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Concentration-fluctuation model of a doped semiconductor in the nonmetallic regime. II. Excitation spectrum

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With the use of the unrestricted Hartree-Fock scheme developed by us earlier, the excitation spectra are calculated for doped semiconductors in the nonmetallic regime. The excitation spectrum suggests the possible self-compensation effect proposed by Bhatt and Rice. The spectral density so derived explains the dependence of the photoconducting current on the impurity concentration.

I. INTRODUCTION

Substitutional shallow level impurities in semiconductors, such as phosphorous in silicon, provide a convenient system to investigate the interplay between the electron correlation and the disorder effects. When the impurity concentration (N) varies in a wide range enclosing the critical concentration for the metal-nonmetal transition (N_c), a number of interesting phenomena show up in the transport, magnetic, and thermodynamic properties of highly correlated electrons under the influence of a random potential. Any attempt to construct a unified theory for the entire range of impurity concentration so far has not been successful. However, in the low-concentration nonmetallic regime, both experimental suggestions and theoretical calculations lead to the presently accepted picture that the system consists of statistically distributed clusters of impurities of various sizes. A summary of the existing results in this area has been given in a previous paper[1] (referred to as I).

In I we have performed an improved unrestricted Hartree-Fock pseudocluster calculation with a correlated two-electron wave function for the D^- state (D^- represents a negatively charged isolated impurity) to investigate the microscopic structure of the impurity states. A *sample* of doped semiconductor in the nonmetallic regime is simulated with a computer such that the positions of the impurities $\{\vec{R}_i;\ i=1,2,\ldots,\mathcal{N}\}$ are spatially random. Clusters of impurities (defined purely as topological clusters of the *positions* $\vec{R}_i$'s) of various sizes are formed and statistically distributed throughout the entire sample. Single-particle eigenstates were then derived numerically. It is found that each state is localized on a finite cluster of impurities, and we define such states as *cluster states.* The distribution function of the cluster states (which may not be the same as the distribution function of the clusters of impurities) agrees with the recent conclusion derived from analyzing a variety of experimental data.

It is well known that in any Hartree-Fock—type calculation the total energy of the system is not a simple summation over all the single-particle energies of occupied states. One must make a correction on the double counting of the electron-electron interaction energy, which depends crucially on the wave functions. Let the single-bare-particle excitation energy be $E=E_{f\sigma}-E_{i\sigma}$, where $E_{f\sigma}$ and $E_{i\sigma}$ are, respectively, the final and initial Hartree-Fock energies. For the cluster states considered here, the correction on the electron-electron interaction energy turns out to be extremely important and so the single-quasiparticle (as well as multi-quasiparticle) excitation spectrum E^* differs substantially from the bare excitation energy spectrum E. In I we found a gap separated the occupied and the empty parts of the bare-particle density of states in the nonmetallic regime. The same gap appears in the single-bare-particle excitation spectral density $\rho(E)$. Nevertheless, it is the gap of the single-quasiparticle excitation spectral density $\rho^*(E^*)$ that determines the dynamic properties of the cluster states.

When one electron is excited from the initial single-particle Hartree-Fock state $\psi_i(\vec{r})$ in the Fermi sea to the final Hartree-Fock state $\psi_f(\vec{r})$ outside the Fermi sea, the difference $\Delta E=E^*-E$ comes from the different amounts of total electron-electron interaction energy in the final (Ψ_f) and the initial (Ψ_i) *many-electron* states. It is obvious that the electron-electron interaction energy is rather sensitive to the degrees of localization of all the single-particle Hartree-Fock states in a many-electron wave function used in the calculation. A careful analysis in the later sections leads to the fact that ΔE is negative in most cases with very few exceptions.

We consider a simple case in which $\psi_i(\vec{r})$ is a very localized cluster state (for example, a state localized on a cluster A of only one impurity) and $\psi_f(\vec{r})$ is a less-localized cluster state (for example, a state localized on a cluster B of six impurities). Assume that initially both clusters A and B are electrically neutral with $\psi_i(\vec{r})$ occupied but $\psi_f(\vec{r})$ empty. The excitation of one electron from $\psi_i(\vec{r})$ to $\psi_f(\vec{r})$ makes the cluster A positively charged and the cluster B negatively charged. Bhatt and Rice[2] suggested that after the relaxation of the entire many-electron wave function Ψ_f (mostly the relaxation of the part of wave function localized on cluster B), it is possible to have the total energy of the system in the final state lower than that in the initial state Ψ_i. Then the cluster B plays the role of an *acceptor,* and the donor (cluster A) loses its electron even without the intentional compensation with acceptors. Bhatt and Rice called this phenomenon the *self-compensation,* which may occur only at *very low impurity concentration.* In our calculation the set of basis functions is fixed and so the orbital relaxation is not taken into account. Consequently, we cannot obtain a negative E^* for self-compensation. On the other hand, if very small values of E^* emerge from our calculation, it can be interpreted as a precursor of the onset of self-compensation.

