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Impurity cluster states in disordered two-dimensional systems: A self-consistent Hartree-Fock-Roothaan model

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We have investigated the microscopic structure of the impurity states in a two-dimensional disordered system by using a self-consistent Hartree-Fock-Roothaan formalism with spin-polarized potentials which has previously been used to study the three-dimensional systems. It is shown that all the matrix elements are very sensitive to a change in the dimensionality of the system. For impurity concentrations in a large range of interest, the electronic states are localized and the system is dominated by isolated donor impurities or pairs of donor impurities. The results of other models are discussed.

The purpose of this work is to investigate the impurity states in a two-dimensional (2D) disordered system in the light of our previous work,[1] hereafter denoted by I, which has used a self-consistent Hartree-Fock-Roothaan (HFR) formalism with spin-polarized potentials to 3D disordered systems.

We basically assume the bound state as a hydrogenic wave function in two dimensions, as in the work of Stern and Howard[2] (SH), who carried out a calculation for an unscreened impurity located at a thickness inversion layer. On the basis of their work, da Cunha Lima and Ferreira da Silva[3] have calculated the 2D impurity bands assuming a Hubbard-type Hamiltonian in their calculation. They have used a proper 2D hopping matrix

$$V_{ij}=\langle\phi(\mathbf{r}-\mathbf{R}_i)\,|\,V(\mathbf{r}-\mathbf{R}_i)\,|\,\phi(\mathbf{r}-\mathbf{R}_j)\rangle$$

associated with the site i and j, 2D wave function $\phi(\mathbf{r}-\mathbf{R}_i)^2$ and the impurity ion potential $V(\mathbf{r}-\mathbf{R}_i)\equiv V^{\text{ion}}(\mathbf{r}-\mathbf{R}_i)=1/(\mathbf{r}-\mathbf{R}_i)$. Such an ion potential will also appear in our scheme. Recently da Cunha Lima *et al.*,[4] with a one-band formalism have calculated the 2D density of impurity states, based also on the SH work, taking into account the overlap effects, screening length, and the distance from the impurities to the inversion layer. It is worthwhile also to mention that Debney,[5] Kikuchi,[6] and Puri and Odagaki[7] have also calculated the 2D one-band density of states but with a V_{ij} in three dimensions.

In what follows, we will carry out the 2D calculation of the impurity states by a numerical cluster formalism instead. For a given impurity concentration N, we generate M random impurity sites $\{\mathbf{R}_i;i=1,2,\ldots,M\}$ on a plane surface of side L as the location of M hydrogenic atoms, with $N=M/L^2$. Since at high concentrations the number of impurities near the cluster boundary is not small, we surround these M impurities with additional M_s impurities similarly generated, in such a way as to keep N unchanged. These M_s impurities reduce the surface effects and provide a mean field.[1,8] With each impurity is associated a donor wave function $\phi_i(\mathbf{r})$. The Hamiltonian of the cluster of M impurities is

$$H=\sum_i\frac{P_i^2}{2m}+\sum_i V^{\text{ion}}(\mathbf{r}_i)+\tfrac{1}{2}\sum_{i,j}V^{e\text{-}e}(\mathbf{r}_i-\mathbf{r}_j)\ , \tag{1}$$

where $V^{\text{ion}}(\mathbf{r}_i)$ is the impurity ion potential acting on the ith electron, $V^{e\text{-}e}(\mathbf{r}_i-\mathbf{r}_j)$ is the Coulomb interaction between the ith and jth electron, and the summations are over all of the M electrons. In the unrestricted HFR formalism we get a set of coupled Schrödinger equations for each spin:[1]

$$H_\sigma(\mathbf{r})\Psi_{n\sigma}(\mathbf{r})=E_{n\sigma}\Psi_n(\mathbf{r})\ ,\qquad \sigma=\uparrow,\downarrow \text{ and } n=1,2,\ldots,M\ , \tag{2}$$

where

$$H_\sigma(\mathbf{r})=\frac{P^2}{2m}+V^{\text{ion}}(\mathbf{r})+V^C(\mathbf{r})+V^{\text{ex}}(\mathbf{r})\ , \tag{3}$$

$$V^C(\mathbf{r})=\sum_s\sum_m\int|\Psi_{ms}(\mathbf{r}')|^2V^{e\text{-}e}(\mathbf{r}-\mathbf{r}')d^2r',\quad s=\sigma,-\sigma \tag{4}$$

is the Coulomb potential, and

$$V_\sigma^{\text{ex}}(\mathbf{r})\Psi_{n\sigma}(\mathbf{r})=-\sum_s\sum_m\delta_{s\sigma}\int\Psi_{ms}^*(\mathbf{r}')V^{e\text{-}e}(\mathbf{r}-\mathbf{r}')\times\Psi_{n\sigma}(\mathbf{r}')\Psi_{ms}(\mathbf{r})d^2r'\ , \tag{5}$$

is the spin-dependent exchange potential.

