(r_2),\end{aligned} \tag{19}$$

$$H_{bc}^1 = -(e^2/K_0)(1/r_{1a} + 1/r_{2a}), \tag{20}$$

and

$$H = H_{ac}^0 + \lambda H_{ac}^1 = H_{bc}^0 + \lambda H_{bc}^1 \quad \text{if } \lambda = 1 \quad . \tag{21}$$

Here we must understand that the perturbation Hamiltonian is not small in itself, but that it has a small *effect* on the wave function. This is due to the random potential term present in the zero-order Hamiltonian. If this were not present, the perturbation Hamiltonian would have a very large effect due to the degeneracy of the single-site energies.

If we consider only the perturbation by site b on the one-electron wave function localized on the site a, we have $\Psi = \Psi^0 + \lambda\Psi^1$, where Ψ^0 is given by Eq. (10) and Ψ^1 by the first term of Eq. (16).

Inserting this into

$$(H - E)\Psi = 0\,, \tag{22}$$

where

$$E = E_0 + \lambda E_1\,, \tag{23}$$

we get to first order in λ

$$\delta_{ab}^{(ac)} H_{cb}^0 |\Psi^1\rangle - \delta_{ab}^{(ac)} E_0 |\Psi^1\rangle \equiv H_{ac}^1 |\Psi^0\rangle - E_1 |\Psi^0\rangle\,. \tag{24}$$

The operation $\langle\Psi^1|$ on both sides of the equation gives

$$\delta_{ab}^{(ac)} = \frac{\langle\Psi^1 | H_{ac}^1 | \Psi^0\rangle - E_1\langle\Psi^1|\Psi^0\rangle}{E_0 - \langle\Psi^1 | H_{bc}^0 | \Psi^1\rangle} \equiv \frac{A - B}{E_0 - C}\,, \tag{25}$$

with

$$A = -\langle\phi_a | e^2/K_0 r_{1b} | \phi_b\rangle - \langle\phi_c | e^2/K_0 r_{1b} | \phi_c\rangle\langle\phi_a|\phi_b\rangle\,, \tag{26}$$

$$B \approx -[\langle\phi_a | e^2/K_0 r_{1b} | \phi_a\rangle + \langle\phi_c | e^2/K_0 r_{1b} | \phi_c\rangle] \times[\langle\phi_a|\phi_b\rangle + O(|\phi_a|\phi_b\rangle|^2)]\,, \tag{27}$$

$$C = \mathcal{E}_b + \mathcal{E}_c + e_{bc} + X_{bc}\,, \tag{28}$$

$$E_0 = \mathcal{E}_a + \mathcal{E}_c + e_{ac} + X_{ac}\,, \tag{29}$$

where

$$\mathcal{E}_b = \langle\phi_b | T_1 - e^2/K_0 r_{1b} - e^2/K_0 r_{1a} + V(r_1) | \phi_b\rangle\,, \tag{30}$$

$$e_{bc} = \langle\phi_b(1)\phi_c(2) | e^2/K_0 r_{12} | \phi_b(1)\phi_c(2)\rangle\,. \tag{31}$$

and

$$X_{bc} = \pm\langle\phi_c(1)\phi_b(2) | e^2/K_0 r_{12} | \phi_b(1)\phi_c(2)\rangle\,. \tag{32}$$

Thus

$$\delta_{ab}^{(ac)} = -\frac{\langle\phi_a | e^2/K_0 r_{1b} | \phi_b\rangle + \langle\phi_a | e^2/K_0 r_{1b} | \phi_a\rangle\langle\phi_a|\phi_b\rangle}{\mathcal{E}_a - \mathcal{E}_b + e_{ac} - e_{bc} \pm X_{ac} \mp X_{bc}}\,. \tag{33}$$

If we can neglect the exchange terms X_{ac} and X_{bc} in Eq. (33), we get the same result for $\delta_{ab}^{(ac)}$ as we would get if we were treating the ab pair as an one-electron problem. From Eq. (32) we see that the exchange terms are of second order in the overlap and can be neglected. Hence we can disregard the antisymmetrized character of the two-electron wave function. We will accordingly adopt the form

$$\Psi_{ac} \approx (\phi_a(1) + \delta_{ab}^{(ac)}\phi_b(1))(\phi_c(2) + \delta_{cd}^{(ac)}\phi_d(2))\,, \tag{34}$$

where the δ's have the form as in Eq. (33), e.g.,

$$\delta_{ab}^{(ac)} = \frac{L_{ab} - S_{ab}J_{ab}}{\mathcal{E}_a - \mathcal{E}_b + e_{ac} - e_{bc}} = \frac{W_{ab}}{\mathcal{E}_a - \mathcal{E}_b + e_{ac} - e_{bc}}\,, \tag{35}$$

with L, S, and J defined by MA. In this form we are neglecting any interaction between minor components of the wave function. Including these interactions would only add exchange terms of the order of δ^4. The form of the wave function in Eq. (34) is tailored to our needs. We are considering only the minor components on sites to which a transition is to be made. We are interested in the difference between one- and two-electron transitions. Considering all possible combinations of indices suggested by Eq. (34) constitutes an exhaustive treatment of all possible four-site configurations.

Following the previous works on the two-site problem, we will consider concentrations where $\delta_{ab}^{(ac)}$ (and all like terms) of Eq. (34) are small. This condition is more restrictive than the neglect of exchange because the exchange energy includes the product of two overlaps but W_{ab} includes only a single overlap. Thus we can safely assume here that if $\delta_{ab}^{(ac)}$ is small, the exchange effects can be neglected in the derivation of the wave functions.

III. PHONON-INDUCED TRANSITION RATES OF TWO ELECTRONS

To be consistent with the outline of the treatment in the Introduction, we want to consider the transition of electron 1 from site a to site b with electron 2 either remaining in place (at c) or making a transition (to d). Hence we consider transitions from Ψ_{ac} to Ψ_{bc} and Ψ_{bd}.

In the derivation of the form of the wave function of the two-electron system, we have shown that the exchange effects are unimportant. But exchange effects still may be of importance when considering transitions between such states. The direct and exchange transitions will be found to be of the same order in overlap integrals and we must discuss this in some detail, going to an enlarged configuration. For this purpose we use a Slater determinant to describe a configuration with $2N$ sites and N electrons:

$$\Psi_\alpha = \frac{N}{\sqrt{N!}}\begin{vmatrix} \Psi_1^\alpha(1) & \Psi_2^\alpha(1) & \cdots & \Psi_p^\alpha(1) & \cdots \\ \Psi_1^\alpha(2) & & & & \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ \Psi_1^\alpha(q) & & & & \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ \Psi_1^\alpha(N) & \cdots & & \cdots & \Psi_N^\alpha(N) \end{vmatrix}\,. \tag{36}$$

The Ψ_i^α are generalizations of Eqs. (12) and (13), i.e., a major component of the wave function is on the one site i and minor components are on the "empty" sites j. α denotes which of the $2N$ sites have large amplitudes. Transitions in such a system are given by the matrix elements connecting Ψ_α to some Ψ_β,

$$M=\langle\Psi_\alpha|H'|\Psi_\beta\rangle, \tag{37}$$

where H' is the perturbation Hamiltonian. When we consider an n-electron transition, β has n indices that differ from α. Thus, if a one-electron transition from i to i' occurs then Ψ_i in Eq. (36) is replaced by $\Psi_{i'}$. If a two-electron transition occurs, i and j (say) are replaced by i' and j'; for three, ijk to $i'j'k'$, etc. In addition, all minor components change accordingly.

We now partition the problem i.e., move the n columns that differ in the initial and final states to the first n columns in the determinants below. We then consider

$$\left\langle \begin{vmatrix} \Psi_i^\alpha(1) & \cdots & \Psi_p^\alpha(1) & \cdots \\ \vdots & & \vdots & \\ \Psi_i^\alpha(n) & \cdots & \Psi_p^\alpha(n) & \\ \vdots & & & \vdots \\ \Psi_i^\alpha(N) & \cdots & & \Psi_N^\alpha(N) \end{vmatrix} \right\| H' \left\| \begin{vmatrix} \Psi_{i'}^\beta(1) & \cdots & \Psi_{p'}^\beta(1) & \cdots \\ \vdots & & \vdots & \\ \Psi_{i'}^\beta(N) & \cdots & \Psi_{p'}^\beta(n) & \\ \vdots & & & \vdots \\ \Psi_{i'}^\beta(N) & \cdots & & \Psi_N^\beta(N) \end{vmatrix} \right\rangle , \tag{38}$$

which reduces to

$$\frac{1}{n!}\left\langle \begin{vmatrix} \Psi_i^\alpha(1) & \cdots & \Psi_p^\alpha(1) \\ \vdots & & \vdots \\ \Psi_i^\alpha(n) & \cdots & \Psi_p^\alpha(n) \end{vmatrix} \right\| H' \left\| \begin{vmatrix} \Psi_i^\beta(1) & \cdots & \Psi_{p'}^\beta(1) \\ \vdots & & \vdots \\ \Psi_{i'}^\beta(n) & \cdots & \Psi_{p'}^\beta(n) \end{vmatrix} \right\rangle , \tag{39}$$

when only terms of order n in overlap are kept. This form has $(n!)^2$ terms of which $n!$ are distinct. Figure 4 illustrates examples of terms kept and the n-electron matrix elements to which they correspond. Figure 5 illustrates examples of terms which are dropped when the partitioning is used.

In the remainder of this work we will concentrate on the treatment of terms like those in Figs. 4-1 and 4-2. Figure 4-1 is the one-electron transition considered in previous works.[6] We will incorporate the two-electron transitions into the treatment as follows: Consider a percolation path such that the transition from i to i' comprises one step in the path. In that context we call the transition in Fig. 4-2a the direct transition, i.e., the charge that was on site i is the charge that moves along the percolation path. Figure 4-2b is then termed the exchange transition.