It was also found in I that the distribution probability of the cluster states varies with the impurity concentration. Since the excitation energy E^* depends on the sizes of the relevant cluster states, the peak position of $\rho^*(E^*)$ shifts when the impurity concentration is altered. Therefore, the cluster states should manifest themselves in optical measurements such as the photoconductivity.

The calculation of the excitation spectrum in doped semiconductors is certainly a very difficult task, yet it must be done in order to have a deeper understanding of this complicated correlation-disorder system. This is the purpose of the present work, in general, and, in particular, its purpose is to investigate the possible self-compensation phenomenon proposed by Bhatt and Rice,[2] as well as the concentration dependence of the photoconductivity spectra observed by Taniguchi *et al.*[3] and Taniguchi and Narita.[4]

II. EXCITATION SPECTRA

Since the present computation of the excitation spectra is based on the self-consistent unrestricted Hartree-Fock ground state obtained in I, we will first outline the calculation scheme briefly. With a computer we simulate a sample of doped semiconductor containing $\mathcal{N}$ impurities in a volume Ω. The positions of the impurities $\{\vec{R}_i;\ i=1,2,\ldots,\mathcal{N}\}$ are random. We further generate $M=\xi N$ more impurities located randomly in a volume of $\xi\Omega$ outside Ω. Then the overall impurity concentration $N=\mathcal{N}/\Omega$ is unchanged. A localized orbital $\phi_{i\sigma}(\vec{r})$ is attached to the ith impurity for $i=1,2,\ldots,\mathcal{N}$. The effect of the M surrounding impurities (impurity ions plus the electrons in localized orbitals) on the $\mathcal{N}$ impurities in Ω is approximated by an effective field. The inner $\mathcal{N}$ impurities embedded in this effective field will be solved numerically using an improved Hartree-Fock scheme with a spin-polarized potential.

A. Calculation scheme

The Hamiltonian of the $\mathcal{N}$-impurity system is

$$H=\sum_i p_i^2/2m+\sum_i [V^{\text{ion}}(\vec{r}_i)+V^{\text{eff}}(\vec{r}_i)] + \tfrac{1}{2}\sum_{i,j} V^{e-e}(\vec{r}_i-\vec{r}_j)\ , \tag{1}$$

where $V^{\text{ion}}(\vec{r})$ is the impurity-ion potential and $V^{\text{eff}}(\vec{r})$ is due to the effective field mentioned above. The Coulomb interaction between the ith and the jth electrons is $V^{e-e}(\vec{r}_i-\vec{r}_j)$. With the unrestricted Hartree-Fock approximation, one chooses a set of basis functions $\{\phi_{i\sigma}(\vec{r});\ \sigma=\uparrow,\downarrow;\ i=1,2,\ldots,\mathcal{N}\}$ and constructs the single-particle Hartree-Fock states as

$$\psi_{i\sigma}(\vec{r})=\sum_j \phi_{j\sigma}(\vec{r})B_{\sigma ji}\ . \tag{2}$$

These Hartree-Fock states must satisfy $2\mathcal{N}$ coupled equations,

$$[p^2/2m+V^{\text{ion}}(\vec{r})+V^{\text{eff}}(\vec{r})+V^{\sigma}_{Cx}(i;\vec{r})]\psi_{i\sigma}(\vec{r}) = E_{i\sigma}\psi_{i\sigma}(\vec{r}) \tag{3}$$

for $\sigma=\uparrow,\downarrow$ and $i=1,2,\ldots,\mathcal{N}$. The Coulomb exchange potential $V^{\sigma}_{Cx}(i;\vec{r})$ is nonlocal and depends on the sets $\Gamma(\uparrow)$ and $\Gamma(\downarrow)$ of single-particle states occupied by the up-spin and the down-spin electrons, respectively.

