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Ferromagnetism in the Nearly-Half-Filled-Band Hubbard Model at Nonzero Temperatures

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Nagoaka's result that the ground state of the near-neighbor-hopping Hubbard model, for a nearly half-filled band and for interaction strength much greater than hopping energy, is ferromagnetic, is shown to be valid for bosons with spin, as well as fermions, in a finite system. In the thermodynamic limit, the boson system is shown to be nonmagnetic. Ferromagnetism is argued to exist at nonzero temperatures for fermions in an infinite system, and upper and approximate lower bounds are obtained for the Curie temperature.

Nagaoka has shown that the near-neighbor-hopping Hubbard model,[1] with infinite-interaction energy, has a ferromagnetic ground state if the band contains one less than one electron per lattice site.[2] In the infinite-interaction limit, the Hubbard Hamiltonian reduces to

$$\mathcal{H} = \sum_{ij\sigma} h_{ij}\, a^{\dagger}_{i\sigma}\, a_{j\sigma}, \tag{1}$$

where $h_{ij} = h$ if i and j are near neighbors, and zero otherwise, and where

$$a_{i\sigma} = (1 - n_{i,-\sigma})\, c_{i\sigma}, \qquad n_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma},$$

where $c_{i\sigma}$ is an annihilation operator for an electron of spin σ on site i.[3,4] Nagaoka's proof depends on considering the motion of the "hole" (i.e., site not containing an electron) over all possible paths over which it may hop. The number of paths contributing to Nagaoka's Green's function, involving a given number of hops of the hole, does not depend on the fact that we have fermions, but only on the fact that we have a variable such as spin which makes some particles distinguishable. Therefore, Nagaoka's result should also be applicable to bosons with spin. Thus, we have a case of ferromagnetism not caused by the Pauli exclusion principle either directly or indirectly.

At nonzero temperatures, we consider the canonical partition function in order to discuss the magnetic properties of the system. If we write the partition function as

$$Z = \sum_{i\alpha} \langle i\alpha | e^{-\beta\mathcal{H}} | i\alpha \rangle = \sum_{i\alpha} \sum_{m=0}^{\infty} \langle i\alpha | (-\beta\mathcal{H})^n / n! \, | i\alpha \rangle, \tag{2}$$

where i is the position of the hole and α is the spin configuration, we can see using Eq. (1) that a term of order n in Eq. (2) can be found by finding the total number of paths in which in n hops the hole returns to the site i and at the same time returns the spins to their original configuration α. It is easy to see that for simple-cubic (sc) and bcc lattices only even terms contribute to Eq. (2) and hence all terms are positive. For a fcc lattice, all terms are positive if $h > 0$. We will assume all terms positive in this discussion. If we have N_h "holes" in the system whose concentration is sufficiently small that their paths do not intersect (i.e., $N_h \ll N_a$, the number of atoms), Eq. (2) becomes

$$Z = \sum_{\{i\}\alpha} \left\langle \{i\}\alpha \left| \prod_{l=1}^{N_h} \sum_{n_l} \frac{(-\beta\mathcal{H})^{n_l}}{n_l!} \right| \{i\}\alpha \right\rangle, \tag{3}$$

where $\{i\}$ denotes the locations of the N_h holes. (This is easily shown by dividing the hops contributing to the nth-order term among the N_h holes in all possible ways.) Since we expect the Curie temperature to be small for very low densities, we will consider $KT \ll h$ in this discussion. Each factor in

the product over l in Eq. (3) will give a contribution equal to the number of paths of a "hole" which in the end return the hole to its original site and return the spins of the system to their original configuration after n_l hops. As pointed out in Ref. 5 (in which we treat this same system away from the $N_h \ll N_a$ limit) when the "hole" paths do overlap, there are also exchange paths in which two or more "holes" exchange places. Each exchange path which involves interchange of an odd number of "holes" will appear with a negative sign for the fermion case and will be equal in magnitude to at least one of the nonexchange paths. For example, it will be equal to a path in which one hole travels over the same sites as in the exchange path and the other holes remain stationary. Thus, each "exchange"-path contribution will cancel one nonexchange-path contribution, and thus the remaining nonexchange-path contributions will all be positive. Using Eq. (9) in Ref. 5 and performing a saddle point integration over the $\vec{k}$'s, we find at low temperatures for all spins aligned for fermions