When considering at most two-electron transitions, it is easily seen that the large majority of configurations encountered have one two-electron transition (as defined above) that predominates. Figures 6(a) and 6(b) show two two-electron transitions that may have comparable rates, because the overlaps are similar. Figures 6(c) and 6(d) show two transitions with much different rates to the same final state. Since configurations like those in Fig. 6(c) are much more numerous, we do not include exchange effects in the transition.

We will now consider a one-electron percolation path. This is shown as the dashed line in Fig. 6(a). The fact that we can neglect exchange such as in Fig. 6(b) or Fig. 6(d) justifies our previous division of the four-site configuration into a primary and auxiliary pair. In this treatment the electron in the second pair serves as an assistant or auxiliary to the "carrier."

Using a perturbation in the form of a deformation potential induced by acoustic phonons,[6] we have

$$H'(i)=E^1\left(\frac{2\hbar}{sp V}\right)^{1/2}\sum_q q^{1/2}\left(b_q e^{i\vec{q}\cdot\vec{r}_i}-b_q^* e^{-i\vec{q}\cdot\vec{r}_i}\right), \tag{40}$$

$$\mathcal{H}'=H'(1)+H'(2), \tag{40a}$$

where the notation is that of MA.

We calculate the transition rate between states Ψ_α and Ψ_β using a generalization of MA's form using two-electron Hartree wave functions:

$$\Psi_\alpha = (\alpha_a\phi_a(1) + \alpha_b\phi_b(1))(\alpha_c\phi_c(2) + \alpha_d\phi_d(2)) , \qquad (41)$$

$$\Psi_\beta = (\beta_a\phi_a(1) + \beta_b\phi_b(1))(\beta_c\phi_c(2) + \beta_d\phi_d(2)) . \qquad (42)$$

We find

$$\langle\alpha\,|\mathcal{H}'|\,\beta\rangle = \tfrac{1}{2}[n(q)]^{1/2}Cq^{1/2}\langle e^{i\vec{q}\cdot\vec{r}}\rangle \times[(\alpha_a\beta_a + \alpha_b\beta_b\, e^{i\vec{q}\cdot\vec{R}_{ab}})(\alpha_c\beta_c + \alpha_d\beta_d) + e^{i\vec{q}\cdot\vec{R}_{ac}}(\alpha_a\beta_a + \alpha_b\beta_b) \times(\alpha_c\beta_c + \alpha_d\beta_d\, e^{i\vec{q}\cdot\vec{R}_{cd}})] , \qquad (43)$$

where

$$\vec{R}_{ij} = \vec{r}_j - \vec{r}_i ,$$
$$\langle e^{i\vec{q}\cdot\vec{r}}\rangle = \langle\phi_i\,|e^{i\vec{q}\cdot\vec{r}}|\,\phi_i\rangle \approx [1 + (\tfrac{1}{2}aq)^2]^{-2} , \qquad (44)$$

where $n(q)$ is the number of phonons of wave vector q:

$$n(q) = (e^{\hbar sq/kT} - 1)^{-1} . \qquad (45)$$

Using this form, we find for the transition rate

$$U_{\alpha\beta} = \frac{V}{\hbar(2\pi)^2}\, n(q_{\hbar\beta})\frac{4\pi(\Delta_{\alpha\beta}/\hbar S)^3}{[1 + (\frac{1}{2}aq)^2\,]^{-4}}\Bigg[[(\alpha_a\beta_a)^2 + (\alpha_b\beta_b)^2][\alpha_c\beta_c + \alpha_d\beta_d]^2 + [\alpha_a\beta_a + \alpha_b\beta_b]^2[(\alpha_c\beta_c)^2 + (\alpha_d\beta_d)^2]$$
$$+ 2\alpha_a\beta_a\alpha_b\beta_b\frac{\sin q_{\alpha\beta}|Rab|}{q_{\alpha\beta}|Rab|}[\alpha_c\beta_c + \alpha_d\beta_d]^2 + 2\alpha_c\beta_c\alpha_d\beta_d\frac{\sin q_{\alpha\beta}|R_{cd}|}{q_{\alpha\beta}|R_{cd}|}[\alpha_a\beta_a + \alpha_b\beta_b]^2 + 2(\alpha_a\beta_a + \alpha_b\beta_b)$$
$$\times(\alpha_c\beta_c + \alpha_d\beta_d)\Bigg(\alpha_a\beta_a\alpha_c\beta_c\frac{\sin q_{\alpha\beta}|R_{ac}|}{q_{\alpha\beta}|R_{ac}|} + \alpha_a\beta_a\alpha_d\beta_d$$
$$\times\frac{\sin q_{\alpha\beta}|R_{ac} + R_{cd}|}{q_{\alpha\beta}|R_{ac} + R_{cd}|} + \alpha_b\beta_b\alpha_c\beta_c\frac{\sin q_{\alpha\beta}|R_{bc}|}{q_{\alpha\beta}|R_{bc}|} + \alpha_b\beta_b\alpha_d\beta_d\frac{\sin q_{\alpha\beta}|R_{bc} + R_{cd}|}{q_{\alpha\beta}|R_{bc} + R_{cd}|}\Bigg)\Bigg] , \qquad (46)$$

where $n(q_{\alpha\beta}) \rightarrow n(q_{\alpha\beta}) + 1$ for emission and $q_{\alpha\beta} = \Delta_{\alpha\beta}/\hbar s$.

We consider now the terms $(\alpha_a\beta_a)^2 + (\alpha_b\beta_b)^2$ and $(\alpha_a\beta_a + \alpha_b\beta_b)^2$ in Eq. (46). If the transition involves a movement of charge from a to b, then $\alpha_a = 1$, $\alpha_b = \delta^\alpha_{ab}$ and $\beta_a = \delta^\beta_{ba}$, $\beta_b = 1$. Here δ^α_{ab} is as Eq. (35) where $\alpha = (ij)$. Thus,

$$(\alpha_a\beta_a)^2(\alpha_b\beta_b)^2 = (1\cdot\delta^\alpha_{ba})^2 + (\delta^\alpha_{ab}\cdot 1)^2$$
$$= \delta^{\beta\,2}_{ba} + \delta^{\alpha\,2}_{ab} . \qquad (47a)$$

$$(\alpha_a\beta_a + \alpha_b\beta_b)^2 = (1\cdot\delta^\beta_{ba} + \delta^\alpha_{ab}\cdot 1)^2 = (\delta^\beta_{ba})^2 + (\delta^a_{ab})^2$$
$$+ 2\cdot\delta^\alpha_{ab}\delta^\beta_{ba} . \qquad (47b)$$

If there is only motion from a to b, then $\delta^\alpha_{ab} = -\delta^\beta_{ba}$ and (47b) is equal to zero.

If the transition involves movement of charge from c to d with no major movement of charge from a to b, then $\alpha_a = 1$, $\beta_a = 1$, $\alpha_b = \delta^\alpha_{ab}$, and $\beta_b = \delta^\beta_{ab}$. Then,

$$(\alpha_a\beta_a)^2 + (\alpha_b\beta_b)^2 = 1 + (\delta^\alpha_{ab}\delta^\beta_{ab})^2 \approx 1 ,$$
$$(\alpha_a\beta_a + \alpha_b\beta_b)^2 = (1 + \delta^\alpha_{ab}\delta_{ab})^2 \approx 1 . \qquad (48)$$

Similar arguments hold for $(\alpha_c\beta_c)^2 + (\alpha_d\beta_d)^2$ and $(\alpha_c\beta_c + \alpha_d\beta_d)^2$. Thus, for a one-electron transition $a \rightarrow b$, the first and third terms of Eq. (46) reduce to MA's form. For $c \rightarrow d$, the second and fourth terms reduce to MA's form. The third, fourth, and fifth terms of Eq. (46) will be neglected here for reasons given by MA. In addition, we neglect terms $O(\delta^4)$ for the one-electron transitions. The energy difference between the different states $\Delta_{\alpha\beta}$ is given by

$$\Delta_{\alpha\beta} = \mathcal{E}_\beta - \mathcal{E}_\alpha , \qquad (49)$$

$$\mathcal{E}_\beta = \mathcal{E}_{(jl)} = \mathcal{E}_j + \mathcal{E}_l + e_{jl} , \qquad (50)$$

$$\mathcal{E}_\alpha = \mathcal{E}_{(ik)} = \mathcal{E}_i + \mathcal{E}_k + e_{ik} , \qquad (51)$$

$$\Delta_{\alpha\beta} = \Delta_{(ik),(jl)} = \Delta_{ij} + \Delta_{kl} - e_{ik} + e_{jl} , \qquad (52)$$

$$\Delta_{ij} = \mathcal{E}_j - \mathcal{E}_i . \qquad (53)$$

The first two terms in Eq. (52) are due to all fixed charges plus all electrons other than the two treated, and the last two are the electron-electron interaction of the two charges treated. The fact that Δ_{ij} and e_{ik} are of the same order opens the possibility that $\Delta_{\alpha\beta}$ may be made smaller by the correlated movement of more than one electron.

In this context let us confine ourselves to a single type of transition, i.e., the transitions that involve movement of charge from sites a to b. In the two-electron four-site system there are four states of the system of the form of Eq. (41) of interest to us.

