RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 15 15 NOVEMBER 1987-II

Quantum electron glass

G. Vignale
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
and Department of Physics, University of Tennessee, Knoxville, Tennessee 37996
(Received 8 September 1987)

A model of localized interacting electrons is studied numerically, under conditions in which the electron wave functions significantly overlap in space. A Coulomb gap in the one-particle density of states is found to persist throughout the localized regime. From the calculated rise of a quantum-mechanical order parameter, and from the increase in the number of metastable "pseudo-ground" states, evidence is obtained of a glass transition, occurring at zero temperature, as the overlap is varied.

The long-range Coulomb repulsion between electrons in localized states leads to a number of remarkable effects, of which the best known is the "Coulomb gap"[1] in the density of states (DOS). The density of one-particle excitations is reduced in the vicinity of the Fermi energy E_F, in such a way that it tends to zero at E_F, but it is nonzero elsewhere. The original arguments in favor of this effect, as well as the computer simulations[2-4] which subsequently confirmed it, were formulated for the infinitely dilute regime, in which the spatial overlap between localized states is negligibly small. This is *not*, however, the regime in which experimental studies are usually conducted. In the experiments of Zabrodskii[5] and Zabrodskii and Zinov'eva,[6] where the presence of a Coulomb gap is inferred from the temperature dependence of the resistivity in n-doped germanium, almost all the samples are very close to the metal-insulator transition, and therefore the overlap of wave functions is far from negligible.[7] Quite generally, overlap effects are now believed to be important whenever the concentration of impurities exceeds $\frac{1}{10}$ of the critical Mott concentration.[8] Other experiments which have recently been interpreted[9] as prime evidence for the Coulomb gap are photoemission studies[10] of compensated sodium tungsten bronzes. Here again the concentration of uncompensated electrons is much larger than $\frac{1}{10}$ of the critical concentration. It is therefore relevant to undertake a study of the disordered insulator under conditions in which the overlap between localized wave functions is not negligible. This problem is addressed in the present Rapid Communication.

The method employed is an extension of the numerical energy-minimization programs of Baranovskii, Efros, Gelmont, and Shklovskii[2] (BEGS) and Davies, Lee, and Rice[3] (DLR). The crucial difference is that the electrons are allowed to tunnel between neighboring impurities, with a tunneling amplitude t. The two other parameters characterizing the system are the disorder bandwidth B and the magnitude of the Coulomb interaction $E_0 \cong B$. It will be shown that a Coulomb gap in the DOS persists up to values of t/B at which the localization length becomes comparable to the size of the sample. We shall then discuss the possibility of a glass-ordering transition occurring at the absolute zero of temperature when t/B is varied; for example, by doping or by compensation. The onset of glasslike order is suggested by two different facts: (a) rise of an order parameter which we define as a quantum modification of the one of Edwards-Anderson,[3,11] and (b) the rapid increase of the number of metastable "pseudo-ground-states" of similar energy. The transition appears to occur at $t/B=0.04$ in three dimensions (3D) and $t/B=0.06$ in 2D, which are both within the localized regime.

A simplified Hamiltonian for localized interacting electrons has the form (in dimensionless units)

$$H=H_0+\tfrac{1}{2}\sum_{\substack{i,j\\ i\neq j}}\frac{1}{r_{ij}}(a_i^\dagger a_i-K)(a_j^\dagger a_j-K)\ ,$$
$$H_0=\sum_i \phi_i a_i^\dagger a_i + t\sum_{\langle i,j\rangle} a_i^\dagger a_j\ , \tag{1}$$

where $a_i^\dagger$ (a_i) is the creation (annihilation) operator of an electron at site i, ϕ_i is the random site energy, and K is the compensating charge per site. To make comparison with previous results for the classical version of the Hamiltonian ($t=0$), we also choose to ignore spin. The tunneling term can be formally eliminated, transforming to the basis of the exact eigenstates $|\alpha\rangle=\sum_i C_{\alpha i}|i\rangle$ of the noninteracting Hamiltonian H_0. The transformed Hamiltonian has the form

$$H=\sum_\alpha E_\alpha a_\alpha^\dagger a_\alpha+\tfrac{1}{2}\sum_{\alpha,\beta,\gamma,\delta} e_{\alpha\beta\gamma\delta}(a_\alpha^\dagger a_\beta-K\delta_{\alpha\beta})(a_\gamma^\dagger a_\delta-K\delta_{\gamma\delta}). \tag{2}$$

