Correlation and Magnetic Effects in Narrow Energy Bands. II*

LAURENT G. CARON†
University of Sherbrooke, Sherbrooke, Québec
GEORGE W. PRATT, JR.
Massachusetts Institute of Technology, Cambridge, Massachusetts

Correlation and magnetic effects in narrow bands are studied using a generalized self-consistent cluster treatment of the narrow-band Hamiltonian. Here the dynamics consists of electron hopping between nearest-neighbor sites and Coulomb interaction between electrons on the same site and nearest-neighbor sites. In the simpler case, where the neighbor interactions are neglected, i.e., the Hubbard model, the environment of the cluster is regarded as a particle reservoir, one for each spin. Hopping between the cluster and reservoirs is described by fermion source terms. It is required that the thermodynamic average of the particle currents of each spin within the cluster equal the corresponding particle exchange between cluster and reservoir. Electron motion in the system is examined for varying ratios of the strength of the hopping to the intrasite Coulomb repulsion. A discontinuous transition from an antiferromagnetic insulator to a metal is found under dynamical conditions close to those predicted by Hubbard and Kemeny. The effect of the intersite Coulomb interaction on the transition is next studied. These added terms are seen greatly to influence the transition and the magnetic properties of the cluster.

The metal–nonmetal transition is very intimately entwined with the electron-correlation problem. Since band theory has failed to account for the discontinuous transition from insulator to metal with increasing bandwidth as postulated by Mott[1] for partically filled bands, correlations brought about by electron–electron interaction have to be considered as active ingredients for the phenomenon. The narrow-band Hamiltonian introduced by Hubbard[2] proved to be a breakthrough in the correlation problem because of its apparent simplicity and inherent physical value. Itinerant electron as well as localized approaches have been tried on this Hamiltonian using various techniques of modern many-body theory. What we propose is a generalization of the self-consistent cluster theory of spin-interacting systems[3] to correlation in narrow bands.[4]

MODEL HAMILTONIAN AND THE CLUSTER APPROXIMATION

As was Hubbard, we are interested in the problem of a narrow band. We write down a narrow-band Hamiltonian in the Wannier representation restricting it to nearest-neighbor interatomic terms. This is justifiable in narrow energy bands:

$$\mathcal{H}=T\sum_{ij}^{nn}\sum_{\sigma}c_{i\sigma}{}^{+}c_{j\sigma}+K\sum_{ij}^{nn}\sum_{\sigma}(c_{i\sigma}{}^{+}c_{j\sigma}n_{j-\sigma}+\text{h.c.})$$
$$+\tfrac{1}{2}I\sum_{i}\sum_{\sigma}n_{i\sigma}n_{i-\sigma}+\tfrac{1}{2}C\sum_{ij}^{nn}\sum_{\sigma\sigma'}n_{i\sigma}n_{j\sigma'}$$
$$+\tfrac{1}{2}J\sum_{ij}^{nn}\sum_{\sigma\sigma'}c_{i\sigma}{}^{+}c_{j\sigma'}{}^{+}c_{i\sigma}c_{j\sigma}, \quad (1)$$

apart from a constant. In the Hubbard notation

$$T=N^{-1}\sum_{\mathbf{k}}\exp[i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)]$$
$$\times\{\mathcal{E}_{\mathbf{k}}-(2J-c)v_{\mathbf{k}}-2Kv_{\mathbf{k}}\exp[-i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)]\},$$
$$I=(ii\mid 1/r\mid ii);\qquad K=(ij\mid 1/r\mid ii),$$
$$c=(ij\mid 1/r\mid ij);\qquad J=(ij\mid 1/r\mid ji), \quad (2)$$

where

$$(ij\mid 1/r\mid kl)=e^2\int d\mathbf{r}d\mathbf{r}'$$
$$\times\frac{\phi^*(\mathbf{r}-\mathbf{R}_i)\phi^*(\mathbf{r}'-\mathbf{R}_j)\phi(\mathbf{r}'-\mathbf{R}_l)\phi(\mathbf{r}-\mathbf{R}_k)}{|\mathbf{r}-\mathbf{r}'|}.$$

The extra terms aside, the one-electron energy $\mathcal{E}_{\mathbf{k}}$ appearing in the definition of T compensate for that part of the electron–electron interaction which is included in the Hartree–Fock field determining the band energy.