We treat the state ac as the ground state. This simply corresponds to labeling the sites so that ac is the lowest-lying state in energy. We assume that the transition of charge between a and b is necessary for transport. We treat the problem in such a way that all excitations of interest require the absorption of a phonon, i.e., they are all exci-

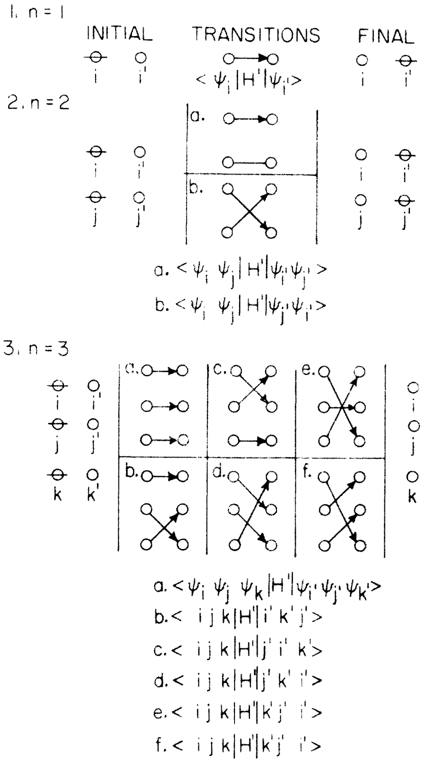

FIG. 4. Illustration of the various direct and exchange transitions, for some n-electron $2n$-site configurations.

tations up in energy. Hence, for any four-site two-electron system we will label the sites so that (ac) is the ground state and the charge on a moves to b to make a step in the percolation path.[16] The remaining site is labeled d. Thus, we are interested in the four transitions

$$(ac) \rightarrow (bc), \tag{54}$$

$$(ad) \rightarrow (bd), \tag{55}$$

$$(ac) \rightarrow (bd), \tag{56}$$

$$(ad) \rightarrow (bc). \tag{57}$$

The transition $(ac) \rightarrow (bc)$ corresponds to the one-electron transition as discussed by MA. We define for our purposes a one-electron transition to be an excitation[17] from the ground state of the two-electron system, i.e., $(ac) \rightarrow (bc)$. By contrast, $(ad) \rightarrow (bd)$, the movement of a single charge from an excited state, is defined here as an adiabatic transition.

For the moment we will consider the transitions of the system in terms of an energy-level scheme, only, and disregard matrix elements. This will give us some idea how the electron-electron interaction can alter the one-electron picture. The transitions considered are seen in Fig. 7.

The figure enumerates all the possible energy diagrams of the four-center configurations, consistent with the annotation of the ground state by ac; and the conservation of one electron on each of the pairs ab and cd. For each of the six possibilities, the current-carrying transitions most likely to contribute to the conductivity are indicated. Transitions from ac to bc (annotated MA) are the one-electron transitions, those from ac to bd (annotated 2) are the two-electron transitions, and those from ad to bd (annotated a) are the adiabatic transitions. In studying the figure one may be misled by the relatively small number of diagrams in which the two-electron transitions may be important. It must be born in mind, that many possible "auxiliary" pairs may exist around a given primary pair ab. It is enough that one of them be in a configuration in which a two-electron transition is favored to make the two-electron transition important.

The figure also clarifies somewhat the importance of the adiabatic transitions. Since their matrix element is the same as for the MA transition, they will be important irrespective of the temperature, whenever the compensation is high enough to make the presence of at least one auxiliary of the type (a) or (b) around most "main" pairs very probable.

It will be noted that the two-electron transitions in Fig. 7 always appear with an additional transition. This is because the smaller matrix element for the two-electron transition may make the other transition more important, even if it may involve a larger energy.

However, as T goes to zero, the matrix elements become unimportant and all that must be asked is which energy level represents the lowest-lying excitation of the system. In this limit, we would

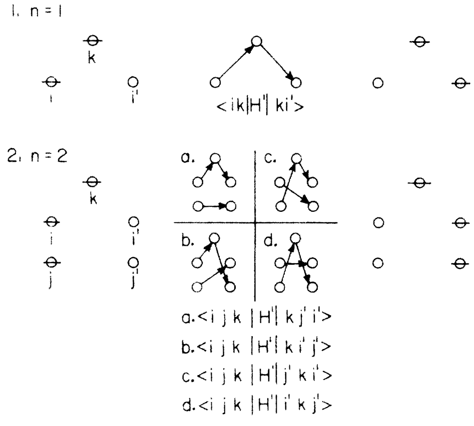

FIG. 5. Illustration of some transitions for configurations where the number of sites is not twice the number of electrons. The figure shows the case where the number of electrons is larger than one-half the number of sites, if bars represent electrons, or the case where the number of electrons is smaller than one-half the number of sites, if bars represent electron deficiencies.

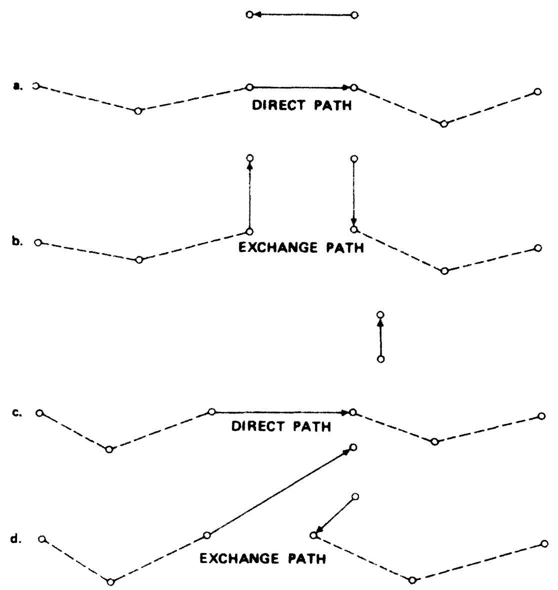

FIG. 6. Two examples of direct and exchange two-electron transitions in the percolation path.

have to treat many more than two electrons. This will become clear below when a temperature-dependent volume in space is defined wherein correlation effects are important. This volume will be seen to go to infinity when T goes to zero.

IV. MICROSCOPIC ADMITTANCES

We pick the $(ac)\rightarrow(bc)$ process as a guide. What are the energy conditions for the other processes to predominate over $(ac)\rightarrow(bc)$? To discuss this properly we put the problem into the form of effective admittances for any given transition $(ij)\rightarrow(kl)$.

For each transition $\alpha\rightarrow\beta$ involving transfer of charge from a to b, the admittance is

$$Y_{ab,\alpha\beta}=(e^2/kT)f^0_\alpha U_{\alpha\beta t}\,. \tag{58}$$

$U_{\alpha\beta t}$ is the absorption rate for the transition $\alpha\rightarrow\beta$. For several such transitions,

$$Y_{ab,\,\mathrm{total}}=\sum_{\alpha\beta} Y_{ab,\alpha\beta} \tag{59}$$

$$=\frac{e^2}{kT}\sum_{\alpha\beta}{}' f^0_\alpha U_{\alpha\beta}\,, \tag{60}$$

where the $\sum'$ always sets α to the lower energy of α and β. The sum is over not only the transitions of a given primary-auxiliary pair, but over all possible auxiliaries. The factor f^0_α is then the probability that the primary electron and the given auxiliary are in the state α.

Using the form for the transition rates of Eq. (46) and the form for the wave functions of Eq. (34) we calculate the transitions of interest, using the first term of Eq. (46). In all cases we write the absorption rate,

$$U_{(ac),(bc)}=Cn(q_{(ac),(bc)})\Delta^3_{(ac),(bc)}\left(\frac{W_{ab}}{\Delta_{ab}+e_{bc}-e_{ac}}\right)^2$$
$$=CW^2_{ab}\left|\Delta_{ac,bc}\right|e^{-\Delta_{(ac),(bc)}/kT}\,, \tag{61}$$

where we have set the second part of the first term of Eq. (46) equal to 1 and neglected all but the first term. We have set the factor $(e^{\beta\Delta}-1)^{-1}\approx e^{-\beta\Delta}$ in the phonon density $n(q)$, since in the cases we treat $\beta\Delta>1$,

$$U_{(ad),(bd)}=CW^2_{ab}\Delta_{(ad),(bd)}\exp(-\Delta_{(ad),(bd)}/kT) \tag{62}$$

and

$$\begin{aligned}U_{(ac),(bd)}={}&CW^2_{ab}W^2_{cd}\left|\Delta_{(ac),(bd)}\right|^3[(\Delta_{ab}+e_{bc}-e_{ac})^{-2}+(\Delta_{ab}+e_{bc}+e_{ad})^{-2}][(\Delta_{cd}+e_{ad}-R_{ac})^{-1}\\&+(\Delta_{cd}+e_{bd}-e_{bc})^{-1}]^2+\{[(\Delta_{cd}+e_{ad}-e_{ac})^{-2}+(\Delta_{cd}+e_{bd}-e_{bc})^{-2}]\,[(\Delta_{ab}+e_{bc}-e_{ac})^{-1}\\&+(\Delta_{ab}+e_{bc}-e_{ad})^{-1}]^2\}\exp[-\Delta_{(ac),(bd)}/kT]\,.\end{aligned} \tag{63}$$

We write

$$W_{ij}=C'(e^2/K_0a)(R_{ij}/a)\,e^{-R_{ij}/a}\,. \tag{64}$$

Miller and Abrahams give $C'=2/3n$ where n is the number of equivalent indirect minima ($n=6$ for Si, $n=4$ for Ge). This is for an exactly isotropic ground-state wave function. Inserting Eq. (64) into Eqs. (61), (62), and (63), we have

$$U_{(ac),(bc)}=CC'^2\Delta_{(ac),(bc)}\left(\frac{e^2}{K_0a}\frac{R_{ab}}{a}\right)^2\exp(-\alpha R_{ab}-\beta\Delta_{(ac),(bc)})\,, \tag{65}$$

$$U_{(ad),(bd)}=CC'^2\Delta_{(ad),(bd)}\left(\frac{e^2}{K_0a}\frac{R_{ab}}{a}\right)^2\exp(-\alpha R_{ab}-\beta\Delta_{(ad),(bd)})\,, \tag{66}$$

$$U_{(ac),(bd)}=CC'^2\left(\frac{e^2}{K_0a}\right)^4\left(\frac{R_{ab}}{a}\right)^2\left(\frac{R_{cd}}{a}\right)^2\exp(-\alpha R_{ab}-\alpha R_{cd}-\beta\Delta_{(ac),(bd)})$$

$$\times|\Delta_{(ac),(bd)}|^3[(\Delta_{ab}+e_{bc}-e_{ac})^{-2}+(\Delta_{ab}+e_{bd}-e_{bc})^{-2}][(\Delta_{cd}+e_{ad}-e_{ac})^{-1}+(\Delta_{cd}+e_{bd}-e_{bc})^{-1}]^2$$
$$+[(\Delta_{cd}+e_{ad}-e_{ac})^{-2}+(\Delta_{cd}+e_{bd}-e_{bc})^{-2}][(\Delta_{ab}+e_{bc}-e_{ac})^{-1}+(\Delta_{ab}+e_{bd}-e_{bc})^{-1}]^2\,. \tag{67}$$