If we define the matrices $\tilde{E}_\sigma$ with the element $E_{\sigma ij}=E_{i\sigma}\delta_{ij}$ and $\tilde{B}$ with the element $B_{\sigma ji}$, then (3) can be rewritten as a matrix equation,

$$\tilde{B}^{\dagger}_{\sigma}\tilde{H}_{0\sigma}\tilde{B}_{\sigma}=\tilde{E}_{\sigma}\ , \tag{4}$$

where

$$H_{0\sigma ij}=\int \phi^{*}_{i\sigma}(\vec{r})[p^2/2m+V^{\text{ion}}(\vec{r})+V^{\text{eff}}(\vec{r})]\phi_{j\sigma}(\vec{r})d\vec{r}+\sum_{s}\sum_{l\in\Gamma(s)}[\tilde{B}^{\dagger}_{\sigma}\tilde{V}(\sigma,s;i,j)\tilde{B}_{\sigma}]_{ll}\ , \tag{5}$$

with the electron-electron interaction matrix element defined as

$$[V(\sigma,s;i,j)]_{tq}=\int\int \phi^{*}_{i\sigma}(\vec{r})\phi^{*}_{ts}(\vec{r}\,')V^{e-e}(\vec{r}\,'-\vec{r})[\phi_{qs}(\vec{r}\,')\phi_{j\sigma}(\vec{r})-\phi_{qs}(\vec{r})\phi_{j\sigma}(\vec{r}\,')\delta_{s\sigma}]d\vec{r}\,d\vec{r}\,'\ . \tag{6}$$

With a chosen set of localized orbitals $\{\phi_{i\sigma}(\vec{r});\ i=1,2,\ldots,\mathcal{N}\}$ all matrix elements can be calculated either analytically or numerically. Equation (4) is then solved by iteration to reach a self-consistent solution of the coefficients $B_{\sigma ji}$'s. At extremely low impurity concentration, each impurity can be treated as isolated. The associated localized impurity orbital in a many-valley semiconductor is very complicated owing to the anisotropic effective mass and the central-cell correction. Even assuming an isotropic effective mass and ignoring the central-cell correction in the present calculation, the computation of the matrix elements requires a great effort and the self-consistent solution needs much computer time. Such accurate calculation gives the correct characteristic features, though they can be further improved quantitatively.

The localized impurity orbital $\phi_{i\sigma}(\vec{r})$ is then approximated by a hydrogenic 1s wave function with an effective Bohr radius a_0 (which can be determined from the measured ionization energy when we compare our results with experimental data). However, this set of basis functions is inadequate to describe the structure of impurity energy spectrum. A negatively charged isolated impurity D^- has been discovered to be bound.[5] Furthermore, the photoconductivity data[3,4] strongly suggest that the stability of a negatively charged small cluster of n impurities, D_n^- increases with n, provided n is small. On the other hand, a simple wave function like $\phi_{i\uparrow}(\vec{r}_1)\phi_{i\downarrow}(\vec{r}_2)$ does not give a bound state for D^-. The variational wave function proposed by Chandrasekhar[6] for H^-,

$$\Phi_i(\vec{r}_1,\vec{r}_2)=\eta[\exp(-\alpha|\vec{r}_1-\vec{R}_i|-\beta|\vec{r}_2-\vec{R}_i|)+\exp(-\alpha|\vec{r}_2-\vec{R}_i|-\beta|\vec{r}_1-\vec{R}_i|)]\times[1-\gamma(|\vec{r}_1-\vec{r}_2|)]\,, \qquad (7)$$

with $\alpha=1.074\,78$, $\beta=0.477\,58$, and $\gamma=0.312\,14$, yields a rather accurate binding energy 0.0259 hartree for a free H^- ion as compared to the measured value 0.0275 hartree. In (7), η is the normalization constant. Consequently, we will use the Chandrasekhar wave function (7) properly scaled with the effective Bohr radius a_0 to describe the D^- state.

The unrestricted Hartree-Fock scheme (4)—(6) has to be modified in order to take into account the correct D^- feature. In the calculation of the matrix elements (5) and (6), whenever $\phi_{i\uparrow}(\vec{r}_1)\phi_{i\downarrow}(\vec{r}_2)$ appears, it is replaced by the Chandrasekhar wave function $\Phi_i(\vec{r}_1,\vec{r}_2)$. For the special case $i=j=t=q$, the single-particle-operator part in (5) should also be modified to treat the two correlated electrons on the ith impurity simultaneously. Since the potential is spin polarized, there is an exchange Coulomb gap in the energy spectrum when the concentration is low. As the concentration approaches zero, the split density of states approaches two δ spikes with energies corresponding to the ionization energies of an isolated neutral impurity D^0 and a negatively charged isolated impurity D^-, respectively. Only with such modification on the Hartree-Fock scheme the D^- is bound and the observed optical excitation from the D^- level to the semiconductor conduction band[3,4] can be explained. By the same token, the cluster states localized on a small cluster of few impurities should also be treated including the relaxation of the orbitals. However, such correlated many-particle wave functions for more than two electrons are too difficult to construct. In this paper, we do not go beyond the two-electron Chandrasekhar wave function.