The cluster eigenfunction of Eq. (2) can be expressed as

$$\Psi_{n\sigma}(\mathbf{r})=\sum_j\phi_{j\sigma}(\mathbf{r})B_{jn\sigma}\ , \tag{6}$$

where

$$\phi_j(\mathbf{r})=\phi^{2\text{D}}(\mathbf{r}-\mathbf{R}_j)=(8/\pi)^{1/2}a_H^{-1}\exp(-2\,|\,\mathbf{r}-\mathbf{R}_j\,|\,/a_H)\ ,$$

(see Refs. 2—4, 9, and 10). Following the usual HFR procedure, we obtain[1]

$$\sum_j[(\bar{B}_\sigma^\dagger\bar{H}'_\sigma\bar{B}_\sigma)_{ij}-E_{m\sigma}\delta_{ij}]C_{mj\sigma}=0\ , \tag{7}$$

where the matrix elements of $\overline{H}'_{\sigma}$, are given by

$$H'_{ij\sigma}=\int \phi_i^*(\mathbf{r})\left[\frac{p^2}{2m}+V^{\text{ion}}(\mathbf{r})\right]\phi_{\text{j}}(\mathbf{r})\text{d}^2\text{r}+\sum_{\mu,\lambda}\sum_{\text{s}}\text{P}^{\text{s}}_{\mu\lambda}\int\int \phi_{\text{i}}^*(\mathbf{r})\phi_{\mu}^*(\mathbf{r}')\text{V}^{\text{e-e}}(\mathbf{r}-\mathbf{r}')[\phi_\lambda(\mathbf{r}')\phi_{\text{j}}(\mathbf{r})-\phi_\lambda(\mathbf{r})\phi_{\text{j}}(\mathbf{r}')\delta_{\text{s}\sigma}]\text{d}^2\text{r}\,\text{d}^2\text{r}' \tag{8}$$

and

$$P^s_{\mu\lambda}=\sum_m B^*_{\mu m s}B_{\lambda m s}\ . \tag{9}$$

Equations (7) and (8) are solved self-consistently by iteration. As the initial input, we neglect the exchange term in (3) to obtain the Hartree eigensolution $\overline{B}_{\sigma}$. Neglecting the three- and four-center integrals, the diagonal and off-diagonal matrix elements of (8) are written explicitly in terms of the modified Slater[11] integrals S,K,J,L,U,J', and K' for two dimensions:

$$\begin{aligned}H'_{ii\sigma}=E_d&+\sum_{k(\neq i)}J(\mathbf{R}_{ik})+UP_{ii}^{-\sigma}+2\sum_{k(\neq i)}P_{ij}^{-\sigma}L(\mathbf{R}_{ik})\\&+\sum_{s=\sigma,-\sigma}\sum_{k(\neq i)}P^s_{kk}J'(\mathbf{R}_{ik})-\sum_{k(\neq i)}P^{\sigma}_{kk}K'(\mathbf{R}_{ik})\ ,\end{aligned} \tag{10}$$

$$\begin{aligned}H'_{ij\sigma}=E_dS(\mathbf{R}_{ij})&+K(\mathbf{R}_{ij})+(P_{ii}^{-\sigma}+P_{jj}^{-\sigma})L(\mathbf{R}_{ij})\\&+\sum_{s=\sigma,-\sigma}P^s_{ij}K'(\mathbf{R}_{ij})-P^{\sigma}_{ij}J'(\mathbf{R}_{ij})\ ,\end{aligned} \tag{11}$$

where U is the intra-atomic correlation energy; $E_d=-2.0$ effective hartrees is the ground-state level of an isolated impurity for a hydrogenic system in 2D;[2–4,9,10] $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$ is the separation between a pair of donor sites. The overlap integral[10] is

$$S(\mathbf{R}_{ij})=S_{ij}=2(R^*_{ij})^2\left[K_0(2R^*_{ij})+\frac{1}{R^*_{ij}}K_1(2R^*_{ij})\right]\ , \tag{12}$$

where $R^*_{ij}=R_{ij}/a_H$, and K_0 and K_1 are the modified Bessel functions of zero and first order, respectively. The energy for the transfer of electrons between impurity sites[10] (hopping matrix) is