We assume a canonical ensemble for the form of the f^0_α [Eq. (58)] for a single isolated elemental unit of four sites occupied by two electrons. If we then write the form for the admittances of Eqs. (54), (56), and (57) using only the factors of Eqs. (64)–(66) involving energy (i.e., neglecting the R-dependent terms), we have for the prescription of Eq. (58)

$$Y_{(ac),(bc)}=CC'^2|\Delta_{(ac),(bc)}|(e^2/K_0a)^2e^{-\beta\Delta(ac),(bd)}f^0_{(ac)}\,, \tag{68}$$

$$Y_{(ad),(bd)}=CC'^2|\Delta_{(ad),(bd)}|(e^2/K_0a)^2e^{-\beta\Delta(ad),(bd)}f^0_{(ad)} \tag{69}$$

for $\mathcal{E}_{(ad)}<\mathcal{E}_{(bd)}$,

$$Y_{(ad),(bd)}=CC'^2|\Delta_{(ad),(bd)}|(e^2/K_0a)^2e^{-\beta|\Delta(ad),(bd)|}f^0_{(bd)} \tag{70}$$

for $\mathcal{E}_{(ad)}>\mathcal{E}_{(bd)}$,

$$Y_{(ac),(bd)}=CC'^2|\Delta_{(ac),(bd)}|^3(e^2/K_0a)^4\,e^{\beta|\Delta(ac),(bd)|}f^0_{(ac)}$$
$$\times[(\Delta_{ab}+e_{bc}-e_{ac})^{-2}+(\Delta_{ab}+e_{bd}-e_{ad})^{-2}][(\Delta_{cd}+e_{ad}-e_{ac})^{-1}+(\Delta_{cd}+e_{bd}-e_{bc})^{-1}]^2$$
$$\times[(\Delta_{cd}+e_{ad}-e_{ac})^2+(\Delta_{cd}+e_{bd}-e_{bc})^2][(\Delta_{ab}+e_{bc}-e_{ac})^{-1}+(\Delta_{ab}+e_{bd}-e_{ad})^{-1}]^2\,. \tag{71}$$

The object of this work is, of course, to determine the effects of the electron-electron interaction on the transition rates. Thus, we want to know when, in the sum of admittances in Eq. (59), the admittances of the form Eqs. (69)–(71) predominate over those of Eq. (68). For a canonical ensemble,

$$f^0_\alpha/f^0_\beta=e^{\beta\Delta_{\alpha\beta}}\,. \tag{72}$$

The condition for the above to hold is

$$\frac{Y_{(ad),(bd)}}{Y_{(ac),(bc)}}>1 \tag{73a}$$

and

$$\frac{Y_{(ac),(bd)}}{Y_{(ac),(bc)}}>1 \tag{73b}$$

We have, with Eq. (68),

$$\frac{Y_{(ad),(bd)}}{Y_{(ac),(bc)}}=\frac{\Delta_{(ad),(bd)}}{\Delta_{(ac),(bc)}}\exp[-\beta(\Delta_{cd}-\Delta_{ab}+e_{ad}-e_{bc})] \tag{74}$$

for $\mathcal{E}_{(ad)}>\mathcal{E}_{(bd)}$,

$$\frac{Y_{(ad),(bd)}}{Y_{(ac),(bc)}}=\frac{\Delta_{(ad),(bd)}}{\Delta_{(ac),(bc)}}\exp[-\beta(\Delta_{cd}-\Delta_{ab}+e_{ad}-e_{bc})] \tag{75}$$

for $\mathcal{E}_{(ad)}>\mathcal{E}_{(bd)}$,

$$\frac{Y_{(ac),(bd)}}{Y_{(ac),(bc)}}=C'^2(e^2/K_0a)^2\,\frac{|\Delta_{ac,bd}|^3}{\Delta_{ac,bc}}\exp[-\beta(\Delta_{cd}+e_{bd}-e_{bc})]$$
$$\times[(\Delta_{ab}+e_{bc}-e_{ac})^{-2}+(\Delta_{ab}+e_{bd}-e_{ad})^{-2}][(\Delta_{cd}+e_{ad}-e_{ac})^{-1}+(\Delta_{cd}+e_{bd}-e_{bc})^{-1}]^2$$
$$+[(\Delta_{cd}+e_{ad}-e_{ac})^{-2}+(\Delta_{cd}+e_{bd}-e_{bc})^{-2}][(\Delta_{ab}+e_{bc}-e_{ac})^{-1}+(\Delta_{ab}+e_{bd}-e_{ad})^{-1}]^2\,. \tag{76}$$

If we consider the exponents only, we have from Eq. (74),

$$\Delta_{cd}-\Delta_{ab}+e_{ab}-e_{bc}<0\,,\quad \mathcal{E}_{(ad)}<\mathcal{E}_{(bd)}\;; \tag{77}$$

from Eq. (75),

$$\Delta_{cd}-\Delta_{ab}+e_{ad}-e_{bc}<0\,,\quad \mathcal{E}_{(ad)}>\mathcal{E}_{(bd)}\,; \tag{78}$$

and from Eq. (76)

$$\Delta_{cd}+e_{bd}-e_{bc}<0 \tag{79}$$

for Eq. (73) to hold.

In the adiabatic case [Eqs. (74) and (75)], the preexponential term is not of great importance since it is of the order of 1, when all energy terms are equal to within less than an order of magnitude. In the two-electron case [Eq. (76)], however, we have a preexponential term on the order of

$$C'^2(e^2/K_0a)^2\Delta^{-2}\,. \tag{80}$$

This is a number >1, Δ being of the order of $e^2/n'K_0r_s$, where $10>n'>1$. Thus, the preexponential goes like $C'^2(n'r_s/a)^2$, which in all cases we discuss >1 or even ≫ 1. Thus, the energy condition for the two-electron transition to predominate

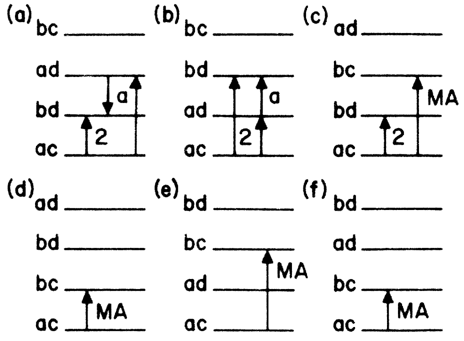

FIG. 7. Six possible energy schemes of the two-electron four-site problem, with *ac* the ground state. Indicated are the excitations from *a* to *b* which are likely to contribute to the conductivity. MA is the one-electron transition, 2 is the two-electron transition, and *a* is the "adiabatic" transition. As explained in the text, *a* is a two-step process.

is somewhat softened. Equation (79) becomes

$$\beta(\Delta_{cd}+e_{bd}-e_{bc})-2\ln(C'n'r_s/a)<0. \tag{81}$$

At sufficiently low temperature the last term can be disregarded, which gives us Eq. (79) again.

From all of the conditions of Eqs. (77)–(79), it is plain that neither of the adiabatic transitions, as far as the energy considerations go, dominates over the two-electron transition. This proves to be an important result at very low temperatures, when the R-dependent terms we neglected here are of relatively minor significance.

Including the R dependence in the above condition changes only Eqs. (79) and (81). This is due to the fact that the same overlap term in all of the first three rates of Eqs. (65) and (66) determines the movement of the conducting charge. Equation (81) now becomes

$$\beta(\Delta_{cd}+e_{bd}-e_{bc})-2\ln(R_{cd}/a)$$
$$+2R_{cd}/a-2\ln(C'n'r_s/a)<0. \tag{82}$$

The second and fourth terms of Eq. (82) both soften the condition for onset of the two-electron transition. Thus, for the condition of Eq. (73) to hold

$$\beta e_{bc}>\beta e_{bd}+\beta\Delta_{cd}+\alpha R_{cd}$$
$$-4\ln r_s/a-2\ln C'n', \tag{83}$$

where we have replaced R_{cd} by the average separation r_s in the second term of Eq. (82). The important factor is the Coulomb interaction between the two electrons while they reside on the *bc* pair. If this is large enough, then a two-electron transition has the possibility of lowering the energy of the excitation by reducing the large intersite Coulomb energy. We rewrite Eq. (83) and define G:

$$G\equiv\beta(e_{bc}-e_{bd})-\alpha R_{cd}$$
$$>\beta\Delta_{cd}-4\ln r_s/a-2\ln C'n'\equiv M. \tag{84}$$

Inserting the expressions for e_{bc}, e_{bd}, and R_{cd},

$$G=\beta\left(\frac{e^2}{K_0 r_{bc}}-\frac{e^2}{K_0 r_{bd}}\right)-\alpha\left|\vec{r}_{bd}-\vec{r}_{bc}\right|. \tag{85}$$

We also define the "gain" Γ as $\Gamma\equiv G-M$.

It can be seen that the two-electron transition will predominate over the adiabatic transition only when $e_{bd}<e_{bc}$, and even then only under certain conditions.