B. Total energy

Since the potential (6) is nonlocal, the self-consistent potential for one many-particle state is different from that for the other many-particle state. Let us for the moment assume that there are $\mathcal{N}_\uparrow$ up-spin and $\mathcal{N}_\downarrow$ down-spin electrons, and $\mathcal{N}_\uparrow+\mathcal{N}_\downarrow=\mathcal{N}$. Then, in (5) the set $\Gamma(\sigma)$ contains $\mathcal{N}_\sigma$ occupied single-particle Hartree-Fock states, and for a given $\Gamma(\sigma)$ one obtains, from (5), $\mathcal{N}$ Hartree-Fock states for each spin. For given values of $\mathcal{N}_\uparrow$ and $\mathcal{N}_\downarrow$, if at each iteration we keep the $\mathcal{N}_\sigma$ lowest-energy σ-spin Hartree-Fock states occupied, then the self-consistent solution of (4)—(6) yields the lowest-energy many-particle state $\Psi_0(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ in the form of a Slater determinant composed of the $\mathcal{N}$ occupied Hartree-Fock states.

To avoid ambiguity, the self-consistent Hartree-Fock solutions for given values of $\mathcal{N}_\uparrow$ and $\mathcal{N}_\downarrow$ are expressed as $\psi_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ and $E_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ with $E_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)\le E_{j\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ if $i\le j$. Then, the lowest-energy state $\Psi_0(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ can be more explicitly expressed as $\Psi(\{\psi_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow);\ i=1,2,\ldots,\mathcal{N}_\sigma;\ \sigma=\uparrow,\downarrow\})$. The second lowest-energy determinental many-particle state $\Psi_1(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ must be orthogonal to $\Psi(\{\psi_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow);\ i=1,2,\ldots,\mathcal{N}_\sigma;\ \sigma=\uparrow,\downarrow\})$ and be a solution of (4)—(6) corresponding to another self-consistent potential. If again we denote the new set of self-consistent Hartree-Fock solutions as $\bar{\psi}_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ and $\bar{E}_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ with $\bar{E}_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)\le\bar{E}_{j\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ if $i\le j$, then $\Psi_1(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ can be similarly written as

$$\Psi(\{\bar{\psi}_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow);\ i=1,2,\ldots,\mathcal{N}_\sigma;\ \sigma=\uparrow,\downarrow\})\,.$$

The orthogonality condition

$$\langle\Psi(\{\psi_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow);\ i=1,2,\ldots,\mathcal{N}_\sigma;\ \sigma=\uparrow,\downarrow\})\,|\,\Psi(\{\bar{\psi}_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow);\ i=1,2,\ldots,\mathcal{N}_\sigma;\ \sigma=\uparrow,\downarrow\})\rangle=0$$

must be satisfied.

All the other higher-energy many-particle states should be derived step by step in the same way as the derivation of $\Psi_1(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$. The process should also be repeated for all possible values of $\mathcal{N}_\uparrow$ and $\mathcal{N}_\downarrow$. Certainly, it is an impossible task. The following conventional approximation has been commonly used. After having obtained the set of self-consistent single-particle Hartree-Fock states $\{\psi_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow);\ i=1,2,\ldots,\mathcal{N};\ \sigma=\uparrow,\downarrow\}$ corresponding to the lowest-energy many-particle state $\Psi_0(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$, the higher-energy states are created from $\Psi_0(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ by electron-hole—pair excitation. In general, the approximated many-particle states can be expressed as

$$\Psi(\{\psi_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow);\ i=k_1,k_2,\ldots,k_{\mathcal{N}_\sigma};\ \sigma=\uparrow,\downarrow\})\,,$$

where

$$\{\psi_{i\sigma}(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow);\ i=k_1,k_2,\ldots,k_{\mathcal{N}_\sigma};\ \sigma=\uparrow,\downarrow\}$$

is a set of $\mathcal{N}$ occupied single-particle states. The orthogonality between different many-particle states is automatically satisfied.

Within this approximation the total energy corresponding to each many-particle state can be readily calculated as

$$\epsilon_i(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)=\langle\Psi_i(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)\,|\,H\,|\,\Psi_i(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)\rangle\,, \qquad (8)$$

where $\Psi_i(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ is the shorthand notation for the ith many-particle state associated to given values of $\mathcal{N}_\uparrow$ and $\mathcal{N}_\downarrow$. By comparing the lowest energies $\epsilon_0(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ of all possible values of $\mathcal{N}_\uparrow$ and $\mathcal{N}_\downarrow$, the ground-state energy is then finally determined. We should mention that in calculating $\epsilon_i(\mathcal{N}_\uparrow,\mathcal{N}_\downarrow)$ the Chandrasekhar wave function must be used whenever the D^- configuration appears.

