Atomic Limit and Projected Hubbard Models for a Linear Chain

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The Hubbard model in the limit of infinite intrasite interaction and a related projected Hubbard model, which includes this extreme limit, are considered. This projected model is that portion of the full Hubbard model which preserves the number of sites of each possible occupancy, 0, 1, and 2. For the linear case, this projected model is solved exactly, both for the eigenvalue spectrum and the static thermodynamic properties. A second-order phase transition is found.

I. INTRODUCTION

The Hubbard model has[1] found wide use in the theoretical description of electronic states in magnetic insulators. It involves a matrix element Δ for electron transfer between neighboring sites and an intrasite Coulomb repulsion matrix element I. For a linear chain of N sites, the Hamiltonian takes the form

$$H=\Delta\sum_{n=1}^{N-1}\sum_{\sigma}(a_{n\sigma}^{\dagger}a_{n+1,\sigma}+a_{n+1,\sigma}^{\dagger}a_{n\sigma}) +I\sum_{n=1}^{N}a_{n\alpha}^{\dagger}a_{n\alpha}a_{n\beta}^{\dagger}a_{n\beta}\,, \qquad (1.1)$$

where $a_{n\sigma}^{\dagger}$ and $a_{n\sigma}$ are fermion creation and annihilation operators for an electron of spin $\sigma=\alpha,\ \beta$ on site n. When $|\Delta|\ll I$, we say we are near the so-called *atomic limit* in which $I\to\infty$. When $\Delta=0$ there generally is not only a high degree of spin or permutation degeneracy, but also a great deal of orbital degeneracy. These degeneracies are largely lifted for finite nonzero values of the intersite and intrasite interactions, Δ and I. Even for $I\to\infty$, $\Delta\neq 0$ much of the degeneracy is[2] lifted. The band energies can vary linearly with the strength Δ of the hopping term, regardless of how much greater the band separation I is. Such properties of this $I\to\infty$, $\Delta\neq 0$ atomic limit render it of special interest. The existence of ferromagnetism for certain lattices has been indicated[3] through the use of perturbation techniques. Moment analyses[2] have helped demonstrate the varying degrees of inadequacy of a number of the conventional many-body solutions near this atomic limit. Numerous Green's-function decoupling schemes have been studied[4] for application to this limit. A few other studies have been made[5,6] in this limit, and some exact results[7] for arbitary Δ and I, but severely restricted numbers of electrons and/or temperature, also apply here.

Here we consider a projected Hubbard Hamiltonian which includes the special $I\to\infty$, $\Delta\neq 0$ case. We let $\mathcal{P}(N_0,N_1,N_2)$ be the projector onto the space with N_0 unoccupied sites, N_1 singly occupied sites, and N_2 doubly occupied sites. Then we define the *projected* Hubbard Hamiltonian

$$H^0\equiv H^{00}+V^0,$$
$$H^{00}\equiv\Delta\sum_{N_0N_1N_2}\mathcal{P}(N_0,N_1,N_2)\sum_{n=1}^{N-1}\sum_{\sigma}(a_{n\sigma}^{\dagger}a_{n+1,\sigma}+a_{n+1,\sigma}^{\dagger}a_{n\sigma})\mathcal{P}(N_0,N_1,N_2), \qquad (1.2)$$
$$V^0\equiv I\sum_{n=1}^{N}a_{n\alpha}^{\dagger}a_{n\alpha}\ a_{n\beta}^{\dagger}a_{n\beta}\ .$$

This projected model H^0 evidently preserves the number of sites with a given occupation number. That is, the usual charge transfer interactions of the full Hubbard model which carry an electron from a doubly occupied site to an unoccupied site are excluded. This projected Hubbard model is then expected to be similar to the full Hubbard model solutions in regimes where there are either very few doubly occupied sites or very few unoccupied sites. Hence, this regime of similarity should include the case when $|\Delta|/I$ is very small and the number of electrons differs significantly from the number of sites.

The projected model has been[6] diagonalized exactly in the $N_2=0$ subspace (where V^0 is effectively zero). In Sec. II we extend this work to obtain the complete eigenvalue spectrum of H^0. In Secs. III and IV we proceed to evaluate the static thermodynamic properties of the projected model. For suitable values of Δ and I and appropriate numbers of electrons a second-order phase transition is found, despite the one-dimensional short-range nature of the model. For fewer electrons than sites one finds a single phase with very few doubly occupied sites on one side on the transition point. On the other side of this point a second phase with many doubly occupied sites and few unoccupied ones is found to condense out.