The condition for the predominance of the adiabatic transition over the one-electron transition is strictly one of energetics [Eqs. (74) and (75)]. The absence of an extra term in the matrix element for the adiabatic transition causes configurations which have a predominant adiabatic transition (relative to the one-electron transition) at one density to have the same predominant transition at another density. This shows qualitatively why the adiabatic transition can lower $\mathcal{E}_3$ at low densities. The predominance of the adiabatic transition will prove to be a function of compensation. In the following we will compare only the two-electron and one-electron transitions. The adiabatic transition will be the subject of a later study.

V. DETERMINATION OF MACROSCOPIC PROPERTIES

This section deals with the counting of configurations where two-electron transitions occur. For a given primary pair, *ab*, we find the probability that there is an auxiliary pair *cd* with properties [Eq. (93)] that allow the two-electron transition to have the predominant rate. The counting procedure must count all configurations once and only once. For a given temperature, density, and compensation the procedure first assumes that there is an *ab* pair that is singly occupied. We then find the probability that there is an occupied site *c* with a given value of r_{bc}. Then, given this site *c* and some gain Γ, we find the probability that there is an unoccupied site *d* which lies at a point such that the two-electron transition has the given gain Γ over the one-electron transition; the two basic ground rules are (i) $r_{bd}>r_{bc}$ and (ii) (*ac*) is the ground state of the two-electron system. This can be seen to exhaust all configurations that need to be counted.

The counting procedure looks for configurations like *abcd* of Fig. 8(a). It does not count *abc'd'* of Fig. 8(b). If *abc'd'* is considered in terms of holes rather than electrons then *abc'd'* can be seen to be exactly like *abcd*. Thus, we include a factor of 2 in counting *cd* pairs in order to account for equivalent *c'd'* pairs that exist. This procedure must be modified somewhat when $K\neq 0.5$.

Figure 8(c) shows a configuration where (*bd*) rather than (*ac*) is the ground state. Once again,

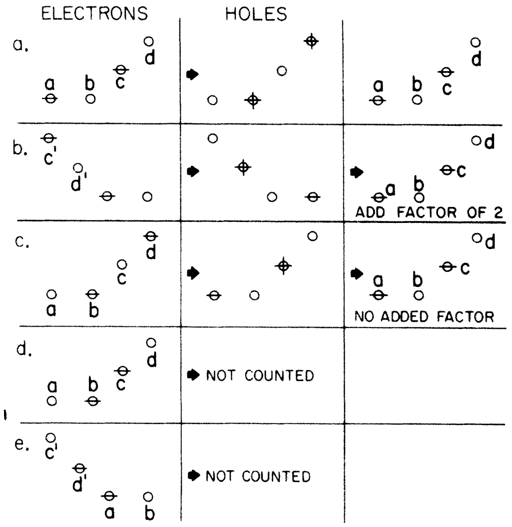

FIG. 8. Aid to text for the enumeration of configurations.

considering this configuration in terms of holes rather than electrons makes it identical to *abcd* and thus it is accounted for by the above counting procedure. In Fig. 8(d) a state where (*bc*) is the ground state is shown. Such a configuration will not have a contributing two-electron transition and is neglected, as is also the case of (*ad*) of Fig. 8(e). Configurations like Figs. 8(d) and 8(e) are counted later as one-electron transitions. Thus, all possible contributing configurations are accounted for by the counting procedure by reducing them all to the form of *abcd* given in the ground rules.

In calculating the gain due to a given auxiliary hop, we must evaluate Eq. (85). The relative contribution of the two-electron transition to the total admittance is

$$Y_{2\text{-el}}/Y_{\text{total}} = e^{\Gamma}/(1+e^{\Gamma}) \,, \tag{86}$$

when only one- and two-electron processes are considered. If $G < M$, the two-electron process does not contribute appreciably to Y_{total} and we shall neglect it. If $G > M$, we approximate $Y_{\text{total}} = Y_{2\text{-el}}$.

There will be the following two conditions on the auxiliary pairs: (i) The *first* condition is imposed by the assumption that the state where *a* and *c* are occupied is the ground state of the particular two-electron system considered. This implies $\mathcal{E}_{(bc)} > \mathcal{E}_{(ac)}$ and $\mathcal{E}_{(bd)} > \mathcal{E}_{(ac)}$. Thus,

$$\Delta_{ab} + e_{bc} - e_{ac} > 0 \tag{87}$$

and

$$\Delta_{ab} + \Delta_{cd} + e_{bd} - e_{ac} > 0 \,. \tag{88}$$

(ii) The *second* condition on the auxiliary pair imposes a minimun separation between sites to be considered. If sites are closer than this distance, a "molecule ion trap" described by Tanaka and Fan[18] is formed. The trap sites do not contribute to conduction. Thus, we will not consider intersite separations between *b* and *c* less than 175–200 Å in Ge where the impurity Bohr radius is approximately 60 Å.

Before considering the implications of the above two conditions on the gain probability function, we will find the conditions for which a configuration has a positive gain. It is clear from Eq. (85) that $G > 0$ only when $r_{bd} > r_{bc}$. The gain is maximized for a given r_{bd} and r_{bc} when sites *c*, *b*, and *d* are colinear because this configuration minimizes the final term in Eq. (85). For a given r_{bc} and r_{bd} the gain falls off as we depart from this configuration.

The simplest way to study the effect of the variation of any one parameter is to study the colinear case. Later this will be generalized to account for all other configurations. We write

$$G = g(r_{bc}) - g(r_{bd}) \,, \quad r_{bd} > r_{bc} \tag{89}$$

where

$$g(r) = (\beta e^2/K_0 r) + \alpha r \,. \tag{90}$$

Figure 9 shows a plot of $g(r)$ vs r. Two obser-

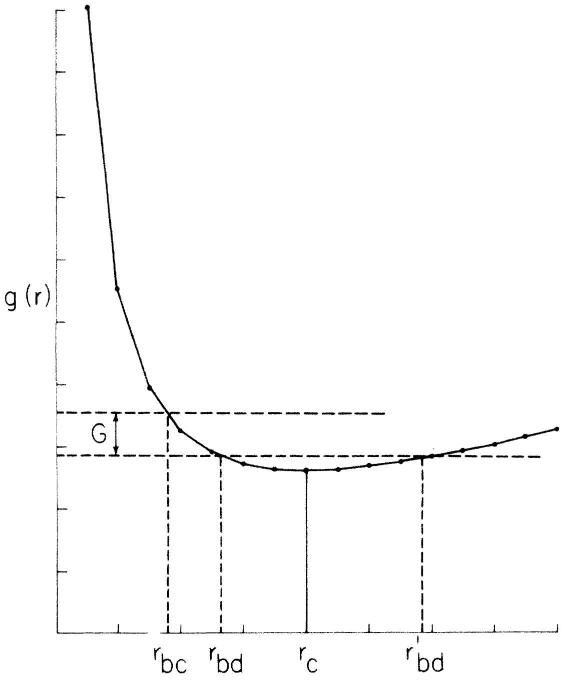

FIG. 9. Graphical representation of Eqs. (89) and (90). Two-electron transitions can be important only if $G = g(r_{bc}) - g(r_{bd})$ is a positive quantity. r_c is the critical value for r_{bc}. If $r_{bc} > r_c$, then no site *d* can exist which would make a two-electron transition probable.

vations are noteworthy:

(i) $G < 0$ unless $r_{bc} < R_c$ where

$$R_c = (\beta e^2/\alpha K_0)^{1/2} . \tag{91}$$

This is a very important point in this discussion. The reduced Coulomb interaction e_{bc}/kT must be large enough to compensate for the loss ($e^{-\alpha R_{cd}}$) in the matrix element before the two-electron transition rate can become comparable with the one-electron rate. If the radius R_c defines a correlation sphere, then only auxiliary pairs that have at least their initial site inside the correlation sphere can contribute to correlated transitions. This is a necessary condition for the two-electron transition to occur. Setting $R_c = r_s$ defines the critical density

$$N_c = (3/4\pi)(1/R_c^3) \tag{92}$$

for the onset of many electron transitions. As a means of orientation, in Ge where $a = 60$ Å and $K_0 = 16$, we find that $R_c = 400$ Å for $T = 2$ K.

(ii) There are two values of r_{bd} for given values of G, r_{bc}, T, K_0, and α [noted r_{bd} and $r_{bd'}$ in Fig. 9]. In three dimensions the surfaces of constant G in r_{bd} space are closed surfaces. In particular, r_{bd} and r'_{bd}, are given by solutions of Eq. (85) for r_{bd}:

$$r_{bd} = \frac{1}{2}\left(r_{bc} - \frac{G}{\alpha} + \frac{R_c^2}{r_{bd}}\right) \pm \frac{1}{2}\left[\left(r_{bc} - \frac{G}{\alpha} + \frac{R_c^2}{r_{bd}}\right)^2 - 4R_c^2\right]^{1/2} . \tag{93}$$

We evaluated Eq. (85) numerically in order to determine the topology of the surfaces of constant G. The results show that for a given value of G, r_{bc}, and R_c the surfaces of constant G in r_{bd} space look like hemispheres to a good approximation for the cases that are of importance here. The radius R of the hemisphere is equal to the difference between the two solutions.

$$R = r_{bd} - r'_{bd} , \tag{94}$$

$$R = [(r_{bc} - G/\alpha + R_c^2/r_{bc})^2 - 4R_c^2]^{1/2} \quad \text{if } G > 0 , \tag{95}$$

$$R = R_c^2/r_{bc} - G/\alpha + (\rho^2 - 4R_c^2)^{1/2} + (\rho'^2 + 4r_c^2)^{1/2} \quad \text{if } G < 0 , \tag{96}$$

where

$$\rho' = r_{bc} + G/\alpha - R_c^2/r_{bc} \tag{97a}$$

$$\rho = r_{bc} - G/\alpha + R_c^2/r_{bc} . \tag{97b}$$

The area of the surface of constant G in r_{bd} space is then

$$A_d(r_{bc}, G, R_c) = 3\pi R^2 . \tag{98}$$

The hemisphere approximation in nearly all cases underestimates the true area and volume. The volume contained in the hemisphere is

$$V(r_{bc}, G, R_c) = \tfrac{2}{3}\pi R^3 . \tag{99}$$

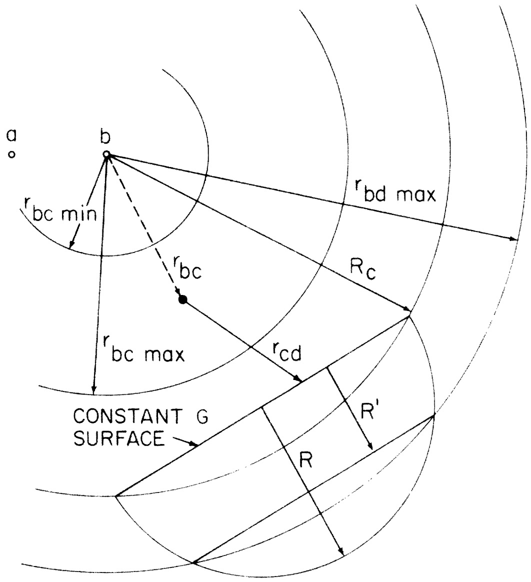

FIG. 10. Illustration of the spatial relationship of the various parameters discussed in the text. For a given value of r_{bc}, α, G and T, the site d lies on the surface of the hemisphere of radius R.