C. Single-particle excitations

The self-consistent computation outlined above is very time consuming. In this paper we only consider the case $\mathcal{N}_\uparrow=\mathcal{N}_\downarrow=\mathcal{N}/2$, and the calculation takes about 35 h CPU (central processing unit) time with a Digital Electronic Computer DEC-20 computer. Including all possible values of $\mathcal{N}_\uparrow$ and $\mathcal{N}_\downarrow$ increases the computing time by a factor of 20, and cannot be realized at the moment. Nevertheless, in doped semiconductors the magnetic coupling (exchange coupling) between electrons in different s orbitals is extremely weak, and can be very easily offset by the disorder effect. This is the generally accepted reason for the absence of magnetic ordering in doped semiconductors. In this respect, it is reasonable to consider only the nonmagnetic case $\mathcal{N}_\uparrow=\mathcal{N}_\downarrow$ since the ground state is nonmagnetic. However, this does not mean that the excited states associated to $\mathcal{N}_\uparrow\neq\mathcal{N}_\downarrow$ are not important. We will return to this point in Sec. IV in connection to the specific heat.

In our calculation with $\mathcal{N}_\uparrow=\mathcal{N}_\downarrow=\mathcal{N}/2$, we use a dimensionless impurity concentration $P=32\pi\mathcal{N}a_0^3/\Omega$, where a_0 is the effective Bohr radius of the impurity atom. The energy is in atomic units with the zero reference energy set at the bottom of the conduction band. Hence, the energy of an isolated neutral impurity D^0 is -0.5 effective hartree, and that of an isolated negatively charged impurity D^- is -0.0275 effective hartree. For given impurity concentration, 12 samples are investigated and the results are configurationally averaged. For most doped semiconductors, the critical concentration for metal-nonmetal transition P_c is around $P_c\simeq0.8$.

For $\mathcal{N}_\uparrow=\mathcal{N}_\downarrow=\mathcal{N}/2$, we simplify the notations and define Γ_0 as the set of occupied single-particle Hartree-Fock states $\{\psi_{j\sigma}(\mathcal{N}/2,\mathcal{N}/2);\ j,\sigma\in\Gamma_0\}$ corresponding to the many-particle ground state $\Psi(\Gamma_0)$. When one electron is excited from $\psi_{j\sigma}(\mathcal{N}/2,\mathcal{N}/2)$ to $\psi_{k\sigma}(\mathcal{N}/2,\mathcal{N}/2)$ with $j,\sigma\in\Gamma_0$ but $k,\sigma\notin\Gamma_0$, the new set of occupied Hartree-Fock states is represented by $\Gamma_{\sigma;j,k}$ and the corresponding many-electron excited state by $\Psi(\Gamma_{\sigma;j,k})$. Then the single-bare-particle excitation energy is

$$E_{\sigma;j,k}=E_{k\sigma}(\mathcal{N}/2,\mathcal{N}/2)-E_{j\sigma}(\mathcal{N}/2,\mathcal{N}/2)\ , \tag{9}$$

while the single-quasiparticle—excitation energy is

$$E^*_{\sigma;j,k}=\epsilon_{\sigma;j,k}(\mathcal{N}/2,\mathcal{N}/2)-\epsilon_0(\mathcal{N}/2,\mathcal{N}/2) \tag{10}$$

where

$$\epsilon_{\sigma;j,k}(\mathcal{N}/2,\mathcal{N}/2)=\langle\Psi(\Gamma_{\sigma;j,k})\,|\,H\,|\,\Psi(\Gamma_{\sigma;j,k})\rangle\ , \tag{11}$$

and

$$\epsilon_0(\mathcal{N}/2,\mathcal{N}/2)=\langle\Psi(\Gamma_0)\,|\,H\,|\,\Psi(\Gamma_0)\rangle\ . \tag{12}$$

The difference of energy

$$\delta\epsilon_0=\sum_{i,\sigma\in\Gamma_0}E_{i\sigma}(\mathcal{N}/2,\mathcal{N}/2)-\epsilon_0(\mathcal{N}/2,\mathcal{N}/2)\ ,$$

as well as

$$\delta\epsilon_{\sigma;j,k}=\sum_{i,\sigma\in\Gamma_{\sigma;j,k}}E_{i\sigma}(\mathcal{N}/2,\mathcal{N}/2)-\epsilon_{\sigma;j,k}(\mathcal{N}/2,\mathcal{N}/2)\ ,$$