$$K_{ij}=-8R^*_{ij}K_1(2R^*_{ij})\ . \tag{13}$$

The Coulomb interaction of an electron in an impurity orbital on nucleus i with nucleus j is

$$J_{ij}=-4[1-4R^*_{ij}I_1(2R^*_{ij})K_0(2R^*_{ij})]\ , \tag{14}$$

where I_1 is Bessel's function of first order. The electron correlations are

$$J'_{ij}=\frac{1}{R^*_{ij}}-\left[\left[\frac{1}{R^*_{ij}}-3.1R^*_{ij}+1.1(R^*_{ij})^2-0.3(R^*_{ij})^3\right]\exp(-2.36R^*_{ij})\right] \tag{15}$$

and

$$\begin{aligned}L_{ij}=2.36\{&\Theta(R^*_{ij}-1.1)\exp(-1.72R^*_{ij}+0.78)\\&+\Theta(1.1-R^*_{ij})\exp[-0.65(R^*_{ij})^2-0.3R^*_{ij}]\}\ ,\end{aligned} \tag{16}$$

and the exchange is

$$K'_{ij}=(0.41R^*_{ij}+2.776)S^2_{ij}[1-\exp(-0.85R^*_{ij})]/R^*_{ij}\ . \tag{17}$$

We found Eqs. (15), (16), and (17) to be the best-fitted analytical curves for J',[12] L, and K'. The term U which is 0.625 effective hartrees in 3D is equal to 2.36 effective hartrees in 2D.[3,9] We also use the value $U=1.76$ to calculate the impurity density of states (IDOS). This value is obtained through the calculation of Phelps and Bajaj,[13] who, using a trial wave function with many terms in its expansion, calculated the ground-state energy of a D^- ion in a 2D semiconductor, and found it to be -2.24 effective hartrees. Since the ground-state energy of an isolated impurity is $E_d=2.0$ effective hartrees, the binding energy $E_B(D^-)$ of the D^- ion becomes equal to -0.24 and $U=E_B(D^-)-E_d=1.76$. The 2D and 3D Slater integrals as a function of R^*_{ij} are shown in Fig. 1. All of the above 2D energy integrals as well as overlap on two neighboring donors are much reduced for $R^*_{ij}>2$ and substantially enhanced for $R^*_{ij}<2$, compared to their values in 3D. For $R^*_{ij}\geq 3$ the effects of such integrals in the IDOS will be of minor importance, except for U, which will play the major effect. Even for smaller R^*_{ij} (higher concentrations), U will be the major importance in the disordered systems in 2D.

Taking a given value of N and a particular configuration of random impurity distribution, we can calculate the matrix elements from (10) and (11) and solve (7) for the eigenenergies. In our calculation we use a cluster of $M=40$ impurities with $M_s=960$ impurities and average over a large number of random configurations.[1] The IDOS $D(E)$ is normalized to

$$\int D(E)dE=\frac{P}{64\pi}=Na_H^2\ . \tag{18}$$

The Fermi energy E_F, at 0 K, is calculated with the assumption made in the HFR calculation, namely, that the first M states of low energy were occupied in each configuration. When this condition is not satisfied, we expect an internal charge transfer between different configurations, and the HFR calculations would have to be performed accordingly. This "charge inhomogeneity" generations called "inner compensation" in I is caused by the

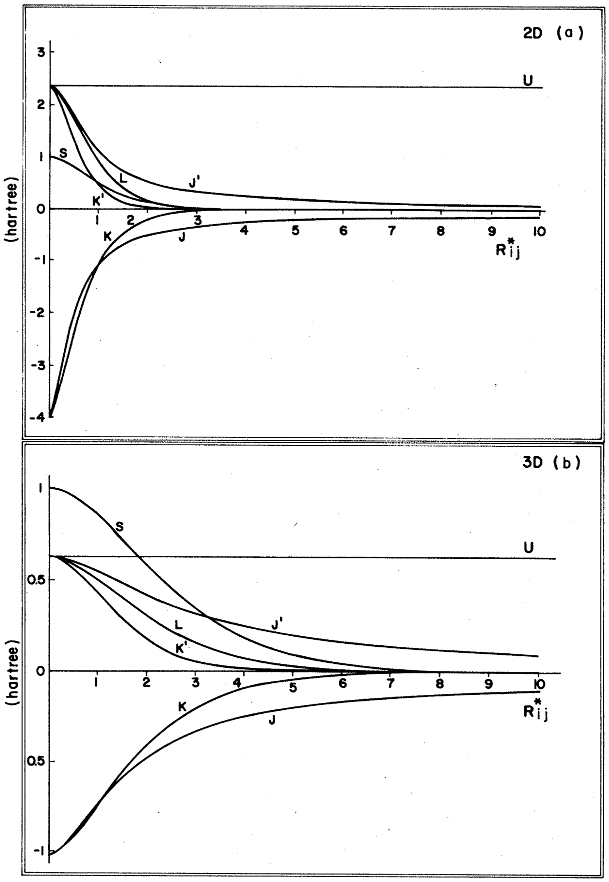

FIG. 1. Slater integrals in two (a) and three (b) dimensions.