E_α are the exact eigenvalues of H_0. The matrix elements of the Coulomb interaction are defined as

$$e_{\alpha\beta\gamma\delta}=\sum_{\substack{i,j\\ i\neq j}}\frac{1}{r_{ij}}C_{\alpha i}^* C_{\beta i} C_{\gamma j}^* C_{\delta j}\ . \tag{3}$$

The many-body problem in Eq. (2) cannot be solved exactly for a system of reasonable size. The present work is based on the following approximation: We only keep the components of the interaction in which the indices $\alpha,\beta,\gamma,\delta$ are equal in pairs, i.e., $\alpha=\beta$ and $\gamma=\delta$, or $\alpha=\delta$ and $\gamma=\beta$. This is equivalent to the Hartree-Fock (HF) approximation, with neglect of the off-diagonal elements $\sum_{\alpha\beta}(\alpha\neq\beta)$

of the self-energy. In other words, we seek an approximate ground-state as a single Slater determinant of noninteracting eigenstates. The treatment becomes rigorous in the extremely localized ($t \to 0$) and in the extremely delocalized ($t \to \infty$) limit. Among the neglected self-energy terms, the most important are the off-diagonal Hartree ones $\sum_{\alpha\beta} = \sum_{\gamma} e_{\alpha\beta\gamma\gamma} n_\gamma$ ($\gamma \neq \alpha, \beta$). These terms are considerably smaller than typical differences of diagonal energies, and their signs alternate randomly (at $t/B = 0.04$, the variance is $\simeq 0.01 B^2$ and the average is $\simeq 0$). Therefore, a complete solution of the HF equations is not expected to change substantially the character of the one-electron eigenstates.[12] The present treatment does not take into account the decay rate of excitations, which is due to terms beyond the Hartree-Fock. This effect has been shown[13] to be exponentially small in the insulating regime. The effective Hamiltonian takes the form

$$H \cong \sum_{\alpha} E_\alpha a_\alpha^\dagger a_\alpha + \tfrac{1}{2} \sum_{\alpha\beta} (e_{\alpha\alpha\beta\beta} - e_{\alpha\beta\beta\alpha})(n_\alpha - K)(n_\beta - K) \ , \tag{4}$$

where $n_\alpha = a_\alpha^\dagger a_\alpha$. Since the n_α's are constants of the motion, this is effectively a classical problem, each eigenstate being determined by one set of occupation numbers. In the localized regime the direct interaction $e_{\alpha\alpha\beta\beta}$ remains long ranged as the separation between the centers of eigenstates α and β is increased. Thus, the Efros-Shklovskii stability criterion, which now reads $E_\alpha - E_\beta - e_{\alpha\alpha\beta\beta} + e_{\alpha\beta\beta\alpha} > 0$ ($E_\alpha > E_F, E_\beta < E_F$) leads to a Coulomb gap with the usual power-law behavior.[1] At short range, however, the quantum interaction is weaker than the classical one, due to the partial delocalization of the electronic charge. Therefore, one expects that the width of the Coulomb gap should be reduced.

The method of solution of the Hamiltonian of Eq. (4) is a straightforward extension of the energy-minimization program employed by BEGS and DLR. The sites are put on a square or simple cubic lattice of parameter a, and the site energies ϕ_i are drawn from a rectangular distribution of width $B = e^2/\kappa a = 1$. Periodic boundary conditions are used as introduced by DLR. The noninteracting eigenstates are determined by direct numerical diagonalization of H_0. The electrons in the noninteracting eigenstates are rearranged, starting from a random initial configuration, until a self-consistent state is obtained, which is stable with respect to all one- and two-particle excitations. Most of the numerical effort goes into the evaluation of the Coulomb matrix elements [Eq. (3)], which involve huge summations. This severely restricts the size of the samples which can be studied. The results presented here are for 5^3 cubic and 11^2 square lattices. It is encouraging to see that, in the limit $t = 0$, they are not very different from those obtained by DLR for larger samples.