is the well-known correction on the double counting of the electron-electron interaction energy. It also contains a correction on the self-consistent potential for the excited states. We have found in I that due to the electron correlation effect all the Hartree-Fock (cluster) states in $\Psi(\Gamma_0)$ avoid one another in order to reach the lowest total energy. When one electron is excited from $\psi_{j\sigma}(\mathcal{N}/2,\mathcal{N}/2)$ with $j,\sigma\in\Gamma_0$ to $\psi_{k\sigma}(\mathcal{N}/2,\mathcal{N}/2)$ with $k,\sigma\notin\Gamma_0$, $\psi_{k\sigma}(\mathcal{N}/2,\mathcal{N}/2)$ is forced to be near to some other Hartree-Fock (cluster) states in Γ_0. The so induced electron-electron interaction energy is the origin of the Coulomb gap in the density of states (Fig. 2 of I). Therefore, $\delta\epsilon_0$ is generally less than $\delta\epsilon_{\sigma;j,k}$, and

$$\begin{aligned}E^*_{\sigma;j,k}&=\left[\sum_{i,\sigma\in\Gamma_{\sigma;j,k}}-\sum_{i,\sigma\in\Gamma_0}\right]E_{i\sigma}(\mathcal{N}/2,\mathcal{N}/2)\\&\quad-(\delta\epsilon_{\sigma;j,k}-\delta\epsilon_0)\\&=[E_{k\sigma}(\mathcal{N}/2,\mathcal{N}/2)-E_{j\sigma}(\mathcal{N}/2,\mathcal{N}/2)]\\&\quad-(\delta\epsilon_{\sigma;j,k}-\delta\epsilon_0)\\&=E_{\sigma;j,k}-(\delta\epsilon_{\sigma;j,k}-\delta\epsilon_0)\end{aligned} \tag{13}$$

is generally less than $E_{\sigma;j,k}$.

For both spins the quasiparticle excitation energies $E^*_{\sigma;j,k}$ versus the bare excitation energies $E_{\sigma;j,k}$ are shown in Figs. 1(a)—1(f) with every dot representing one excitation. Almost all of the 9600 values of $E^*_{\sigma;j,k}$ for each concentration are substantially less than the values of the corresponding $E_{\sigma;j,k}$. It has been shown in I that in the nonmetallic regime the single-particle Hartree-Fock states are cluster states. When one electron-hole pair is created from the many-particle ground state, one electron is transferred from a neutral cluster state localized on m impurities (represented by D_m) to another cluster state localized on n impurities (represented by D_n). Therefore, the final many-particle state contains one D_m^+ cluster state and one D_n^- cluster state. Bhatt and Rice[2] have conjectured that for very low concentration, if $m=1$ and $n>4$, then the excitation energy E^* can become negative and so self-compensation occurs. In our calculation we do find many extremely small excitation energies for the concentration $P\leq0.393$. As we have mentioned earlier, we cannot obtain negative excitation energy because the orbital relaxation has not been taken into account in our calculation. We should also point out that one condition for having the self-compensation phenomenon is that both D_m and D_n should be rather isolated. This requires a sample much larger than the one we have used in our calculation, and perhaps too large to be handled by the commonly available computer. From our calculation we can only draw the conclusion that self-compensation is very likely to occur in a large sample.

III. OPTICAL PROPERTIES

In the low-concentration regime there are two channels contributing to the photoconductivity. By using Fig. 2 of