II. EXACT EIGENSOLUTIONS

We denote N as the number of sites, N_i as the number of sites with occupancy i $(=0,1,2)$, N_e as the number of electrons, and N' as the number of nonsingly occupied sites. We expect $N=N_0+N_1$

$+N_2$, $N_e = N_1 + 2N_2$, and $N' = N_0 + N_2$. The basis kets for our calculation are to be single determinants. Each of these basis kets is then uniquely labeled by a set of indices

$$\begin{aligned}\vec{n} &\equiv (n_1, n_2, \ldots, n_N),\\ \vec{p} &\equiv (p_1, p_2, \ldots, p_{N'}),\\ \vec{\sigma} &\equiv (\sigma_1, \sigma_2, \ldots, \sigma_{N_1}),\end{aligned} \tag{2.1}$$

where

$$n_i \equiv \begin{cases} 0, & \text{site } i \text{ is nonsingly occupied} \\ 1, & \text{site } i \text{ is singly occupied;} \end{cases}$$

$$p_i \equiv \begin{cases} 0, & i\text{th nonsingly occupied site is empty} \\ 2, & i\text{th nonsingly occupied site has 2 electrons;} \end{cases} \tag{2.2}$$

$$\sigma_i \equiv \begin{cases} \alpha, & i\text{th singly occupied site has up-spin} \\ \beta, & i\text{th singly occupied site has down-spin.} \end{cases}$$

The basis kets are thus expressed as $|\vec{n}; \vec{p}; \vec{\sigma}\rangle$, and the total vector space can be broken up into subspaces $\upsilon(N_0, N_1, N_2)$, with N_0, N_1, and N_2 being exact quantum numbers. For example, in the two-site case we have

$$\begin{aligned}&\upsilon(2,0,0): \{|00;00;\rangle\},\\ &\upsilon(1,1,0): \{|10;0;\sigma\rangle, |01;0;\sigma\rangle; \sigma = \alpha, \beta\},\\ &\upsilon(1,0,1): \{|00;02;\rangle, |00;20;\rangle\},\\ &\upsilon(0,2,0): \{|11;;\sigma\tau\rangle; \sigma, \tau = \alpha, \beta\},\\ &\upsilon(0,1,1): \{|10;2;\sigma\rangle, |01;2;\sigma\rangle; \sigma = \alpha, \beta\},\\ &\upsilon(0,0,2): \{|00;22;\rangle\}.\end{aligned} \tag{2.3}$$

To complete the description of the basis kets we specify a phase convention which shall prove convenient. The kets $|\vec{n}; \vec{p}; \vec{\sigma}\rangle$ are formed by applying a product of $a^\dagger_{n\sigma}$ creation operators to the vacuum with $a^\dagger_{m\sigma}$ to the left of $a^\dagger_{n\tau}$ if $m < n$; in the case in which both $a^\dagger_{n\alpha}$ and $a^\dagger_{n\beta}$ occur in the product, we place $a^\dagger_{n\alpha}$ to the left, or right, of $a^\dagger_{n\beta}$ as n is odd, or even. As an example, the basis kets for $\upsilon(0,1,1)$ are

$$\left.\begin{aligned}|01;2;\sigma\rangle &\equiv a^\dagger_{1\alpha} a^\dagger_{1\beta} a^\dagger_{2\sigma} |0\rangle \\ |10;2;\sigma\rangle &\equiv a^\dagger_{1\sigma} a^\dagger_{2\beta} a^\dagger_{2\alpha} |0\rangle\end{aligned}\right\} \sigma = \alpha, \beta, \tag{2.4}$$

and the basis kets for $\upsilon(1,1,0)$ are

$$\left.\begin{aligned}|01;0;\sigma\rangle &\equiv a^\dagger_{2\sigma} |0\rangle \\ |10;0;\sigma\rangle &\equiv a^\dagger_{1\sigma} |0\rangle\end{aligned}\right\} \sigma = \alpha, \beta. \tag{2.5}$$

Having introduced the notation we now check to see how the Hamiltonian H^0 acts on these basis kets. The V^0 term of (1.2) acts very simply on the basis kets, just giving IN_2 times the same basis ket back. The H^{00} term gives zero unless it can move an electron without changing N_2; that is, it gives zero unless a singly occupied site is adjacent to a nonsingly occupied site. Thus for the two-site case, H^{00} gives zero unless the basis ket is in $\upsilon(1,1,0)$ or $\upsilon(0,1,1)$. For the basis kets (2.4) of $\upsilon(0,1,1)$ we have

$$\begin{aligned}H^{00}|01;2;\sigma\rangle &= \Delta a^\dagger_{2,-\sigma} a_{1,-\sigma} a^\dagger_{1\alpha} a^\dagger_{1\beta} a^\dagger_{2\sigma} |0\rangle \\ &= \Delta |10;2;\sigma\rangle,\\ H^{00}|10;2;\sigma\rangle &= \Delta a^\dagger_{1,-\sigma} a_{2,-\sigma} a^\dagger_{1\sigma} a^\dagger_{2\beta} a^\dagger_{2\alpha} |0\rangle \\ &= \Delta |01;2;\sigma\rangle.\end{aligned} \tag{2.6}$$

For the basis kets (2.5) of $\upsilon(1,1,0)$ we have

$$\begin{aligned}H^{00}|01;0;\sigma\rangle &= \Delta a^\dagger_{1\sigma} |0\rangle = \Delta |10;0;\sigma\rangle,\\ H^{00}|10;0;\sigma\rangle &= \Delta a^\dagger_{2\sigma} |0\rangle = \Delta |01;0;\sigma\rangle.\end{aligned} \tag{2.7}$$

In fact, since the intersite interactions only involve transfer between nearest-neighbor pairs we see that for general N the H^{00} operator does not affect the $\vec{p}$ or $\vec{\sigma}$ indices in the basis kets. It is this property of the open one-dimensional chain with nearest-neighbor interactions which enables our solution.