* Part of this work is from a Ph.D. dissertation submitted to the department of Electrical Engineering at the Massachusetts Institute of Technology in October 1967. It is supported in part by the U. S. Office of Naval Research.
† Supported in part by the Canadian National Research Council.

[1] N. F. Mott, Phil. Mag. **6**, 287 (1961).
[2] J. Hubbard, Proc. Roy. Soc. (London) **A276**, 238 (1963); **A281**, 401 (1964); **A285**, 542 (1965).
[3] For general information and references to the cluster theories, see J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Co., Philadelphia, Pa., 1966).
[4] G. W. Pratt, Jr. and L. G. Caron, J. Appl. Phys. **39**, 485 (1968), first paper in this series.

We propose to approximate a solution to this Hamiltonian by a self-consistent cluster treatment. In the spirit of the cluster theories, let us look at one particular atomic site. Electrons can interact with one another on this site but they are not stationary. The hopping terms in the Hamiltonian allow them to jump on and off the bordering sites. The immediate and crucial consequence is that electrons are not conserved on this site. Moreover, the intersite exchange mechanism will couple the spins of the site electrons to the neighboring ones. What is sought is a way to pull the cluster out of its environment and replace the severed links between it and its surroundings by coupling to electron reservoirs and effective fields. The reservoirs would give and take electrons from the cluster site thus preserving the physical picture of electronic motion, while the effective field would describe the exchange coupling with the environment. Conventionally the cluster technique consists in thermodynamically averaging over the operators outside the cluster. Those terms that are independent of the cluster indices can be regarded as constants and dropped. Doing just this, the resulting tentative cluster Hamiltonian is

$$\begin{aligned}\mathcal{H}_{\rm cl}=&T\sum_{\alpha}^{nn}\sum_{\sigma}(c_{i\sigma}^{+}\langle c_{\alpha\sigma}\rangle+\langle c_{\alpha\sigma}^{+}\rangle c_{i\sigma})\\&+K\sum_{\alpha}^{nn}\sum_{\sigma}(c_{i\sigma}^{+}\langle c_{\alpha\sigma}n_{\alpha-\sigma}\rangle+c_{i\sigma}^{+}n_{i-\sigma}\langle c_{\alpha\sigma}\rangle\\&+\langle c_{\alpha\sigma}^{+}n_{\alpha-\sigma}\rangle c_{i\sigma}+\langle c_{\alpha\sigma}^{+}\rangle c_{i\sigma}n_{i-\sigma})+\tfrac{1}{2}I\sum_{\sigma}n_{i\sigma}n_{i-\sigma}\\&+c\sum_{\alpha}^{nn}\sum_{\sigma\sigma'}n_{i\sigma}\langle n_{\alpha\sigma'}\rangle-J\sum_{\alpha}^{nn}\sum_{\sigma}n_{i\sigma}\langle n_{\alpha\sigma}\rangle,\end{aligned}\tag{3}$$

where the Latin index refers to the cluster site and the Greek one to sites outside. The $\langle\cdots\rangle$ terms are thermodynamic averages.

(1) That part which involves the term

$$-J\sum_{\alpha}^{nn}\sum_{\sigma}n_{i\sigma}\langle n_{\alpha\sigma}\rangle,$$

i.e., the exchange between like-spin electrons, is the familiar molecular-field approximation. The $\langle n_{\alpha\sigma}\rangle$ averages act like a magnetic field trying to line up the cluster electrons. On the other hand, the

$$c\sum_{\alpha}^{nn}\sum_{\sigma\sigma'}n_{i\sigma}\langle n_{\alpha\sigma'}\rangle$$

term contributes only a constant to the cluster Hamiltonian and can thus be dropped.