The condition (i) discussed above and expressed in Eqs. (87) and (88) truncates the surface. Figure 10 illustrates the spatial relationship of the parameters discussed above. The sphere of radius $r_{bd_{\max}}$ determined from Eq. (88) truncates the surface of constant G.

We define a function $P_n(G)$ such that $P_n(G)\,dG$ is the differential probability that the nth nearest occupied neighbor of the site b is site c of an auxiliary pair with gain $\Gamma = G - M$. The nth-nearest site c will interact with the first site available in the volume [Eq. (99)]. The volumes of Eq. (99) connected to different sites c will rarely overlap. The probability that the nth-nearest occupied site c lies at r_{bc} is given by the Poisson distribution

$$d\eta_n(r_{bc}) = [\gamma(r_{bc})]^{n-1} e^{-\gamma(r_{bc})}\, d\gamma(r_{bc})/(n-1)! , \tag{100}$$

where

$$\gamma(r_{bc}) = \tfrac{4}{3}\pi(r_{bc}^3 - r_{bc,\min}^3) N_i \tag{101}$$

where for compensation K, $N_i = KN_s$ and $N_f = (1-K)N_s$ are the density of full initial and empty final auxiliary sites, respectively. To find the site d we look for the first available site in moving away from R_c. Thus, we use

$$\frac{dn_i^f(R)}{dG} = N_f\, 3\pi R^2 \frac{dR}{dG} \exp(-\tfrac{1}{3} N_f\, 2\pi R^3) . \tag{102}$$

Implying that for site c at some r_{bc}, d will be the site with the largest possible G. We then have

$$dP_n(G) = [(n-1)!]^{-1} N_i\, 4\pi r_{bc}^2\, dr_{bc} [\tfrac{4}{3}\pi N_i (r_{bc}^3 - r_{bc,\min}^3)]^{n-1}$$

$$\times \exp[-N_i \tfrac{4}{3}\pi(r_{bc}^3 - r_{bc,\,\mathrm{min}}^3)]N_f$$

$$\times 3\pi R^2 \frac{dR}{dG} \exp[-N_f 2\pi R^3/3], \qquad (103)$$

where, by Eq. (95),

$$\frac{dR}{dG} = -\frac{1}{R}\frac{1}{\alpha}\left(r_{bc} - \frac{G}{\alpha} + \frac{R_c^2}{r_{bc}}\right), \quad G > 0. \qquad (104)$$

Suitable modifications are made for $G < 0$.

Thus,

$$P_n(G, R_c, N_i, N_f) = \int_{r_{bc}} dP_n(G, r_{bc}, R_c, N_i, N_f), \qquad (105)$$

where the integration is over the volume available to site c. The lower limit of r_{bc} is determined from the molecular ion consideration. The upper limit is such that the final site d, with $G = 0$, lies at R_c. Thus,

$$r_{bc,\,\max} = \frac{1}{2}\left(\frac{G}{\alpha} + 2R_c\right) - \left[\left(\frac{G}{\alpha} + 2R_c\right)^2 - 4R_c^2\right]^{1/2}. \qquad (106)$$

If $G < 0$, then $r_{bc,\,\max}$ is set equal to R_c.

We now look at Eq. (87). The left-hand side of the inequality corresponds to the MA value of Δ_{ab}, since it is the energy difference between sites a and b when the auxiliary electron is frozen on site c. This quantity is related to the value of E_{ab} for the impedance Z_{ab} in the following way.[13] When site a and b are on the same side of the Fermi energy, the energy E_{ab} can be considered to consist of two parts, an activation energy generally occurring in the probability for the single occupation of a pair of sites and the energy difference between these sites.[13] The former energy clearly vanishes when the compensation is one-half. Thus, for the case considered here, the left-hand side of Eq. (87) can be identified with E_{ab} of the one-electron theory.

We are now interested in the modification of the one-electron impedances by the correlated motion. The magnitude of an impedance in the percolation theory depends primarily on the two random variables E_{ab}/kT, and $2r_{ab}/a$. The effect of the correlated motion is to reduce the value of E_{ab}, so the above discussion implies that we need not consider impedances with an unreduced E_{ab} larger than E_m, the largest value of E_{ab} in the critical paths of the one-electron theory. Generally, E_m is a temperature-dependent quantity. However, a temperature-independent value of E_m is implied when in the uncorrelated limit the conductivity shows a definite activation energy. This appears to be so in the impurity conduction case under discussion. Thus, we can assume a definite value of E_m, which depends only on the material and not on temperature. Another argument for this assumption is as follows. Since E_m related to the one-electron transport, we can refer to the density of states in Fig. 3. The fact that the density curve for the conducting electrons peaks away from E_F, suggests that E_m is close to the distance between E_F and the peak and is insensitive to temperature.

We can now further simplify the set of impedances which we must discuss because it is primarily the largest impedance of the critical paths which determines the conductivity of the material. Therefore we need not consider in this semiquantitative paper impedances with the value of E_{ab} smaller than E_m, and we can focus our attention only on the impedances with $E_{ab} \approx E_m \equiv \mathcal{E}$.

It remains to determine the value of $\mathcal{E}$. In principle, this can be theoretically obtained from the one-electron percolation theory if the density of states is known. The problem of the density of states is quite complicated, and we prefer to take a more heuristic approach here. The Coulombic nature of the problem dictates that $\mathcal{E}$ has the form

$$\mathcal{E} \approx \theta e^2/K_0 r_D, \qquad (107)$$

where for reasons explained earlier θ is a number much closer to unity than that obtained by MA. We chose to use it as a slightly variable parameter and wish to ascertain whether we can adequately reproduce the experimental results with a reasonable value of θ.

To summarize the above discussion, we have made the following three points: (i) The energy E_{ab} which occurs in the expression for the one electron impedance Z_{ab} can be identified with the left-hand side of Eq. (87). (ii) Only those impedances in the one-electron network which have $E_{ab} \approx \mathcal{E}$ need to be considered. (iii) The value of $\mathcal{E}$ is given by Eq. (107), with θ not much smaller than unity. We thus change the inequality of Eq. (87) to

$$\Delta ab + e_{bc} - e_{ac} = \mathcal{E}. \qquad (108)$$

The integral [Eq. (105)] was carried out using the technique of Gaussian quadrature. A temperature range from 1 to 5 K was covered. An average effective interimpurity separation, r_s, of from 200 to 600 Å was used. We used a dielectric constant of $K = 16$ and an isotropic Bohr orbital radius of 60 Å. In this calculation we used $N_i = N_f$ which corresponds to a compensation of 0.5.

Some typical results of the calculation are shown for the first auxiliary in Figs. 11 and 12. We show $P(\Gamma)$ where Δ_{cd} has been set $= 0$. Figure 12 shows the first auxiliary probability for $T = 1.8$ K, $r_s = [(3/4\pi)N_s]^{1/3}$, as the parameter. Figure 11 shows the first auxiliary probability for $r_s = 360$ Å with T as a parameter. In this particular series we set $\mathcal{E} = 0.8e^2/K_0 r_s$.

From the percolation problem we have the general result[13]

$$Q(Z_c) = Q(\xi_c) = \int_0^{\xi_c} p(\xi)\, d\xi = \gamma, \qquad (109)$$

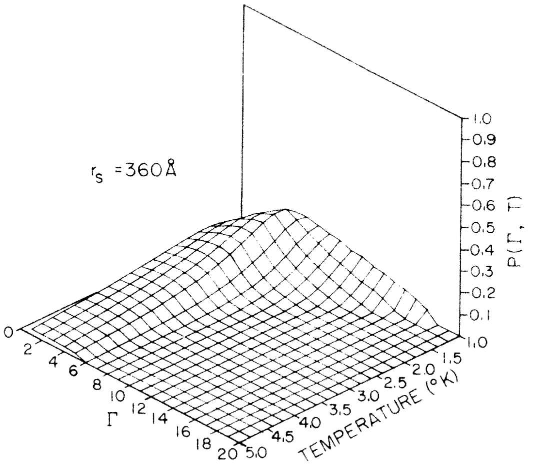

FIG. 11. Computational results of the probability gain function $P(G)$ of Eq. (105), as a function of temperature, for a fixed value of the average intersite separation r_s = 360 Å.

where

$$p(\xi) = \tfrac{4}{3}\pi N(1/\alpha^3)(\xi - \mathcal{E}/kT)^2 \tag{110}$$

is the average number of impedances less than Z_c when moving away from any site in a system. γ is some number between $\frac{1}{2}$ and 1.