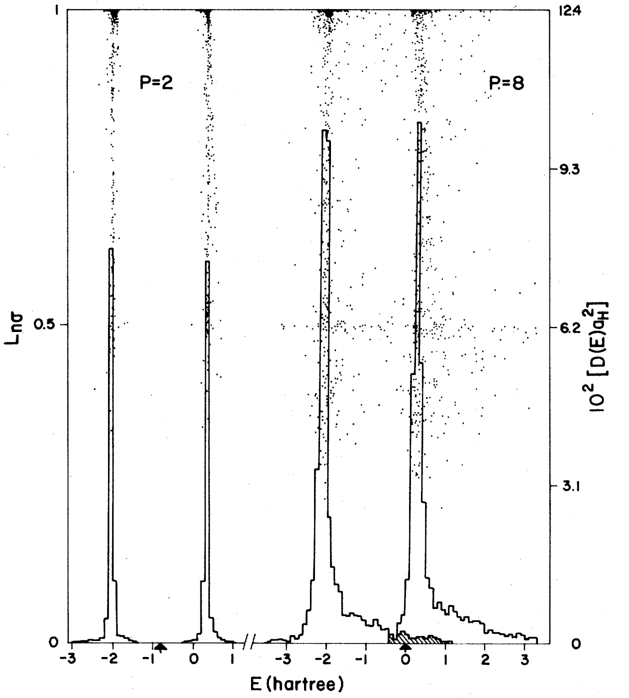

FIG. 2. IDOS for $P=2(N^{1/2}a_H=0.10)$ and $P=8\times(N^{1/2}a_H=0.20)$. The CB is set at zero energy. Shaded area represents the overlap of split bands. The arrow indicates E_F. The dots correspond to the IPR $L_{n\sigma}$.

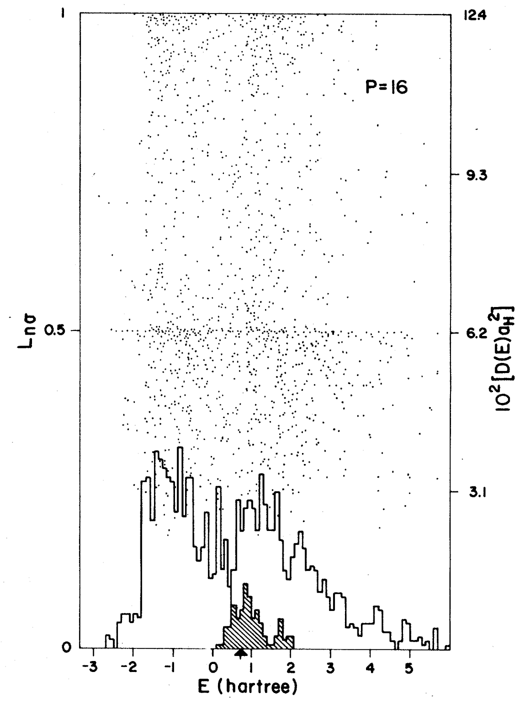

FIG. 3. Same as Fig. 2 for $P=16(N^{1/2}a_H=0.28)$.

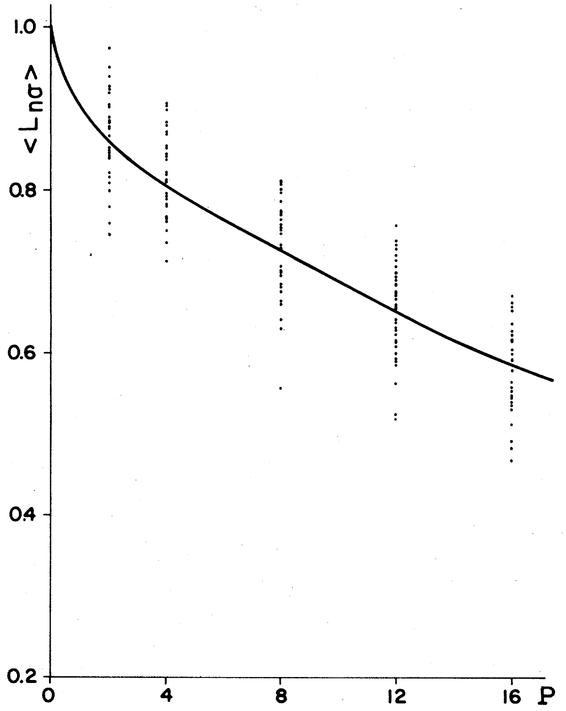

FIG. 4. $\langle L_{n\sigma}\rangle$ for various values of the impurity concentration P. Details are discussed in the text.