(2) The hopping between the cluster and the immediate neighborhood has been replaced by fermion source terms which can create or annihilate electrons in the cluster. It is this new concept in cluster theories which will allow electron correlation to be preserved between the cluster site and its surroundings. Since electrons are not conserved within the cluster, such cluster averages as $\langle c_{i\sigma}\rangle$ and $\langle c_{i\sigma}n_{i-\sigma}\rangle$ do become meaningful in the cluster context. These averages are a measure of the likelyhood for an electron to move off or onto the cluster site. The fermion anticommutation rules and the requirement of Hermiticity for the cluster Hamiltonian imposed the rule used in the cluster separation in Eq. (3). The fermion source turns out not to be simple classical reservoirs.

The self-consistency conditions directly follow the lines of conventional cluster theory. The reservoir averages should be set equal to their cluster counterparts. The following self-consistency rules are then proposed:

$$\begin{aligned}&\langle n_{\alpha\sigma}\rangle=\langle n_{i\sigma}\rangle;\qquad|\langle c_{\alpha\sigma}\rangle|=|\langle c_{i\sigma}\rangle|;\\&|\langle c_{\alpha\sigma}n_{\alpha-\sigma}\rangle|=|\langle c_{i\sigma}n_{i-\sigma}\rangle|.\end{aligned}\tag{4}$$

The absolute value on the unconventional reservoir averages comes from the fact they cannot be assigned a definite phase on each site.

Finally, as was pointed out previously, the cluster does not conserve particles. This implies particle fluctuation and, as such, grand canonical statistics must be used. This demands the introduction of a chemical potential μ. In view of this and the self-consistency conditions, the final form of the cluster Hamiltonian is

$$\begin{aligned}\mathcal{H}_{\rm cl}=&ZT\sum_{\sigma}(c_{i\sigma}^{+}\langle c_{i\sigma}\rangle+\langle c_{i\sigma}^{+}\rangle c_{i\sigma})\\&+ZK\sum_{\sigma}(c_{i\sigma}^{+}\langle c_{i\sigma}n_{i-\sigma}\rangle+c_{i\sigma}^{+}n_{i-\sigma}\langle c_{i\sigma}\rangle\\&+\langle c_{i\sigma}^{+}n_{i-\sigma}\rangle c_{i\sigma}+\langle c_{i\sigma}^{+}\rangle c_{i\sigma}n_{i-\sigma})\\&+\tfrac{1}{2}I\sum_{\sigma}n_{i\sigma}n_{i-\sigma}-ZJ\sum_{\sigma}n_{i\sigma}\langle n_{i\sigma}\rangle-\mu\sum_{\sigma}n_{i\sigma},\end{aligned}\tag{5}$$

where Z is the number of nearest neighbors.

HUBBARD HAMILTONIAN

By far the simplest application of this new cluster approach is to the model used extensively by Hubbard and followers, that is, an s band where the only form of interaction considered is between electrons on the same site. The corresponding cluster Hamiltonian is

$$\begin{aligned}\mathcal{H}_{\rm cl}=&ZT\sum_{\sigma}(c_{i\sigma}^{+}\langle c_{i\sigma}\rangle+\langle c_{i\sigma}^{+}\rangle c_{i\sigma})\\&+\tfrac{1}{2}I\sum_{\sigma}n_{i\sigma}n_{i-\sigma}-\mu\sum_{\sigma}n_{i\sigma}.\end{aligned}\tag{6}$$

We now proceed to find the free energy of this single-site cluster Hamiltonian. The unperturbed cluster states are $|0\rangle$ cluster empty, $|\uparrow\rangle$ spin-up electron in

the cluster, $|\downarrow\rangle$ spin-down electron in the cluster, and $|\uparrow\downarrow\rangle$ cluster full. Thus the energy matrix is

$$\begin{array}{c} \\ |0\rangle \\ |\uparrow\rangle \\ |\downarrow\rangle \\ |\uparrow\downarrow\rangle \end{array} \begin{array}{c} \begin{array}{cccc} |0\rangle & |\uparrow\rangle & |\downarrow\rangle & |\uparrow\downarrow\rangle \end{array} \\ \begin{bmatrix} 0 & ZT\langle c_{i\sigma}{}^{+}\rangle & ZT\langle c_{i\downarrow}{}^{+}\rangle & 0 \\ ZT\langle c_{i\uparrow}\rangle & -\mu & 0 & -ZT\langle c_{i\downarrow}{}^{+}\rangle \\ ZT\langle c_{i\downarrow}\rangle & 0 & -\mu & ZT\langle c_{i\uparrow}{}^{+}\rangle \\ 0 & -ZT\langle c_{i\downarrow}\rangle & ZT\langle c_{i\uparrow}\rangle & -Z\mu+I \end{bmatrix}. \end{array} \tag{7}$$