In the multielectron case, where we solve for a new critical impedance $Z_c' \propto e^{\xi_c'}$,

$$Q_i(\xi_c') = \int_0^\infty d\Gamma \int_0^{\xi_c'} p_i(\xi', \Gamma)\, d\xi' = \gamma , \tag{111}$$

where Q_i is the counterpart of Eq. (109) for the first i auxiliaries and

$$P_i(\xi', \Gamma) = P(\xi + \Gamma) P_i(\Gamma) , \tag{112}$$

where $P_i(\Gamma)$ is the probability that i auxiliaries modify the impedance by the gain Γ:

$$P_i(\Gamma) = S\delta(\Gamma) + P_i(\Gamma) , \tag{113}$$

where $P_i(\Gamma)$ is given by Eq. (105) and

$$S = 1 - \int_0^\infty P_i(\Gamma)\, d\Gamma \tag{114}$$

is the probability that $\Gamma < 0$.

Thus,

$$Q_i(\xi_c') = \int S\delta(\Gamma)\, d\Gamma \int p(\xi' + \Gamma) + \int P_i(\Gamma)\, d\Gamma \int p(\xi' + \Gamma)\, d\xi' , \tag{115}$$

which becomes

$$SQ(\xi_c') + \int_0^\infty P_i(\Gamma) p(\xi_c' + \Gamma)\, d\Gamma = \gamma . \tag{116}$$

Equation (116) was solved by setting $\xi_c' = \xi_c - X(T, r_s)$ and using the one-electron result of Eqs. (109) and (110) and the form for $P_i(\Gamma, T, r_s)$ computed above to solve for $X(T, r_s)$.

In the case where there are two auxiliaries involved, we convolute the probabilities for the first and second auxiliaries, thus

$$P_{1+2}(\Gamma, T, r_s) = P_1(\Gamma, T, r_s)\Big(1 - \int_0^\infty P_2(\Gamma', T, r_s)\, d\Gamma'\Big) + \int_{\Gamma_1 < \Gamma}^\infty P_1(\Gamma, T, r_s) P_2(\Gamma - \Gamma_1, T, r_s)\, d\Gamma_1 . \tag{117}$$

$P_{1+2}(\Gamma, T, r_s)$ is then the normalized probability that there are two auxiliaries with total gain Γ at temperature T and average majority separation r_s. It should be understood here that the $P_n(\Gamma, T, r_s)$ we use here, is a function of many variables that must be used as discussed in Sec. IV. Among the most important of these are $\mathcal{E}$, Δ_{cd}, N_i, N_f. All four of these quantities are poorly known. All of them require a detailed knowledge of the density of states in order to be properly determined. At present, the density of states when ion pairing is taken into account has not been treated at any but very small[13] and very large compensation[12]; we consider it outside the scope of this study.

VI. RESULTS AND SUMMARY

Perhaps our most important result is the criterion for the onset of the two-electron hopping, contained in Eq. (91) and explained below that equation. The critical density obtained from Eq. (91) above which many-electron transitions should be included in the hopping conduction, is plotted in Fig. 13. To use this figure, one matches the appropriate localized radius a and temperature T and reads off the critical density on the ordinate. The example of impurity conduction in germanium, with $a = 60$ Å, and at $T = 2$ K, is indicated in the figure. The critical density is seen to be ~ 3×10^{15} cm^{-3}. The figure is plotted for a dielectric constant of 16. For other dielectric constants K_0 the critical

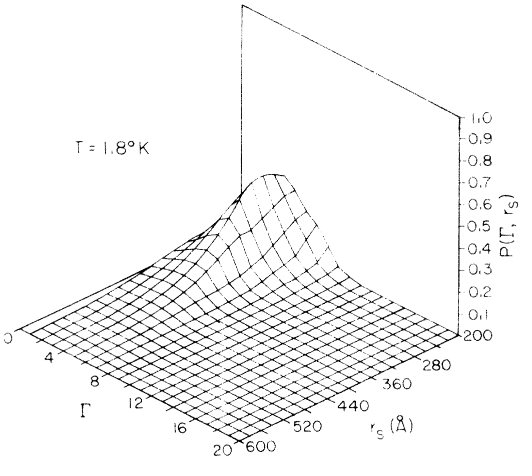

FIG. 12. Computational results of the probability gain function as a function of the average intersite separation, for the fixed value of temperature T = 1.8 K.

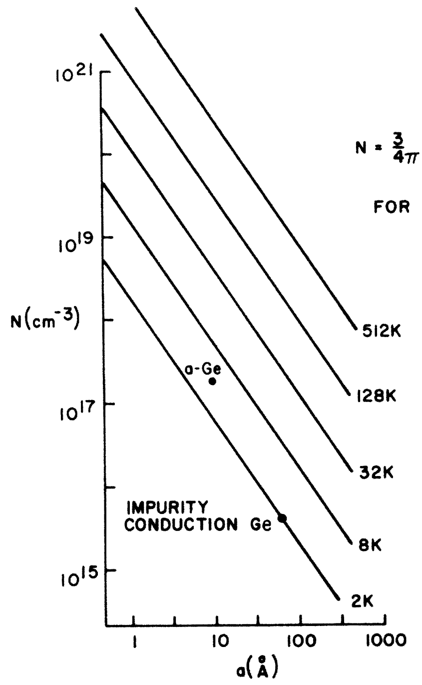

FIG. 13. Criterion for the onset of many-electron transitions in the dc conductivity. Two of the variables in the graph determine the critical value of the third one. For the example of impurity conduction in germanium, with $a = 60$ Å, and at $T = 2$ K, many-electron excitations will be important for concentrations above $N = 3\times10^{15}$ cm^{-3}. For a-Ge, with $a = 10$ Å, and $N \approx 10^{17}$ cm^{-3} (Refs. 19 and 20) these effects appear below 2 K. Further details will be found in the text.

density should be multiplied by $(\frac{1}{16}K_0)^{3/2}$. In addition, the figure corresponds to compensation 0.5. For other compensations the critical concentration is larger.

It is of some interest to apply the criterion to conduction in amorphous semiconductors. We can ask ourselves what the temperature is below which many-electron hopping must be important. For most amorphous semiconductors we lack the necessary knowledge of N and of a. However, for amorphous germanium these quantities are known[19,20] to be $a \approx 10$ Å, and $N \approx 2\times10^{17}$. Figure 13 then implies that many-electron excitations are not important for the conductivity down to 2 K.

A comparison between our many-electron theory and a one-electron theory is shown in Figs. 14–17. The solid lines in Fig. 14 are plots of

$$\rho \propto (R_s/a)^2 \exp[2.65(R_s/a) + \mathcal{E}/kT]; \qquad \mathcal{E} = 0.6e^2/K_0 r_s \tag{118}$$

which is the result of a one-electron percolation theory for a conductivity which exhibits an activation energy. The dashed lines are plots of the FC results. The two sets of curves are not necessarily plotted with magnitude on the same scale. They are made to coincide, rather arbitrarily, at $r_s = 190$ Å, at high temperatures. The figure thus does not test the absolute value of the predicted resistivity, but rather tests the functional dependence of the resistivity on temperature and concentration of dopant.

Even though the activation energy chosen in Eqs. (118) is rather low in view of the earlier discussion on the subject, the agreement between the experimental results and Eqs. (118) is seen to be rather poor. For example, the variation of the resistivity for material with $N = 3.5\times10^{16}$ cm^{-3} ($r_s = 190$ Å) in the temperature range of Fig. 14 is off by seven orders of magnitude and for material with $N = 2.6\times10^{15}$ cm^{-3} ($r_s = 448$ Å), it is off by 2.4 orders of magnitude. Another conspicuous feature of the theoretical curves in Fig. 14 is the crossing of the curves, which is clearly absent from the observed data.

Figures 15 and 16 are our results for the conductivity when two-electron transitions (i.e., one auxiliary pair per configuration) are included. Figure 15 uses $\mathcal{E} = 0.6e^2/K_0r_s$ to enable comparison with the one-electron theory, and Fig. 16 uses $\mathcal{E} = 0.7e^2/K_0r_s$ to show the effect of $\mathcal{E}$ on the results. The trend of the theoretical curves towards the experimental curves is obvious when comparing

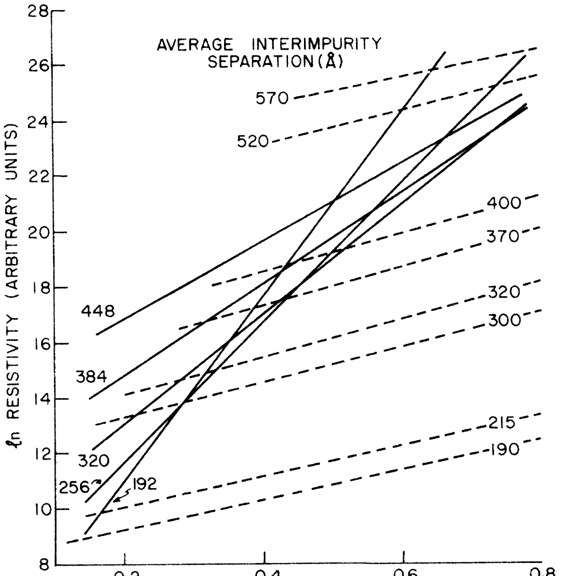

FIG. 14. Results of a dc impurity conduction theory for $K = 0.5$ when correlation motion is neglected. As is explained in detail in the text there is a slight arbitrariness in the slope of the solid theoretical curves. The dashed lines reproduce the results of Fritzsche and Cuevas (Ref. 1).