We define operators $c^\dagger_j$ and c_j which act only on the $\vec{n}$ indices in the basis kets

$$\begin{aligned}c^\dagger_j |\vec{n}; \vec{p}; \vec{\sigma}\rangle &\equiv \delta(n_j, 0) \exp\left(i\pi \sum_{k=1}^{j-1} n_k\right) \\ &\quad \times |n_1, \ldots, n_j + 1, \ldots, n_N; \vec{p}; \vec{\sigma}\rangle,\\ c_j |\vec{n}; \vec{p}; \vec{\sigma}\rangle &\equiv \delta(n_j, 1) \exp\left(i\pi \sum_{k=1}^{j-1} n_k\right) \\ &\quad \times |n_1, \ldots, n_j - 1, \ldots, n_N; \vec{p}; \vec{\sigma}\rangle.\end{aligned} \tag{2.8}$$

$c^\dagger_j$ and c_j are apparently fermion creation and annihilation operators. However, in their definition additional nonphysical kets $|\vec{n}; \vec{p}; \vec{\sigma}\rangle$, for which the sum of the n_i in $\vec{n}$ is different from the number of σ_j in $\vec{\sigma}$, and for which the number of zeroes in $\vec{n}$ is different than the number of p_j in $\vec{p}$, are implicitly introduced. These $c^\dagger_j$ and c_j thus do not represent the creation or annihilation of any conventional electronic orbital. Now a product as $c^\dagger_i c_j$ does not mix physical and nonphysical kets. Further in the physical space, $c^\dagger_i c_j$ merely represents the transfer of an electron from a singly occupied site j to a site i singly occupied after the operation. Indeed it is seen that

$$H^{00} \approx \Delta \sum_{j=1}^{N-1} (c^\dagger_j c_{j+1} + c^\dagger_{j+1} c_j), \tag{2.9}$$

at least when the right-hand side is restricted to the physical spaces. The nonphysical spaces in principle offer no problem, since the projected Hamiltonian H^0 does not mix physical and nonphysical spaces, and one may simply discard the nonphysical solutions.

The V^0 operator acts only on the $\vec{p}$ indices and

then only in the manner of a number operator. Thus to solve H^0 all one need do is diagonalize the quadratic H^{00} by a suitable[8] canonical transformation. Noting that the matrix

$$\underline{\Delta}_{ij} \equiv \Delta(\delta_{i-1,j} + \delta_{i,j-1}) \tag{2.10}$$

is simply diagonalized,[9]

$$\sum_{jk} \underline{U}^*_{ji} \underline{\Delta}_{jk} \underline{U}_{kl} = \delta_{il} \epsilon_i ,$$

$$\epsilon_i = 2\Delta \cos \pi l/(N+1), \tag{2.11}$$

$$\underline{U}_{jk} = [2/(N+1)]^{1/2} \sin \pi jk/(N+1),$$

we obtain

$$H^{00} = \sum_{il} c_i^\dagger \underline{\Delta}_{il} c_l = \sum_j \epsilon_j \xi_j^\dagger \xi_j . \tag{2.12}$$

Here we have defined the canonical creation operators

$$\xi_j^\dagger \equiv \sum_i \underline{U}_{ij} c_i^\dagger . \tag{2.13}$$

The eigenvalues spectrum for H^0 is

$$E_{\vec{j}}^0(N_0, N_1, N_2) = N_2 I + 2\Delta \sum_j^{\text{occ}} \cos \frac{\pi j}{N+1} , \tag{2.14}$$

where $\vec{j}$ indicates the occupancy scheme, which for the physical states involves occupying N_1 of the c orbitals.

From (2.14) we see that a simple band picture describes the eigenvalue spectrum of the projected Hamiltonian H^0. The band structure is independent of the number N_2 and positions of doubly occupied sites. The degree of occupancy in the band is determined solely by the number of singly occupied sites.

In the limit of an infinite number N of sites we find it convenient to define

$$r_i \equiv N_i/N, \quad i = 0, 1, 2, e,$$
$$\theta \equiv \pi j/N, \tag{2.15}$$

so that the energy expression becomes

$$E_{\vec{j}}^0(N_0, N_1, N_2) = N_2 I + 2\Delta \frac{N}{\pi} \int_{\text{occ}} \cos\theta \, d\theta . \tag{2.16}$$

For the lowest-lying state of a given N_2 we thus have

$$E_0^0(N_0, N_1, N_2) = N_2 I - 2|\Delta| (N/\pi) \sin r_1 \pi . \tag{2.17}$$

These solutions of (2.17) include the ground-state solution with $N_2 = 0$ as obtained previously.[6] Further we note that the eigenvalue spectrum (2.16) is independent of the sign of Δ, so that from now on we choose $\Delta \geq 0$.