Fortunately this energy matrix can be easily diagonalized and the self-consistency condition easily satisfied at absolute zero. For the interesting case of a half-filled band for which $\mu=I/2$ the zero-temperature free energy F and reservoir coupling $\langle c_{i\sigma}\rangle$ are

$$F=\begin{cases} 0 & \text{if } Z\,|\,T\,|/I<\frac{1}{2} \\ -\frac{1}{2}(Z\,|\,T\,|-I/2) & \text{if } Z\,|\,T\,|/I\geq\frac{1}{2} \end{cases};$$

$$\langle c_{i\sigma}\rangle=\begin{cases} 0 & Z\,|\,T\,|/I\leq\frac{1}{2} \\ (1/2\sqrt{2})[1-(I/2ZT)^2]^{1/2} & Z\,|\,T\,|/I\geq\frac{1}{2} \end{cases} \tag{8}$$

These results are shown in Fig. 1.

It is seen that below a threshold value of $Z\,|\,T/I=\frac{1}{2}$ the interaction with the reservoir is zero. There is no electronic motion in or out of the cluster and as such the system can be labeled a nonmetal or an insulator inasmuch as there are no transport properties. But past this threshold value, the reservoir coupling increases very fast. There is then electronic motion in or out of the cluster. This is our criterion for labeling the cluster metallic. Since the derivative of the free energy is discontinuous at the threshold point, we have a first-order transition from the insulating to the metallic state. The slope of the reservoir coupling is also infinite at the transition.

In the insulating region there is no real electron motion, although we know there can be virtual hopping. This will tend to lower the energy of the antiferromagnetic state in which the cluster spin is opposite to the spin of the neighbor. It can be shown that in the insulating region the effect of the virtual hopping is equivalent to a zero-point energy

$$-(ZT^2/I)\sum_i\sum_\sigma n_{i\sigma} \tag{9}$$

and an antiferromagnetic "kinetic" virtual exchange

$$J'=-2T^2/I. \tag{10}$$

At zero temperature the free energy of such a state would be given by Eq. (9). This is plotted for the simple cubic structure ($Z=6$) against the cluster solution, in Fig. 2. The degeneracy has now been lifted. The effect is to shift the transition point to

$$(Z\,|\,T\,|/I)_c=0.63, \tag{11}$$

at which point the transition is definitely first order with a noticeable discontinuity in the slope of the free energy and in the coupling to the reservoir. This critical value compares favorably well with those obtained by Hubbard[2] and Kemeny[5]:

$$(Z\,|\,T\,|/I)_c=0.577 \quad \text{(Hubbard)}, \tag{12}$$

$$(Z\,|\,T\,|/I)_c=0.63 \quad \text{(Kemeny)}. \tag{13}$$

This simple cluster theory has yielded a discontinuous transition from an antiferromagnetic insulator to a nonmagnetic metal for a narrow half-filled band. We now proceed to study the effect of the other terms in the general-cluster Hamiltonian, Eq. (5).

MAGNETIC EXCHANGE

After adding exchange to the Hubbard Hamiltonian, the resulting cluster Hamiltonian is

$$\mathcal{H}_{cl}=ZT\sum_\sigma(c_{i\sigma}{}^{+}\langle c_{i\sigma}\rangle+\langle c_{i\sigma}{}^{+}\rangle c_{i\sigma})+\tfrac{1}{2}I\sum_\sigma n_{i\sigma}n_{i-\sigma} -ZJ\sum_\sigma n_{i\sigma}\langle n_{i\sigma}\rangle-\mu\sum_\sigma n_{i\sigma}. \tag{14}$$