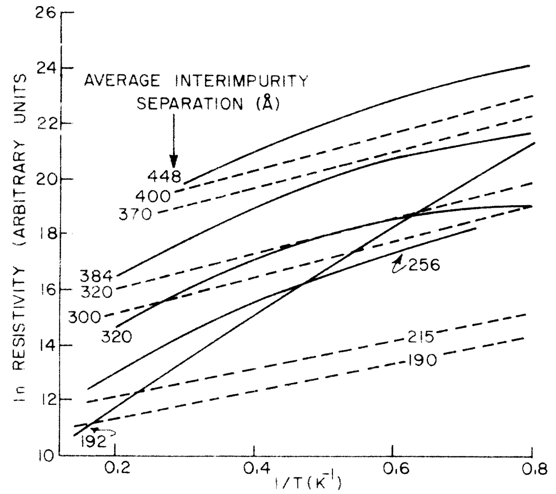

FIG. 15. Our results (solid lines) including two-electron excitations, i.e., one auxiliary hop per configuration. The value of the parameter θ of Eq. (107) is 0.6. The dashed lines are experimental results of Ref. 1.

Fig. 15 with Fig. 14. The discrepancy of approximately seven orders of magnitude at the high concentration is reduced to 2.5 orders of magnitude and a discrepancy of 2.5 orders of magnitude at the low concentration and is reduced to ≈ 0.4 orders of magnitude. Furthermore, most of the theoretical curves cease to cross each other.

Comparison of Figs. 15 and 16 shows that the general improvement of the two-electron theory, as compared to the one-electron theory, is a much more pronounced effect than that caused by an uncertainty in the choice of $\mathcal{E}$.

In Fig. 17 we plot our results when two auxiliaries per configuration are admitted. The plot uses $\mathcal{E} = 0.7e^2/K_0 r_s$. A continued improvement of the predicted behavior is apparent. Because of the approximations made in the computations of the resistivity with two auxiliaries, we do not believe that these calculations are reliable beyond showing that a trend in the right direction exists.

It may be noted that the features of the ρ-vs-T^{-1} curves in Figs. 15–17 resemble qualitatively the $T^{-1/4}$ dependence characteristic of the single-electron variable-range hopping theory of Mott.[21] It is of interest to comment on the relationship between the variable-range and the many-electron hopping processes.

The $T^{-1/4}$ process can take place when the Coulomb interaction between the carriers is less than the relevant random fluctuations of the potential. For $T^{-1/4}$ the density of states has to be roughly constant within a certain energy range around the Fermi energy through which the electrons must propagate. Therefore, this energy range must be larger than the gap in Fig. 3. As discussed in the Introduction, this gap is created by the Coulomb interaction between the carriers.

As pointed out by Mott, in the variable range hopping, there is a competition between the overlap (an exponential function of the distance) and an energy term (an exponential function of the energy). At lower temperatuers the carriers tend to hop longer distances with less activation. When the activation becomes comparable to, or less than the gap, the energy factor can no longer be reduced by enlarging the hops. However, as discussed the energy factor can now be reduced by two- or-more electron hops. (It will be remembered that the gap in Fig. 3 relates to one-electron excitations.)

There is a certain qualitative similarity between the variable range hopping and the two-electron hopping. In both cases the optimum process is determined by a trade off between the energy term and the overlap. In both processes the overlap term must increase to decrease the energy term. In the variable range hopping it increases exponentially with the hop distance, and in the many-electron hopping it increases as the exponential of the sum of the hop distances of the involved electrons.

In conclusion, we believe that we have demonstrated the importance of the correlated motion of electrons in general and of many-electron excitations, in particular, in hopping conduction under conditions often prevailing. Specifically, we find many-electron excitations to be important in much of the data on impurity conduction reported in the literature. On the other hand, it does not appear

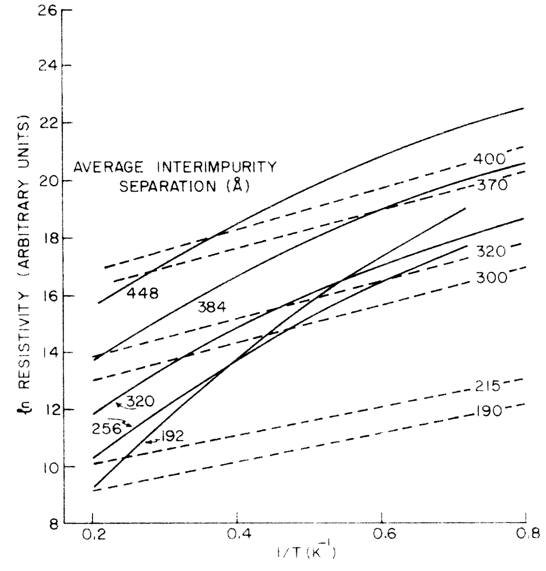

FIG. 16. Figure caption is the same as Fig. 15, but with $\theta = 0.7$.

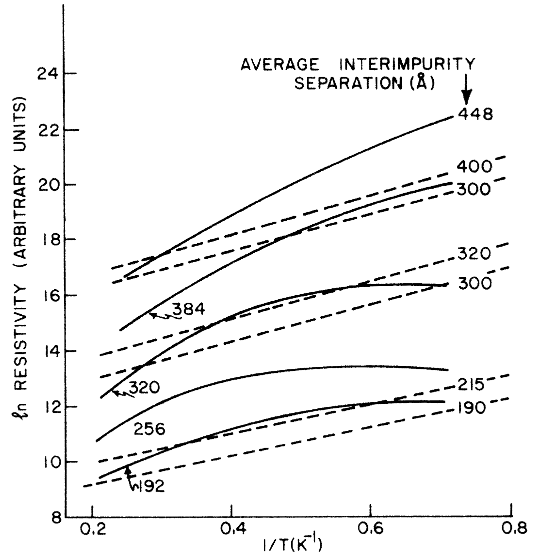

FIG. 17. Figure caption is the same as Fig. 15, but approximately including three-electron excitations, i.e., two auxiliary pairs per configuration.

to be important for the reported measurements on hopping conduction in amorphous germanium.[22]

The following are, we feel, some experimental demonstrations of the importance of many-electron excitations in impurity conduction.

(a) The first is the general agreement of the measurements of FC with this theory.

(b) The second is the work of Gordy[23] who measured impurity conduction in germanium below 1 K. He observed a curvature similar to that we would expect from this effect in that temperature range.

(c) The third is the work of Allen and Adkins[10] who measured impurity conduction down to very low temperatures. They find that in order to interpret their results, they need dielectric constants which are much larger than those of pure germanium. This may be interpreted as the dielectric response of the "auxiliary" carriers to a conducting electron, in accordance with the treatments in Refs. 3 and 2.

(d) The fourth is the work of Emelyanenko *et al.*,[24] where similar measurements on GaAs were reported. Although the authors interpret their results in terms of $T^{-1/4}$, we believe that the alternative interpretation in terms of the theory presented here is likelier. This is particularly true for the low-compensation sample ($K = 0.024$), where $T^{-1/4}$ would not be predicted even with a one-electron theory,[2] because the potential fluctuations are of a longer range than the hopping distance.

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[*] Work supported in part by ONR Grant No. N00014-69-A-0200-5005.

[†] Present Address: Sandia Laboratory, Albuquerque, N. M.

[1] H. Fritzsche and M. Cuevas, Phys. Rev. 119, 1238 (1960).

[2] M. Pollak, Discuss. Faraday Soc. 50, 13 (1970).

[3] M. Pollak and M. L. Knotek, J. Non-Cryst. Solids 4, 465 (1969).

[4] M. Pollak, Proc. Roy. Soc. Lond. 325, 383 (1971).

[5] An extended abstract of part of this work appears in M. L. Knotek and M. Pollak, J. Non-Cryst. Solids 8-10, 505 (1972).

[6] A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960).

[7] P. W. Anderson, Comments Solid State Phys. 2, 193 (1970).

[8] P. W. Anderson, Phys. Rev. 109, 1492 (1958).

[9] G. Srinivasan, Phys. Rev. B 4, 2581 (1971).

[10] F. R. Allen and C. J. Adkins, Phil. Mag. 26, 1027 (1972).

[11] V. Ambegoakar, B. I. Halperin, and J. S. Langer, Phys. Rev. B 4, 2612 (1971).

[12] B. I. Shklovskii and A. L. Efros, Zl. Eksp. Teor. Fiz. 60, 867 (1971) [Sov. Phys.-JETP 33, 468 (1971)].

[13] M. Pollak, J. Non-Cryst Solids 11, 1 (1972).

[14] R. Jones and W. Schaich, J. Phys. C 5, 43 (1972).

[15] C. A. Coulson and J. Fischer, Philos. Mag. 40, 386 (1949).

[16] We do not mean to violate the indistinguishability of particles, but simply imply that

$$|\langle\phi_i(1)\phi_j(2)|H|\phi_{i'}(1)\phi_{j'}(2)\rangle| > |\langle\phi_i(1)\phi_j(2)|H|\phi_{j'}(1)\phi_{i'}(2)\rangle|$$

for most configurations. That this is so is evident from the fact that the one-electron percolation path goes through a and b, not through a and d.

[17] Although we seem to ignore here the transition rates of the phonon emitting process, this will be automatically included when calculating impedances.

[18] S. Tanaka and H. Y. Fan, Phys. Rev. 132, 1516 (1963).

[19] M. L. Knotek, M. Pollak, T. M. Donovan, and H. Kurtzman, Phys. Rev. Lett. 30, 853 (1973).

[20] M. Pollak, M. L. Knotek, H. Kurtzman, and H. Glick, Phys. Rev. Lett. 30, 856 (1973).

[21] N. F. Mott, Philos. Mag. 19, 835 (1969).

[22] The fundamental reason for this appears to be that the random energy fluctuations in amorphous germanium are much larger that the Coulomb interaction between the carriers. Thus the gap created by the interaction is observable only at very low temperatures where kT is comparable with the gap. This is demonstrated by the dot in Fig. 13.

[23] L. Gordy, Bull. Am. Phys. Soc. 17, 305 (1972).

[24] O. V. Emelyanenko, D. N. Nasledov, E. I. Nikulin, and I. N. Tiruchenko, Fiz. Teckh. Poluprovodn. 6, 2283 (1972) [Sov. Phys.-Semicond. 6, 1926 (1973).]