The one-particle DOS is shown in Fig. 1 for two- and three-dimensional samples with $K \cong \frac{1}{2}$. A small size effect is the excessive depression of the DOS, which becomes strictly zero in a region of width $\simeq 1/N^{1/d}$ (N is the number of sites) centered at E_F.[14] Apart from this, the positions and widths of the peaks at $t = 0$ are virtually indistinguishable from those of DLR. The striking feature of Fig. 1 is the considerable reduction of the width of the

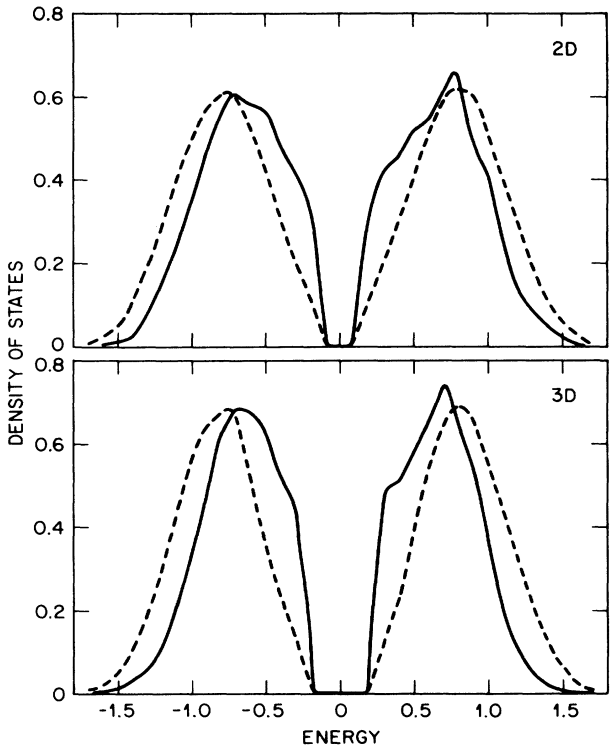

FIG. 1. One-particle density of states for two- and three-dimensional samples at compensation $K = \frac{1}{2}$. Dashed curves: $t = 0$. Solid curves: $t/B = 0.083$ in 3D and $t/B = 0.125$ in 2D.

Coulomb gap, brought about by quantum effects. At $t/B = 0.083$ the 3D quantum DOS in the region of the gap is two to five times larger than the classical DOS. The value of $t/B = 0.083$ was chosen because it is extremely close to that obtained by Licciardello and Economou[15] for the onset of localization in a tight-binding cubic lattice. We have also directly checked that at this point the average extension of the one-electron wave function is about 90% of the limiting value it would reach in a perfectly ordered sample. Therefore, the fact that the DOS still has a sharp two-peak structure strongly suggests that the Coulomb gap persists up to the metal-insulator transition. At larger values of t (i.e., in the metallic regime), the Hartree-Fock calculation predicts a "correlation gap"[16] varying as $(E - E_F)^{1/2}$. Screening effects will modify this result, leading to a finite DOS at the Fermi energy. Unfortunately, the closing of the Coulomb gap cannot be numerically followed in systems of the size considered here. The reason is that when the quantum bandwidth exceeds the disorder bandwidth the noninteracting DOS begins to look like a series of well-separated peaks. The Coulomb two-peak structure is gradually washed out, but it is not possible to obtain a continuous DOS curve.

The results discussed above are in qualitative agreement with the predictions of an analytical theory,[17] which was developed for the $t \to 0$ limit, and which treats disorder in the coherent potential approximation. However, the reduction of the width of the Coulomb gap is more pronounced in the present study.[18]

Coming to the second topic of this Rapid Communication, we now discuss the evidence for the growth of glasslike order as t is decreased at the absolute zero of temperature. The analogy between the classical limit of the Hamiltonian[1] of Eq. (1) (with $K=\frac{1}{2}$) and a classical Ising-spin model, was first explored by DLR,[3] at finite temperature. The variable $\sigma_{iz}=(n_i-\frac{1}{2})$ was interpreted as the z component of a spin. At very high temperature all sites have equal probability of being empty or occupied. As the temperature is lowered, this symmetry eventually breaks down: Some of the sites become preferentially occupied, and others become preferentially empty. In the classical model of a spin glass,[11] in the absence of external fields, a measure of glasslike order can be obtained from the Edwards-Anderson order parameter $\langle\langle 2\sigma_{iz}\rangle_T^2\rangle_S$, where T denotes the thermal average and S an average over samples. In the present system, the random potential breaks the equivalence of sites even in the absence of interactions. This led DLR to modify the definition of the order parameter, subtracting from the thermal average of a spin its value in the absence of interactions: $q_m(T)=2\langle[\langle\sigma_{iz}\rangle_T-\langle\sigma_{iz}\rangle_T^0]^2\rangle_S$.