$$Z \cong \exp[\beta \textstyle\sum_{\vec{k}} \epsilon(\vec{k})], \tag{4}$$

where the summation is taken over the N_h lowest values of $\vec{k}$. For small hole densities, this becomes

$$Z \cong \exp\{\beta[N_h z h - N_h \tfrac{3}{5}(3/4\pi)^{2/3}\, hbC^{2/3}]\}, \tag{5}$$

where C is the "hole" concentration ($C = N_h/N_a$) and $b = (2\pi)^2$ for sc and $4(2\pi)^2$ for fcc and bcc lattices. This approximation is good if KT is much less than the height of the Fermi level. When all spins are aligned, all paths which return the holes to their original configuration contribute. For the paramagnetic state, in which all electron spins are not the same, since only paths in which the spins are returned to their original configuration in the end are allowed, there are fewer paths. Hence, the contribution to each term in the expansion of Z in powers of β in Eq. (3) before taking the trace over spin configurations is smaller in a nonmagnetic state than in the ferromagnetic state. This expansion must then be summed and multiplied by 2^{N_e}, the number of spin configurations of net spin equal to zero. (N_e is the number of electrons in the system.) At sufficiently low temperatures, the difference in the contributions to Z obtained by summing the total number of possible paths without taking the trace in the ferromagnetic and paramagnetic states becomes sufficiently large to make the partition function for the ferromagnetic state dominate over that for the paramagnetic state. Thus if N_a is finite, the system becomes ferromagnetic at sufficiently low T. Strictly speaking, T only has the meaning of temperature in an infinite system. What we have obtained thus far is an alternate proof that the system has a ferromagnetic ground state, which is easier to see through physically than Nagaoko's proof. In this proof, we can see that ferromagnetism comes about because of a reduction in the number of possible "hole" paths in a nonferromagnetic state. In the thermodynamic limit, the fact that the ground state is ferromagnetic does not lead to long-range ferromagnetic order for $T \neq 0$ in a two-dimensional lattice, [6] but short-range order is possible. In three dimensions, the system most likely does order since the spin fluctuations discussed in Ref. 6 are probably not sufficient to destroy the magnetic order at low temperatures. This can be seen roughly by considering that the low-lying excitations of the system involving spin flip are spin waves, whose energy goes as the square of the wave vector, [2] which leads to the well-known $T^{3/2}$ reduction in the magnetization in three dimensions at low temperatures (i.e., $T < T_c$). Thus, ferromagnetism does exist in three dimensions at nonzero temperatures.

In the case of bosons with spin, if we divide the system into a few large, completely ferromagnetic regions each having different spin (e.g., two regions, one of spin up and one of spin down) and place the "holes" in one of these regions, the number of paths of n hops of each "hole" will approach the value that it would have if all spins were aligned, as we take the thermodynamic limit. (Remember that each such region becomes infinitely large in this limit.) Thus, the partition function will have the same value as it did in the ferromagnetic state, or larger and therefore, there will be no ferromagnetism in the thermodynamic limit for bosons. In the case of fermions, we cannot pack many "holes" into the same region of "volume" because the exchange paths, in which two "holes" exchange places, will reduce the partition function since they contribute with a negative sign in Eq. (2), thus making Z lower than if they were not confined to specific regions.

It is possible to obtain an upper bound to the Curie temperature. Consider the system to be in a state not having all spins aligned. At low temperatures, the contributions which dominate Z in Eq. (3) will be from those spin arrangements in which each "hole" is surrounded by electrons having the same spin. Actually, if the regions are cubic, then the energy is lowest if there are two "holes" in such a same-spin region, but the results are not changed significantly by assuming one electron in each region. These arrangements can be shown to give the lowest "hole" energy, as they give rise to so-called "band-tail" states. [7] The electrons are divided evenly among the holes, and each hole will be taken to be at the center of a cube containing C^{-1} electrons, where $C = N_h/N_a$. Consider the n_eth-order term in Eq. (7) of Ref. 5. Clearly, if n_l is less than $\frac{1}{2}C^{-1/3}$, the small radius of such a cube, the result for that term will be the same as in the state