III. THERMODYNAMICS IN ATOMIC LIMIT

We consider the limit in which intrasite Coulomb repulsion I becomes infinite. The number of doubly occupied sites is then a minimum. First we take the number of electrons to be less than the number of sites so that $N_2 = 0$. The grand-canonical partition function is

$$\Xi^{00} = \sum_{N_0 N_1}{}' 2^{N_1} \sum_{\vec{j}}^{\text{occ}}{}' \exp[-\beta E_{\vec{j}}^0(N_0, N_1, 0) + \beta\mu^{00} N_1], \tag{3.1}$$

where μ^{00} is the chemical potential and 2^{N_1} is the spin degeneracy of a level with N_1 electrons. The $\vec{j}$ and $N_0 N_1$ summations in (3.1) are to go only over the physical states. In general for a given N_0 and N_1, there are many nonphysical c-orbital occupation schemes; however, for every c-orbital occupation scheme there is a value for N_0, N_1 that is physical. Letting M different c orbitals be occupied, we see that the physical choice is $N_1 = M$, $N_0 = N - N_1$. Thus, in the partition function (3.1) we may sum over all c-orbital occupation schemes if we change N_0 and N_1 in the proper manner at the same time. Hence,

$$\Xi^{00} = \sum_{\vec{j}}^{\text{occ}} 2^{N_1} \exp[-\beta E_{\vec{j}}^0(N_0 N_1 0) + \beta\mu^{00} N_1]$$
$$= \text{Tr}[2^{N_1} \exp(-\beta H^{00} + \beta\mu^{00} \hat{N}_1)], \tag{3.2}$$

where this time the $\vec{j}$ sum is unrestricted and the trace is over all c-orbital occupation schemes. Also $\hat{N}_1 \equiv \sum_{j=1}^N c_j^\dagger c_j$ is the c-orbital number operator.

Evidently, we may treat much of the present problem in the same way as that for N fermion c-orbitals with a Hamiltonian as in (2.12). In the present case, $\mu^{00} + \ln 2/\beta$ appears in place of the chemical potential in the usual fermion property formulas which are linear in the density matrix. In computing the entropy in the present case we note that there are 2^{N_1} levels with an occupation scheme $\vec{j}$ with N_1 occupied c orbitals, and the probability of any one of these levels being occupied is

$$(\Xi^{00})^{-1} \exp[-\beta E_{\vec{j}}^0(N_0 N_1 0) + \beta\mu^{00}], \tag{3.3}$$

so that this simple replacement is modified for the entropy, or free energy. The internal energy, free energy, entropy, specific heat, and average particle numbers per site are, respectively,

$$\bar{E}^{00} = -\frac{2\Delta}{\pi} \int_0^\pi \cos\theta [1 + \tfrac{1}{2} \exp(2\Delta\beta\cos\theta - \beta\mu^{00})]^{-1} d\theta ,$$

$$F^{00} = \bar{r}_1^{00} \mu^{00} - \frac{1}{\pi\beta} \int_0^\pi \ln[1 + 2\exp(\beta\mu^{00} - 2\Delta\beta\cos\theta)] d\theta ,$$

$$S^{00} = \beta k_B \bar{E}^{00} - \beta k_B F^{00}, \tag{3.4}$$

$$C^{00} = 2\Delta^2 \beta^2 (g_2 - g_1^2/g_0),$$

$$\bar{r}_1^{00} = \frac{1}{\pi} \int_0^\pi [1 + \tfrac{1}{2} \exp(2\Delta\beta\cos\theta - \beta\mu^{00})]^{-1} d\theta .$$

Here k_B is Boltzmann's constant, and we have defined

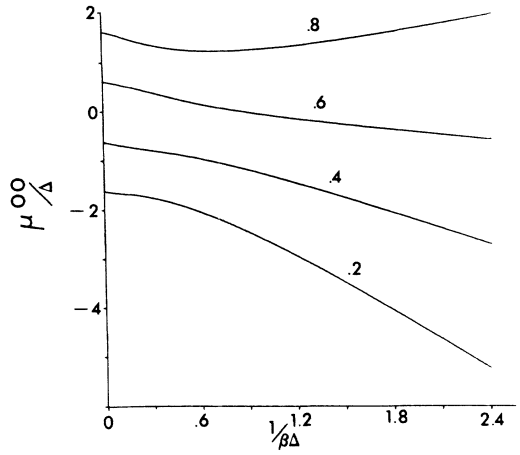

FIG. 1. Chemical potential vs temperature for particle densities 0.2, 0.4, 0.6, and 0.8.