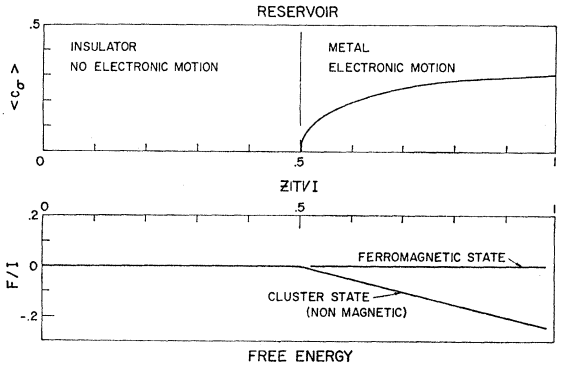

FIG. 1. Zero-temperature results to Hubbard's cluster Hamiltonian.

[5] G. Kemeny and L. G. Caron, Phys. Rev. **159**, 768 (1967).

At zero temperature there are three possible solutions to this cluster problem, neglecting kinetic-exchange effects.

(1) A totally magnetic solution with free energy:

$$F=0 \qquad \text{for antiferromagnetic exchange}$$
$$=-Z\,|\,J\,| \qquad \text{for ferromagnetic exchange.} \qquad (15)$$

(2) A nonmagnetic solution with free energy:

$$F=-ZJ/2 \qquad Z\,|\,T\,|/I\leq\tfrac{1}{2}$$
$$=-ZJ/2-\tfrac{1}{2}(Z\,|\,T\,|-I/2) \qquad Z\,|\,T\,|/I\geq\tfrac{1}{2},$$
$$\langle c_{i\sigma}\rangle=(1/2\sqrt{2})[1-(I/2ZT)^2]^{1/2} \qquad Z\,|\,T\,|/I\geq\tfrac{1}{2}. \qquad (16)$$

(3) A partially magnetized solution. However, its free energy is always greater than the nonmagnetic one and so it is rejected.

These results are shown in Fig. 3, where for purposes of illustration the zero of the free energy has been put at the nonmagnetic cluster solution $Z\,|\,T\,|/I=0$ limit. Again the discontinuous first-order transition is observed from a totally magnetized insulator to a nonmagnetic metal. The magnetic state is seen to be stabilized against hopping. This has the effect of displacing the critical $Z\,|\,T\,|/I$ ratio to larger values, the larger J.

INTERSITE SCATTERING

Finally, the only term left untouched is the intersite scattering K. In its presence the cluster Hamiltonian becomes

$$\mathcal{H}_{\rm cl}=ZT\sum_\sigma (c_{i\sigma}^+\langle c_{i\sigma}\rangle+\langle c_{i\sigma}^+\rangle c_{i\sigma})$$
$$+ZK\sum_\sigma (c_{i\sigma}^+\langle c_{i\sigma}n_{i-\sigma}\rangle+c_{i\sigma}^+n_{i-\sigma}\langle c_{i\sigma}\rangle$$
$$+\langle c_{i\sigma}^+n_{i-\sigma}\rangle c_{i\sigma}+\langle c_{i\sigma}^+\rangle c_{i\sigma}n_{i-\sigma})$$
$$+\tfrac{1}{2}I\sum_\sigma n_{i\sigma}n_{i-\sigma}-\mu\sum_\sigma n_{i\sigma}. \qquad (17)$$

Here we have added a minus sign in front of T since it is normally negative whereas K is positive. By doing this we ensure a correct relationship between T and K. The zero-temperature solution is a bit tedious to obtain. The results of the numerical computations are in Fig. 4, where we have plotted the constant-reservoir coupling curves in the positive ZT/I-versus-ZK/I quadrant. The relationship is surely far from linear, as would have been expected from band theory. The rate of increase of the reservoir coupling is also very strongly affected. We would expect large shifts in the transition point. T and K being of opposite sign, the effect of K is to reduce the effective value of T and thus push back the outset of the metallic phase. Note the region $K>T$ is unphysical. Moreover, the cluster solution is partially ferromagnetic throughout