In the quantum-mechanical situation, at zero temperature, a "freezing" of electrons on certain sites can be induced by decreasing the overlap t. The degree of "freezing" can be measured by a quantum version of the order parameter q_m, in which the thermal average is replaced by a quantum average in a pseudo ground state. At finite temperature one should define q_m with both a thermal and a quantum average. The zero-temperature quantum version of q_m reads

$$q_m(t)=\langle\sum_{\alpha,\beta}(n_\alpha-n_\alpha^0)f_{\alpha\beta}(n_\beta-n_\beta^0)\rangle_S/[2K(1-K)]\ ,$$
$$f_{\alpha\beta}=\frac{1}{N}\sum_i|C_{\alpha i}|^2|C_{\beta i}|^2\ , \tag{5}$$

where n_α^0 are the occupation numbers in the noninteracting ground state (i.e., the $T=0$ Fermi distribution in noninteracting energies).

The calculated values of $q_m(t)$ (averaged over various samples, and various pseudo ground states for each sample) are plotted in Fig. 2 (solid curve). For large t the system is a Fermi liquid (i.e., $n_\alpha=n_\alpha^0$) and $q_m=0$. With decreasing t, the order parameter rises gently, starting at $t/B\cong 0.08$ in 3D and $t/B\cong 0.16$ in 2D. It reaches a value $\simeq 0.4$ at $t=0$. (This limit would be 1 if the ordering process were controlled by interactions alone.) From these data, it is not possible to decide whether a glass transition would occur above, below, or in concomitance of the localization-delocalization transition. Clearly, the two transitions would be related, but they need not be the same.

A more effective way to determine the onset of glasslike order is based on the property of glasses of having a large number of metastable pseudo ground states. These states are local minima of the energy. In the present case they are defined as configurations which are stable with respect to all one- and two-particle excitations. For a given choice of the random site energies a large number of such solutions is found. One can directly count the number N_d of

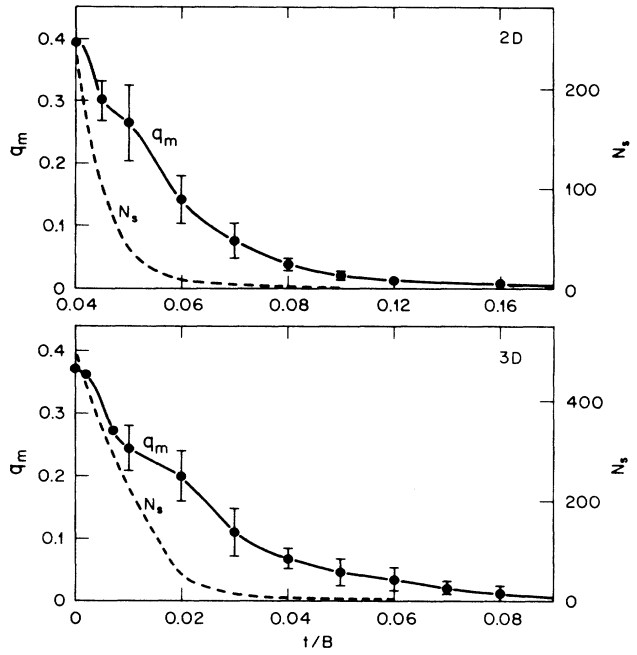

FIG. 2. Solid curve: quantum glass order parameter $q_m(t)$, from Eq. (5). Dashed curves: estimated numbers of pseudo-ground states (scale on the right-hand side).

different solutions obtained by starting the computer program at N_0 different configurations. From this, one can estimate the most probable number of solutions, given by $N_s\simeq N_0N_d/(N_0-N_d)$.