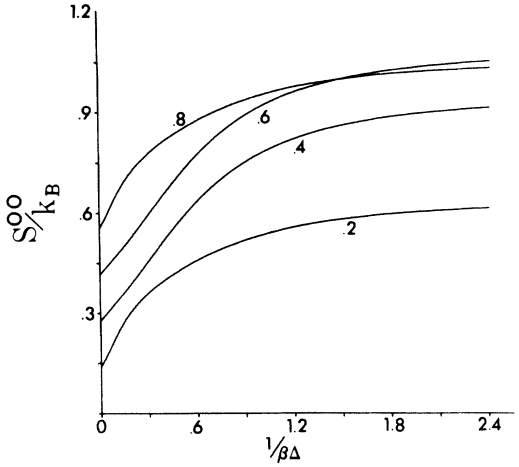

FIG. 3. Entropy vs temperature for particle densities 0.2, 0.4, 0.6, and 0.8.

$$g_m \equiv \frac{1}{\pi}\int_0^{\pi} \cos^m\theta[1+\tfrac{1}{2}\exp(2\Delta\beta\cos\theta-\beta\mu^{00})]^{-2} \times\exp(2\Delta\beta\cos\theta-\beta\mu^{00})\,d\theta. \quad (3.5)$$

We have also taken the infinite site limit $N\to\infty$.

At selected average particle densities $\bar{r}_1^{00}$, the numerical solution of Eqs. (3.4) for the thermodynamic properties is depicted in Figs. 1–5. We see that there is a particle-hole type of symmetry with respect to the c orbitals so that the internal energy and specific heat are identical for $\bar{r}_1^{00}$ and $1-\bar{r}_1^{00}$. The entropy also has this same symmetry except for a constant $\bar{r}_1^{00}\ln 2$ included in its expression. We also note that the average deviation of the number of electrons in our system away from the mean $\bar{r}_1^{00}N$ is

$$\{(\Xi^{00})^{-1}\mathrm{Tr}[(\hat{N}_1-\bar{r}_1^{00}N)^2 2^{\hat{N}_1}\exp(-\beta H^{00}+\beta\mu^{00}\hat{N}_1)]\}^{1/2} = \left((\bar{r}_1^{00}N)^2-\frac{N}{\pi}\int_0^{\pi}[1+\tfrac{1}{2}\exp(2\Delta\beta\cos\theta-\beta\mu^{00})]^{-2}\,d\theta\right)^{1/2}. \quad (3.6)$$

This typical result that the fluctuations of the particle density away from $\bar{r}_1^{00}$ are only of the order of $1/\sqrt{N}$ will be used in Sec. IV.

The more than half-filled case with $N_0=0$ and $N_2\neq 0$ is simply related to the preceding results of this section, because of the particle-hole symmetry with respect to the original a orbitals. In the same way we found (3.2) we also find

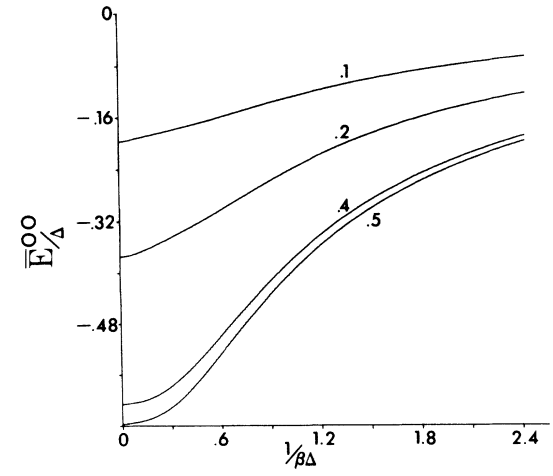

FIG. 2. Internal energy vs temperature for particle densities $\bar{r}_1^{00}=0.1$, 0.2, 0.4, and 0.5. The results at particle densities of $1-\bar{r}_1^{00}$ are identical.

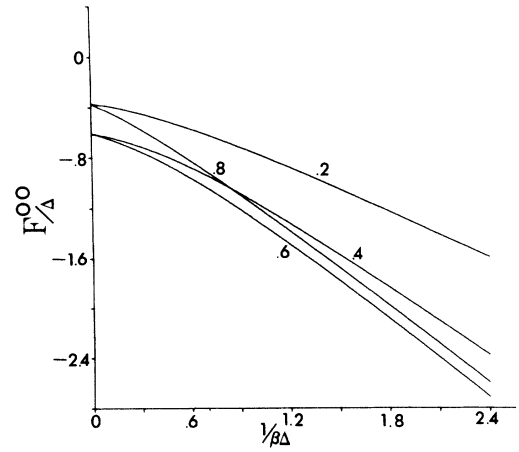

FIG. 4. Free energy vs temperature for particle densities 0.2, 0.4, 0.6, and 0.8.

$$\Xi^{00}=\sum_{\vec{j}}^{\text{occ}} 2^{N_1}\exp[-\beta E^0_{\vec{j}}(0,N_1,N_2)+\beta\mu^{00}(N_1+2N_2)]=\sum_{\vec{j}}^{\text{occ}} 2^{N_1}\exp[-\beta E^0(N-N_1,N_1,0)$$

$$-\beta(N-N_1)I+\beta\mu^{00}(2N-N_1)]=\exp[N\beta(2\mu^{00}-I)]\,\mathrm{Tr}[2^{\hat{N}_1}\exp(-\beta H^{00}+\beta I\hat{N}_1-\beta\mu^{00}\hat{N}_1)]. \quad (3.7)$$