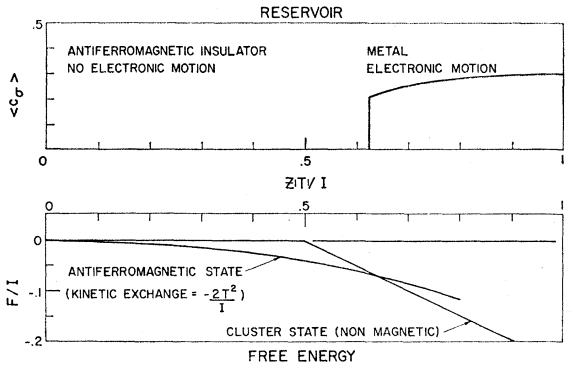

FIG. 2. Zero-temperature results to Hubbard's cluster Hamiltonian including kinetic-exchange effects.

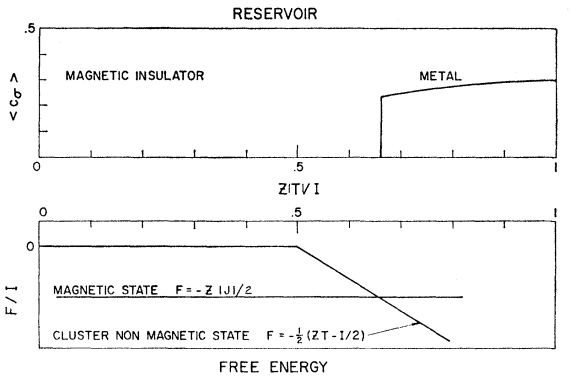

FIG. 3. Zero-temperature results to Hubbard's cluster Hamiltonian including exchange.

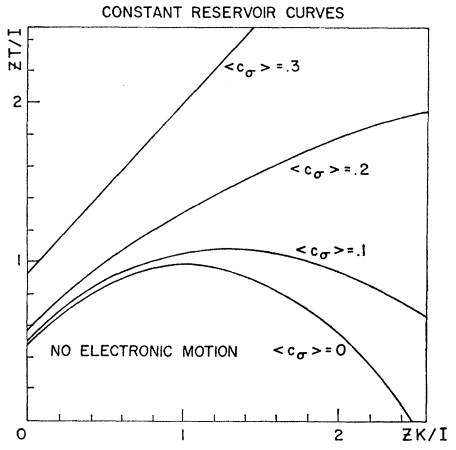

FIG. 4. Zero-temperature results to Hubbard's cluster Hamiltonian including intersite scattering.

the whole plane except, of course, when $K=0$ and in the insulating region where second-order perturbation theory yields an antiferromagnetic state. T and K being of opposite sign, this seems to disfavor hopping from a doubly occupied site or onto an occupied site. The cluster reacts to this by partly polarizing the spins and thus reducing the number of doubly occupied sites.

Extension of the theory to multiband systems as well as larger clusters is quite straightforward.[6] We will shortly present some work on the thermal behavior of certain interesting systems in the cluster approximation.

ACKNOWLEDGMENT

Numerical calculations were performed at the computation center of the University of Sherbrooke.

[6] L. G. Caron, Tech. Rept. No. 6, Materials Theory Group, Massachusetts Institute of Technology, September 1967 (unpublished).

Discussion of Caron and Pratt's Paper

W. KOHN (University of California, San Diego): Do you share my feeling that, while I think this is very physically interesting (I am going to ask you for a copy of your paper), I think that just in trying to determine the order of transition these cluster molecular field methods are generally quite unreliable.

L. G. CARON: I quite agree. As it so happens, I consider this as a zeroth-order approximation to the problem. If it did not give rise to a first-order transition, then it would have been very meaningful. It would have meant that probably such a transition did not occur, but since it does give a first-order transition, this means that such a transition is not at all unlikely. It doesn't reject that result.

G. W. PRATT: I'd like to make a pedagogical point. It seems to me it is of interest here beyond the Mott-transition problem that the machinery of statistical mechanics which is used in magnetism, that is, the Bethe–Peierls–Weiss theory, can be reoriented and steered in the direction of this kind of problem and used to treat correlation. I agree that one has to be very careful to trust it too far, but it's rather an amusing thing.