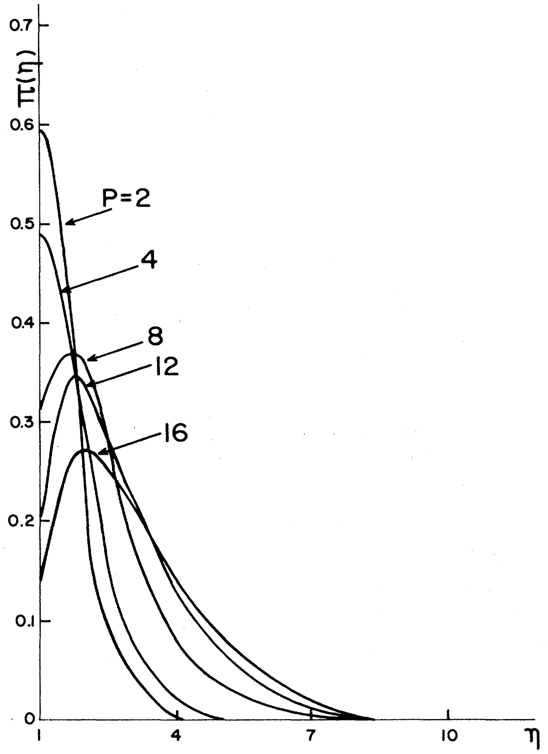

FIG. 5. Probability distribution of cluster as a function of the number of impurities covered by the cluster states, for various values of P,

potential fluctuation of the system itself. The E_F for $U=2.36$ moves into the conduction band (CB) at $P \simeq 10$ (corresponding to $N^{1/2}a_H \sim 0.22$), while for $U=1.76$ it crosses the bottom of the CB at $P \approx 15(N^{1/2}a_H \approx 0.27)$. The calculated IDOS consists of two bands, the lower D^0 band and the upper D^- bands, separated at very low concentration by the intra-atomic Coulomb correlation energy U.

The IDOS are shown in Figs. 2 and 3 as a function of impurity concentration $P=2$, 8, and 16 (corresponding to $N^{1/2}a_H \approx 0.10$, 0.20, and 0.28, respectively). The dots appearing on these figures are the inverse participation ratio (IPR) discussed below.

We use IPR as a measure of localization of the eigenstates.[1,14] It is defined as

$$L_{n\sigma} = \left[\sum_{j=1}^{M} |B_{jn\sigma}|^4 \right] \Big/ \left[\sum_{j=1}^{M} |B_{jn\sigma}|^2 \right]^2 . \qquad (19)$$

for the nth eigenstate with spin σ, where $B_{jn\sigma}$ comes from Eq. (6). The IPR varies from 1, corresponding to a state which is as localized as possible, to $1/M$, corresponding to a state which is as extended as possible. In Figs. 2 and 3, the IPR's are shown as a function of the eigenenergy for different impurity concentrations. For $P \leq 4(N^{1/2}a_H \leq 0.14)$ the great majority of the states are found to be localized. Increasing the concentration up to $P=16(N^{1/2}a_H=0.28)$, although for many of the states the IPR is less than 0.5, we found that most of the occupied states have an IPR between 0.5 and 1.0 indicating an isolated impurity state or a pair state.[1] In Fig. 4 we show the mean value of the IPR for each sample of the cluster, indicated by dots, as a function of concentration, and the configuration average of IPR $\langle L_{n\sigma} \rangle$ over all the sample clusters, indicated by the solid curve. Even for such higher concentrations $(8 < P \leq 16)$, when E_F goes to the region approaching the bottom of the conduction band, where large clusters would become more probable than isolated close pairs I, the localized and extended impurity states coexist in such a way that the conducting states delocalize less rapidly than for a 3D disordered system (I). Since higher density fluctuations are expected with increasing of the impurity concentration, we calculate the probability $\pi(\eta)$ of the eigenstate $\Psi_{n\sigma}(\mathbf{r})$ covering a number of η impurities, which is shown in Fig. 5. For all range of concentrations considered here, we observed that the 2D systems are dominated by isolated donor impurities or donor pairs of impurities.

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