At a given value of $\bar{r}_1^{00}$ we let $\mu_>^{00}$ and $\mu_<^{00}$ denote the chemical potentials for the more than and less than half-filled cases. We then see that

$$I-\mu_>^{00}=\mu_<^{00}. \quad (3.8)$$

For the more than half-filled case, $N_1=0$ and $N_2\neq 0$, one simply adds $(1-\bar{r}_1^{00})I$ to the internal and free energies of (3.4); the entropy and specific-heat expressions remain the same

IV. THERMODYNAMICS FOR PROJECTED MODEL

We now lift the restriction that the intrasite Coulomb repulsion I be infinite, in which case both unoccupied and doubly occupied sites may arise. The grand canonical partition function is

$$\Xi^0=\sum_{N_0N_1N_2} 2^{N_1}\sum_{\vec{j}}^{\text{occ}\,\prime}\exp[-\beta E^0_{\vec{j}}(N_0,N_1,N_2)+\beta\mu^0(N_1+2N_2)]. \quad (4.1)$$

Again requiring only the physical states to be included in the sums, we obtain

$$\Xi^0=\sum_{N_2}\exp(2\beta\mu^0N_2-\beta N_2I)\times\mathrm{Tr}[2^{\hat{N}_1}\exp(-\beta H^{00}+\beta\mu^0\hat{N}_1)] \quad (4.2)$$

in a manner similar to that leading from (3.1) to (3.2). The trace in (4.2) is over different occupation schemes for the c orbitals, just as in (3.2). For exact equality in (4.2) we should restrict the trace to states with N_1 such that $N_e=2N_2+N_1$ is no greater than $2N$. However, the trace is dominated by states with single occupancy particle number N_1 within $1/\sqrt{N_1}$ of the optimal value determined by μ^0. Hence in the limit as N, $N_1\to\infty$, relation (4.2) should be exact. Since the term traced over in (4.2) is just an atomic-limit grand-partition function,

$$\Xi^0=\Xi^{00}\sum_{N_2}\exp[\beta(2\mu^0-I)N_2]$$

$$=\Xi^{00}\,\frac{\exp[\frac{1}{2}\beta(2\mu^0-I)N(1-\bar{r}_1^0)]-1}{\exp[\beta(2\mu^0-I)]-1}. \quad (4.3)$$

Here, approximating the lower and upper limits to the N_2 summation as 0 and $\frac{1}{2}N(1-\bar{r}_1^0)$, again entails errors $\sim\sqrt{N_1}$ in the exponent. This lower-limit approximation applies for the case with fewer electrons than sites; the corresponding lower-limit approximation of $N(\bar{r}_e^0-\bar{r}_1^0)$ applies for the case with more electrons than sites and may be developed in a similar manner.

The average density of doubly occupied sites is

$$\bar{r}_2^0=\frac{1}{N}(\Xi^0)^{-1}\sum_{N_0N_1N_2}N_2\,2^{N_1}\times\sum_{\vec{j}}^{\text{occ}\,\prime}\exp[-\beta E^0_{\vec{j}}(N_0,N_1,N_2)+\beta\mu^0(N_1+N_2)]$$

$$=\frac{1}{N}(\Xi^0)^{-1}\,\Xi^{00}\sum_{N_2}N_2\exp[\beta(2\mu^0-I)N_2]. \quad (4.4)$$

Now denoting

$$\bar{N}'\equiv\tfrac{1}{2}N(1-\bar{r}_1^0), \quad (4.5)$$

and carrying out the summation over N_2 from 0 to $\bar{N}'-1$, we obtain

$$\bar{r}_2^0=\frac{\exp[\beta(2\mu^0-I)\bar{N}']}{\exp[\beta(2\mu^0-I)\bar{N}']-1}\,\frac{\bar{N}'}{N}-\frac{\exp[\beta(2\mu^0-I)]}{\exp[\beta(2\mu^0-I)]-1}\,\frac{1}{N}. \quad (4.6)$$

If $2\mu^0-I$ is negative by a finite amount in the limit as $N\to\infty$ and $\bar{N}'\to\infty$, then $\bar{r}_2^0$ is seen to approach zero. On the other hand if $2\mu^0-I$ is positive by a finite amount, then the right-hand side of (4.6) is computed to approach $\bar{N}'/N=\frac{1}{2}(1-\bar{r}_1^0)$. Evidently, this double-occupancy density $\bar{r}_2^0$ behaves in qualitatively different manners for different signs of $2\mu^0-I$. Now if $2\mu^0-I$ approaches zero as N and $\bar{N}'\to\infty$, say

$$2\mu^0-I\to A/\beta\bar{N}', \quad (4.7)$$

with A/β finite, then we compute

$$\bar{r}_2^0\to\frac{1-\bar{r}_1^0}{2}\left(\frac{1}{1-e^{-A}}-\frac{1}{A}\right), \quad (4.8)$$