with all spins aligned. Then, the n_lth-order term gives a contribution

$$\sum_{\vec{k}} \frac{1}{n_l!} \beta^{n_l} \epsilon(\vec{k})^{n_l},$$

which is dominated by the $\vec{k}=0$ term,

$$\frac{1}{n_l!}(\beta z h)^{n_l} \tag{6}$$

as $T \to 0$. For $\beta h \gg 1$, the summation over n_l is dominated by the term $n_l = \beta h z$, with a standard deviation $\simeq (\beta h z)^{1/2}$, where z is the number of near neighbors. (This is because the terms in the summation represent essentially a Poissen distribution.) Hence, the system will certainly become paramagnetic above a temperature given by

$$\beta z h = \tfrac{1}{2} C^{-1/3}$$

or

$$KT_C = 2hzC^{1/3}. \tag{7}$$

An approximate lower limit can be placed on T_C as follows: Assume that in the paramagnetic state each hole is surrounded by αC^{-1} same-spin electrons, where $0 < \alpha < 1$. We proceed as in Eq. (7) of Ref. 5. Once n_l becomes greater than the radius of this region containing αC^{-1} holes, there are restrictions on the summation in Eq. (7) of Ref. 5. To get an estimate on the lower bound to T_c, let us assume for simplicity that the "hole" cannot hop out of this region. Although this reduces the number of possible "hole" paths more than is necessary, this can be made up for by increasing the size of the region slightly (i.e., increasing α). This restriction is equivalent to a boundary condition that the "hole" wave function vanish at the boundary of the region. Then expressing h_{ij} as in Ref. 5, with the Fourier series defined on this region with αC^{-1} electron sites, we must obtain for each factor in the product over l in Eq. (3) the result for a particle in a box containing αC^{-1} sites which is, if $\alpha C^{-1} \gg 1$,

$$\exp\{\beta h z[1 - (a/z)(C/\alpha)^{2/3}]\} \tag{8}$$

for $\beta h \gg 1$, where a is a numerical factor depending on the shape of the region $\{-hz[1-(a/z)(C/\alpha)^{2/3}]$ is the lowest "hole" energy$\}$. We proceed in the same way for the other holes, take the product of the results, and multiply by the number of possible spin arrangements consistent with each hole being surrounded by αC^{-1} same-spin sites. (This includes counting all possible directions of the total spins of these regions and all possible spin arrangements of the spins not in the regions.) The final result is

$$Z = (\alpha/C)^{N_a C} 2^{N_a(1-\alpha)} \exp\{\beta N_a C[1-(a/z)(C/\alpha)^{2/3}]hz\}. \tag{9}$$

To obtain a lower bound for T_c, we set Eq. (9) equal to Eq. (5). Then we obtain

$$KT_c = \frac{Cha(C/\alpha)^{2/3} - \frac{3}{5}(3/4\pi)^{2/3} hbC^{5/3}}{C\ln(\alpha/C) + (1-\alpha)\ln 2}$$

$$\gtrsim \frac{hC^{5/3}}{\ln 2}[a - \tfrac{3}{5}(3/4\pi)^{2/3} b]. \tag{10}$$

Since spherical regions seem to give the lowest ground-state energy for this particle in a box problem, we use the value of a for a spherical region, i.e., $a = \frac{1}{4}(4\pi/3)^{2/3} b$. In setting Eq. (9) equal to Eq. (5), we have made two errors which have opposite effects on Z. First of all, KT_c is not much smaller than the Fermi energy; rather they are of the same order of magnitude. Then, Eq. (4) gives a partition function for the completely ferromagnetic state at T_c which is too small. Second, the system is certainly not completely magnetically ordered just below T_c, as assumed here. This error makes Z too large. Nevertheless, Eq. (10) should still be a good order of magnitude estimate of T_c for low "hole" concentrations, i.e., a nearly half-filled band.

The assumption used in this calculation that each hole is surrounded by a sphere of same-spin electrons will break down when the second term in the exponent of Eq. (8) is equal to or greater than one-half the first. At this point the treatment in Ref. 5 becomes a better approximation. By a simple calculation we find that this occurs when $C \approx 0.02$ for sc, bcc, and fcc lattices.

If instead of having misaligned spins we had impurities with infinite potentials, the holes would be restricted to nonimpurity sites which is a more restrictive set of paths than we have in this paper. But both in the Hubbard model and the impurity problem, the restriction of particles to certain paths in the lattice results in eigenvalues which cannot be labeled by a wave vector $\vec{k}$. In the case of the infinite-U Hubbard model, unlike the impurity problem, it is not a potential alone which restricts the hole's motion, but rather the requirement that all spins be returned to their original configuration in the calculation of the partition function or Green's function.