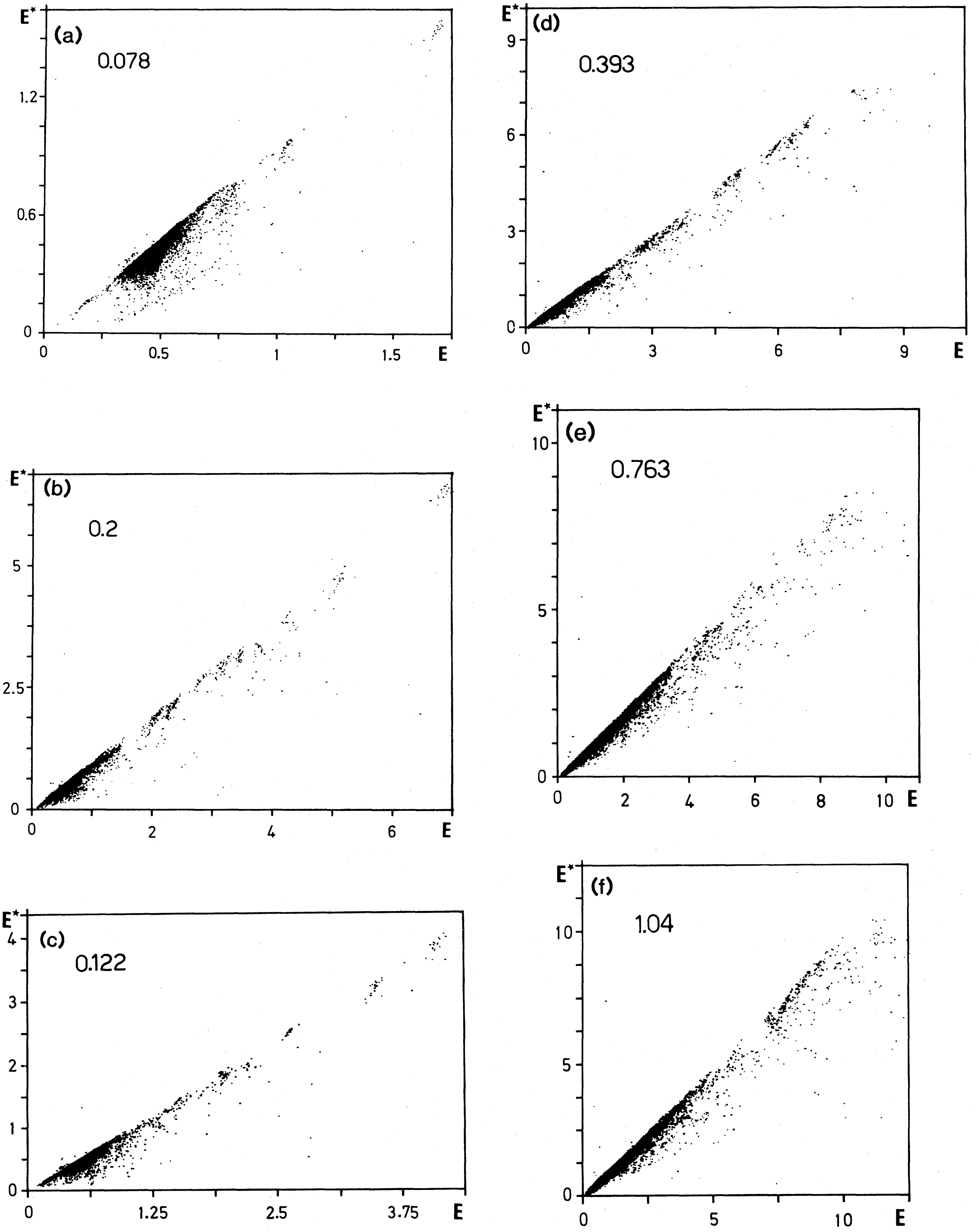

FIG. 1. (a) Single-quasiparticle excitation energy vs the single-bare-particle excitation energy for impurity concentration 0.078. (b) Same as (a) for impurity concentration 0.122. (c) Same as (a) for impurity concentration 0.2. (d) Same as (a) for impurity concentration 0.393. (e) Same as (a) for impurity concentration 0.763. (f) Same as (a) for impurity concentration 1.04.