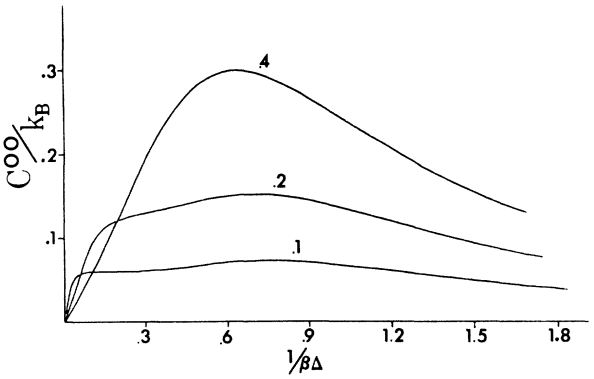

FIG. 5. Specific heat vs temperature for particle densities $\bar{r}_1^{00}=0.1$, 0.2, and 0.4. The results at particle densities of $1-\bar{r}_1^{00}$ are identical.

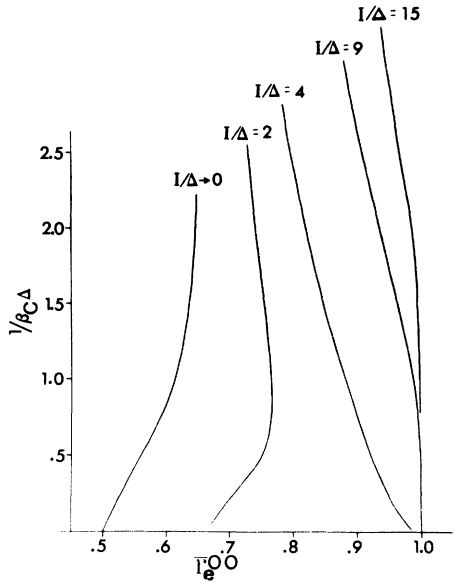

FIG. 6. Critical temperatures for the phase transition as a function of particle density $\bar{r}_e^0$ and interaction ratio I/Δ.

$$\langle r_2^2\rangle^0 \to \left(\frac{1-\bar{r}_1^0}{2}\right)^2\left[\frac{1}{1-e^{-A}}\left(1-\frac{2}{A}\right)+\frac{2}{A^2}\right] \neq (\bar{r}_2^0)^2 \quad .$$

Thus, if a temperature is approached when (4.7) applies, we see that there are large fluctuations in the double-occupancy density.

As a consequence of these considerations the behavior of the projected model is determined in terms of the atomic limit model of Sec. III. As long as the atomic-limit chemical potential μ^{00} is less than $\frac{1}{2}I$, we find $\bar{r}_2^0 = 0$ and $\mu^0 = \mu^{00}$, to order $1/\sqrt{N}$; hence, all the thermodynamic properties for the projected model are the same as those of Sec. III. Values of μ^0 greater than $\frac{1}{2}I$ by a finite amount are not allowed, since $\bar{r}_2^0 \to \frac{1}{2}(1-\bar{r}_1^0)$ and the number of electrons cannot be restricted to a sufficiently small value. Hence for values of $\mu^{00} \geq \frac{1}{2}I$ we expect μ^0 to equal $\frac{1}{2}I$ to order $1/\sqrt{N}$. When $\mu^{00} \geq \frac{1}{2}I$, the average number of particles may be constrained properly if $\mu^0 = \frac{1}{2}I$, although extreme fluctuations in the double-occupancy density appear. Evidently, then we have a phase transition at the temperature for which $\mu^{00} = \frac{1}{2}I$. This critical temperature is plotted in Fig. 6 for various choices of I/Δ. In this figure values of $\mu^{00} < \frac{1}{2}I$ occur to the left of the curve, while values of $\mu^{00} > \frac{1}{2}I$ occur to the right. When the average number of electrons is greater than N, we recall (3.8) so that $2\mu_>^{00} - I = -(2\mu_<^{00} - I)$, and consequently, Fig. 6 may be extended to $\bar{r}_e^0 > 1$ merely by reflection about the $\bar{r}_e^0 = 1$ axis.