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ence is $\langle\{S^+(-\vec{q}), [\mathcal{H}, S^-(\vec{q})]\}\rangle$, which can be found using Eq. (1) of this paper to go as q^2. This implies that there is no long-range order in two dimensions.

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Electric-Field-Induced Quadrupole Splittings of Li^7 Nuclear Magnetic Resonance in KCl: Li^+†

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The electric-field-induced quadrupole splitting of the nuclear magnetic resonance of the off-center impurity ion Li^7 has been observed in KCl: Li^+. Observations of the dependence of the quadrupole splitting upon applied electric field in the [110] direction and upon orientation of the dc magnetic field confirm the value of the quadrupole coupling constant determined by Alderman and Cotts as well as the ⟨111⟩ tunneling model for the Li ion.

Before the observation[1] of stress-induced quadrupole splitting of Li^7 NMR in KCl: Li^+, an unsuccessful attempt was made to observe the splittings induced by a static electric field. Since the completion of the stress experiment and in view of other experiments[2,3] which demonstrate the validity of the ⟨111⟩ tunneling model of Gomez, Bowen, and Krumhansl[4] (GBK), efforts to observe the electric-field-induced splitting were resumed. We have now observed this splitting in samples prepared with special care and annealed to keep internal strains to a minimum.

The functional form of the energy levels of the Li^+ ion in KCl with an electric field applied has been calculated by a number of authors.[2-6] The electric field term in the Hamiltonian is $\mathcal{H}_E = -\vec{\mu}\cdot\vec{E}_0$, where $\vec{\mu}$ is the electric dipole moment of the off-center Li^+ ion and $\vec{E}_0$ is the applied field. The most accurate measure of $\vec{\mu}$ and Δ, the level spacing of the ground-state multiplet, has been made by Herendeen and Silsbee who find, for Li^7, $\vec{\mu} = 5.6 \pm 0.2 \times 10^{-18}$ esu cm and $\Delta = 0.77 \pm 0.03$ cm^{-1}.

The expected value of the electric-field-induced quadrupole splitting is calculated using the same formalism given in Alderman and Cotts.[1] The average value of the electric-field-gradient (EFG) tensor in the crystal axis coordinate system is

$$\langle\overleftrightarrow{V}'\rangle = Z^{-1}\sum_\mu e^{-E_\mu/kT}\,V'_\mu\,, \qquad (1)$$

where

$$Z = \sum_\mu e^{-E_\mu/kT}\,,$$

$$\overleftrightarrow{V}'_\mu = \int \Psi^*_\mu(\vec{r})\,\overleftrightarrow{V}'(\vec{r})\,\Psi_\mu(\vec{r})\,d^3r\,,$$

and the $\Psi_\mu(\vec{r})$ are the exact eigenfunctions of the impurity-ion wave function in the presence of an electric field. The Ψ_μ can be expressed in terms of the basis state functions ψ_n of the ⟨111⟩ tunneling model of GBK:

$$\Psi_\mu = \sum_n c_{n\mu}\psi_n\,, \qquad (2)$$

where n is summed over the eight well sites. The EFG tensor $\overleftrightarrow{V}'(\vec{r})$ is the sum of well-site tensors V'_n which have been transformed to a common coordinate system, the crystal axes (x', y', z') shown in Fig. 1. As in other work, it is assumed that the ψ_n are highly localized on each well site and only the "edge" overlap integrals[4] are important in the ground-state multiplet. The experiment is done for only one direction of the applied field $\vec{E}_0$ parallel to the [110] direction. Solutions to the ⟨111⟩ tunneling model predict that at sufficiently low temperatures a nonzero $\langle\overleftrightarrow{V}'\rangle$ is predicted. In addition, the resulting quadrupole splittings depend upon the direction of $\vec{E}_0$ and the applied dc magnetic field used in the nuclear-magnetic-resonance (NMR) ex-

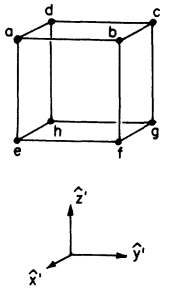

FIG. 1. Crystal axis coordinate system (x', y', z') and ⟨111⟩ potential well sites symmetrically located about vacant cation lattice site. Site labels are the same used by Gomez *et al.* in Ref. 4.