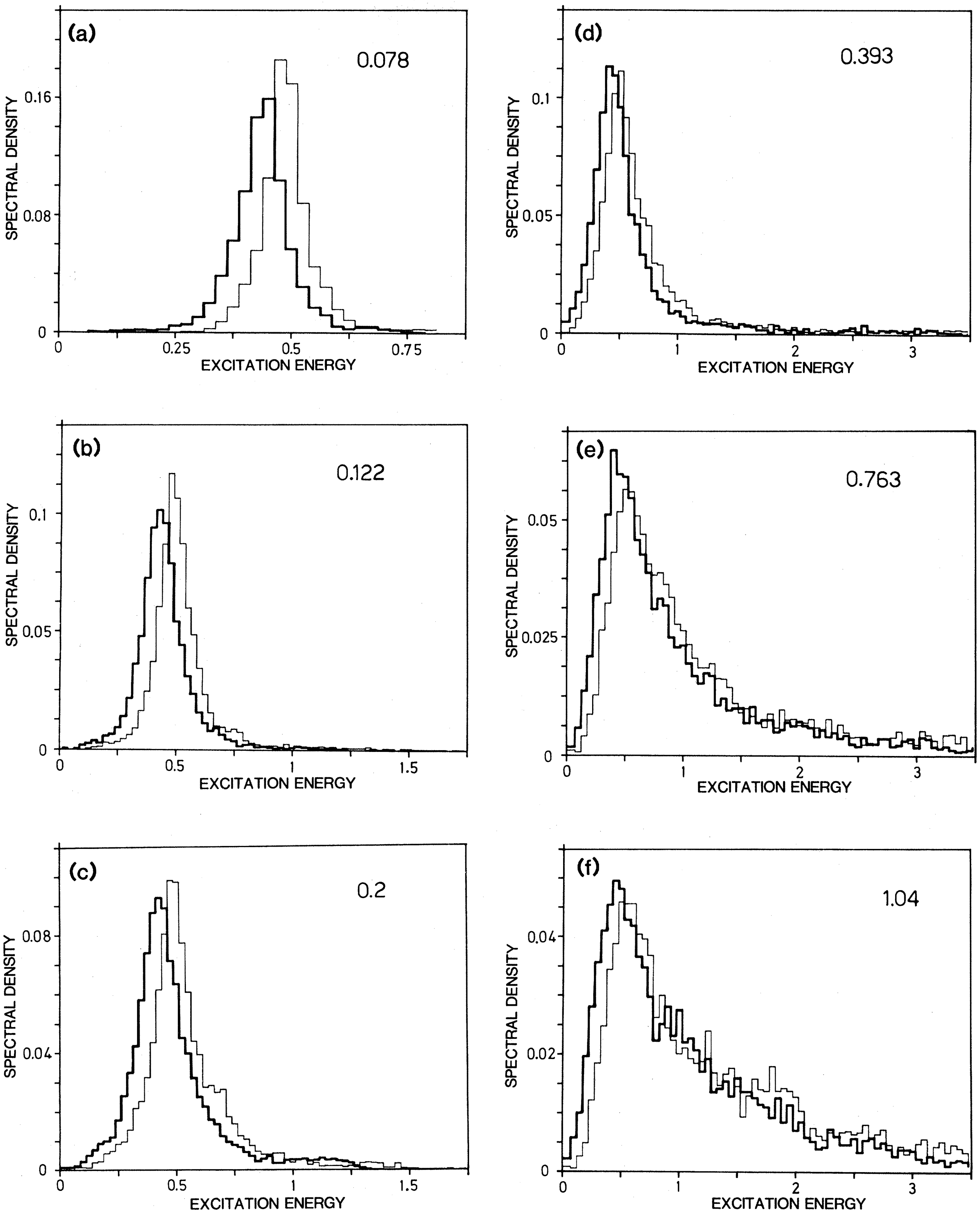

FIG. 2. Spectral density for the single-quasiparticle excitation (thick-lined histogram) and for the single-bare-particle excitation (thin-lined histogram). Impurity concentration is 0.078. (b) Same as (a) for impurity concentration 0.122. (c) Same as (a) for impurity concentration 0.2. (d) Same as (a) for impurity concentration 0.393. (e) Same as (a) for impurity concentration 0.763. (f) Same as (a) for impurity concentration 1.04.

I as the reference, electrons may be optically excited to the host conduction band from either the lower or the upper split impurity subband. Recent interest is focused on the transition from the upper split band because in this case the photoconductive response is very sensitive to the impurity concentration.

To compare our calculation with the experiments, we show the excitation spectral densities $\rho(E)$ and $\rho^*(E^*)$ in Figs. 2(a)–2(f) for the single-bare-particle and the single-quasiparticle excitations, respectively [the subscript $(\sigma;j,k)$ of the energies are omitted for convenience]. The impurity concentrations are marked at the upper right corners. In each figure the thick-lined histogram is for the quasiparticle excitation spectral density $\rho^*(E^*)$ and the thin-lined histogram is for the bare-particle excitation spectral density $\rho(E)$. Since the excitations are from the lower to the upper split impurity subbands, at the limit of impurity concentration approaching zero, both $\rho(E)$ and $\rho^*(E^*)$ reduce to a δ spike situated at the excitation energy 0.4725 (the difference between the ionization energies of D^0 and D^-).

As the concentration increases, we see in these figures that the peak position of the bare-particle excitation spectral density $\rho(E)$ is almost stationary, while that of the quasiparticle excitation spectral density $\rho^*(E^*)$ is shifted toward the lower energy by an amount $\simeq 0.05$. It is found in Fig. 10 of I that the probability of having larger cluster states increases with the impurity concentration. Consequently, this shift of $\rho^*(E^*)$ is due to the increasing number of larger cluster states (D_n^- states) the binding energies of which are larger than that of the D^- state.

We recall that the bottom of the host conduction band is situated at the excitation energy equal to 0.5. Therefore, with increasing concentration to $P=0.078$, the photoconductivity spectrum corresponding to the transition from the upper split impurity band to the host conduction band should shift to higher energies by an amount roughly equal to 10% of the D^0 ionization energy. Furthermore, since there is a finite threshold in the spectral density at very low concentrations, the corresponding photoconductivity spectrum shows a peak. We notice that the finite threshold of $\rho^*(E^*)$ disappears when the concentration increases to $P\simeq 0.2$. At this concentration, the corresponding photoconductivity spectrum should monotonically increase toward higher energies without a peak. If we keep in mind that for both Sb-doped Ge and P-doped Si the critical concentration is around $P_c \simeq 0.8$, then our calculation agrees well with the measured data of Taniguchi *et al.*[3] for Ge:Sb and of Taniguchi and Narita[4] for Si:P. These authors have proposed the formation of D_n^- as the origin of the spectral shift. It is worthwhile to point out that with increasing concentration, the split impurity subbands begin to overlap and so drives the spectral density to become asymmetric.

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