The $\mu^{00} > \frac{1}{2}I$ phase requires some additional consideration. Now when $\mu^{00} \geq \frac{1}{2}I$ we have noted $(\bar{r}_2^0)^2 \neq \langle r_2^2\rangle^0$, but in computing $\bar{r}_1^0$ and $\langle r_1^2\rangle^0$ we find, just as in (3.6), that $(\bar{r}_1^0)^2 = \langle r_1^2\rangle^0$. Hence the different systems in our grand ensemble almost all have nearly the same number of singly occupied sites while all numbers, between 0 and $N - N_1 = N'$, of doubly occupied sites are found comparatively frequently. However, since μ^0 differs from being less than $\frac{1}{2}I$ only very slightly, a slight change in the system Hamiltonian might stabilize these density fluctuations. We thus seek to introduce a symmetry breaking perturbation which may accomplish this stability, take the thermodynamic limit and then take the limit as the perturbation vanishes. (This program of action is similar to that in the theory of magnetism with magnetic field perturbations and in the theory of superconductivity with particle nonconserving perturbations which are allowed to vanish after taking the thermodynamic limit.) Here an appropriate perturbation is

$$\epsilon \sum_{m\in\mathfrak{A}} a_{m\alpha}^\dagger a_{m\alpha} a_{m\beta}^\dagger a_{m\beta} - \epsilon \sum_{n\in\mathfrak{B}} a_{n\alpha}^\dagger a_{n\alpha} a_{n\beta}^\dagger a_{n\beta}\,, \tag{4.9}$$

where $\mathfrak{A}$ and $\mathfrak{B}$ are a partitioning of the sites of a chain into two disjoint sets. In place of I we now have $I+\epsilon$ and $I-\epsilon$ on the $\mathfrak{A}$ and $\mathfrak{B}$ sites so that doubly occupancy is more favorable on the $\mathfrak{B}$ sites. Further, with $I - \epsilon < 2\mu^0 = I < I + \epsilon$, we take the number of $\mathfrak{A}$ and $\mathfrak{B}$ sites to be such that on leaving unoccupied all the nonsingly occupied sites of $\mathfrak{A}$ and doubly occupying all the nonsingly occupied sites of $\mathfrak{B}$ the total number of electrons is $N\bar{r}_e$. Letting $|\mathfrak{A}|$ and $|\mathfrak{B}|$ be the orders of sets $\mathfrak{A}$ and $\mathfrak{B}$, we thus have

$$|\mathfrak{A}| = \frac{\bar{r}_e^0 + \bar{r}_1^0 - 2}{2\bar{r}_1^0 - 2}N, \quad |\mathfrak{B}| = \frac{\bar{r}_e^0 - \bar{r}_1^0}{2\bar{r}_1^0 - 2}N, \tag{4.10}$$

where $\bar{r}_1^0$ is evaluated from the $\bar{r}_1^{00}$ formula of (3.4) with $\mu^{00} = \frac{1}{2}I$. With these choices then the $\mathfrak{A}$ sites will have nearly no double occupancies and the $\mathfrak{B}$ sites will have nearly no unoccupied sites, even in taking the limit $\epsilon \to 0+$ after the thermodynamic limit.

V. DISCUSSION

We thus have obtained the static thermodynamic properties for the linear projected Hubbard model. These results are exact in the thermodynamic limit, while the eigenvalue spectrum is exact even for finite chains. Despite the one-dimensionality of the model, we found a second-order phase transition. On one side of the transition point the condensation of a second phase was found to be induced by a symmetry breaking perturbation which could be allowed to become arbitrarily small after taking the thermodynamic limit. We note that the one-dimensional short-range nature of the model is emphasized if we write

$$H^{00} = \Delta \sum_{n=1}^{N-1} \sum_{\sigma} (a_{n\sigma}^\dagger a_{n+1,\sigma} + a_{n+1,\sigma}^\dagger a_{n\sigma})$$

$$\times(a^{\dagger}_{n,-\sigma}a_{n,-\sigma}a^{\dagger}_{n+1,-\sigma}a_{n+1,-\sigma}+a_{n,-\sigma}a^{\dagger}_{n,-\sigma}a_{n+1,-\sigma}a^{\dagger}_{n+1,-\sigma}) \tag{5.1}$$

in place of the expression of Eq. (1.2). It appears that although the projected model may approximately describe[6] some complex TCNQ salts with $\bar{r}_e < 1$, none have corresponding I/Δ near which a phase transition occurs. Further even if such free radical salts with I/Δ and $\bar{r}_e$ near such a phase transition point for H^0 were obtained, it seems unlikely that they would be well described by H^0, because of the exclusion in H^0 of electron transfers from a doubly occupied site to an empty site. However, the exact solution does have attendant uses indicated in the introduction. Further a perturbative treatment of the linear Hubbard model might be developed in terms of the projected model taken as the zero-order result.

Solubility of the projected model was found to depend on the fact that the Hamiltonian did not affect the "spin distribution" in that the number and order of unpaired spins was preserved. Modifications of the Hamiltonian with additional intrasite interactions and/or different strengths for nearest-neighbor charge transfer interactions could be treated similarly. Next-nearest-neighbor charge transfer interactions, higher dimensionality, or intersite Coulomb interactions would apparently spoil the solution.

Finally, we note the magnetic properties for the atomic limit, and projected models, are simply those of a collection of $N\bar{r}_1^{00}$ and $N\bar{r}_1^{0}$ noninteracting singly occupied doublet sites.

Note added in proof. Recently G. Beni, T. Holstein, and P. Pincus, [Phys. Rev. B 8, 312 (1972)] have obtained via a different approach some of the same results of Sec. III.

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