The value of N_s, averaged over various samples, is plotted in Fig. 2 (dashed curve) as a function of t. The striking feature of this curve is that it rises much more sharply than $q_m(t)$. A relation between q_m and N_s can be anticipated by considering that $Nq_m/2$ is roughly a measure of the number of states whose occupation number differs from the Fermi distribution. The number of energy configurations compatible with a given value of q_m is easily shown to increase exponentially with q_m. A configuration from this set will result in a pseudo-ground state, only if it happens to have a "favorable" spatial arrangement, the probability of this being presumably independent of the energy configuration. Therefore, it is plausible that the number of pseudo-ground states should also increase with increasing q_m.

From the behavior of N_s in Fig. 2, it appears that a glass transition would be taking place at $t/B\simeq 0.04$ in 3D and $t/B\simeq 0.06$ in 2D. At these values of t the average extension of the wave function is, respectively, 60% and 45% of the perfect-crystal limit. It appears, therefore, that the glass transition is distinct from the localization-delocalization transition, and occurs in the localized regime.

In conclusion, we have performed a first numerical study of localized interacting electrons in a quantum-mechanical situation, i.e., near an insulator-metal transition. A Coulomb gap in the one-particle density of states was found to persist throughout the localized regime. The

rise of the quantum glass-order parameter q_m, and the increase of the number of pseudo-ground states, were taken as indications of a glass transition. It occurs when the overlap parameter t/B is varied, for example, by doping, by compensation, or by a mechanical stress. This hypothesis awaits experimental verification.

This work was supported by the University of Tennessee, and by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc. The author wishes to thank Professor G. D. Mahan for many stimulating discussions.

[1]For a recent review, see *Electron-Electron Interactions in Disordered Systems,* edited by A. L. Efros and M. Pollak (North-Holland, Amsterdam, 1985), Chaps. 4 and 5, and references therein.

[2]S. D. Baranovskii, A. L. Efros, B. L. Gelmont, and B. I. Shklovskii, J. Phys. C **12**, 1023 (1979).

[3]J. H. Davies, P. A. Lee, and T. M. Rice, Phys. Rev. B **29**, 4260 (1984).

[4]M. Grünewald, B. Pohlmann, L. Schweitzer, and D. Wurtz, J. Phys. C **15**, L1153 (1982).

[5]A. G. Zabrodskii, Fiz. Tekh. Poluprovodn. **14**, 1130 (1980) [Sov. Phys. Semicond. **14**, 670 (1980)].

[6]A. G. Zabrodskii and K. N. Zinov'eva, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 369 (1983) [JETP Lett. **37**, 436 (1983)].

[7]See the discussion in B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors,* Springer Series in Solid-State Sciences, Vol. 45 (Springer-Verlag, New York, 1984), Sec. 10.1.2.

[8]See Ref. 7, p. 317; see also M. Pollak and M. Ortuño, J. Non-Cryst. Solids **77**, 33 (1985), where a similar criterion is deduced.

[9]J. H. Davies and J. R. Franz, Phys. Rev. Lett. **57**, 475 (1986).

[10]G. Hollinger, P. Pertosa, J. P. Doumerc, F. J. Himpsel, and B. Reihl, Phys. Rev. B **32**, 1987 (1985).

[11]S. F. Edwards and P. W. Anderson, J. Phys. F **5**, 965 (1975).

[12]In particular, the self-consistent eigenstates are expected to remain localized when the noninteracting ones are localized. The possibility of Coulomb-induced delocalization (see Ref. 1, Chap. IV, and Ref. 8) is not considered here.

[13]L. Fleishman and P. W. Anderson, Phys. Rev. B **21**, 2366 (1980).

[14]The Fermi energy is obtained as the average of the highest occupied and lowest empty level.

[15]D. C. Licciardello and E. N. Economou, Phys. Rev. B **11**, 3697 (1975). We refer to the value obtained from the "$L(E)$" criterion for localization at the center of the band.

[16]P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).

[17]G. Vignale, Y. Shinozuka, and W. Hanke, Phys. Rev. B **34**, 3003 (1986).

[18]The theory of Ref. 17 predicts that the density of states at the Fermi energy should remain finite (although exponentially small) in two dimensions if the classical DOS vanishes linearly or more slowly. Since our classical two-dimensional density of states (like the one calculated in Ref. 3) vanishes faster than linear, this prediction cannot be tested in the present study.