

Electronic correlations in narrow-band solids

Ellen J. Yoffa,* Waldyr A. Rodrigues, Jr.,† and David Adler‡

Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 3 March 1978)

The Hubbard Hamiltonian is rederived from the full many-body Hamiltonian with the assumption that only intrasite correlations are important. It is shown to be exact in both the Hartree-Fock and narrow-band limits, provided the appropriate linearization procedure is adopted in the former case. Real-time and imaginary-time Green's functions are derived for the cases intermediate between the Hartree-Fock and narrow-band limits, and a long-standing puzzle with regard to the number of electrons in the upper pseudoparticle band is cleared up. The chemical potential and total energy of the system are calculated in the narrow-band limit and are shown to be identical with those derived from an effective one-electron representation. It is shown that because these quantities depend only on the number of doubly occupied sites, important transport parameters such as electrical conductivity and thermoelectric power can be calculated from the effective one-electron representation, without the necessity of evaluating the two-particle Green's function. For finite bands, the total energy in the Hubbard model is shown to give the exact result, in contradiction to a previous calculation. It is shown that thermodynamic quantities such as the total energy and chemical potential which depend only on derivatives of the grand partition function are independent of the presence or absence of magnetic ordering, but that the entropy is not. Thus a study of the insulator-metal phase transitions is very sensitive to magnetic ordering.

I. INTRODUCTION

It has been many years since Mott^{1,2} first explained why many solids with narrow partially filled conduction bands are insulating rather than metallic. Unfortunately, the resolution of this major puzzle involved correlations between the conduction electrons, thus invalidating the one-electron approximation of conventional band theory and requiring the use of sophisticated many-body techniques. Only one serious attempt has been made to treat the problem in a logical, quantitative manner—in a series of papers, Hubbard³⁻⁵ introduced a Hamiltonian that could be used to analyze major aspects of both the insulating and the metallic states of solids in which electronic correlations are important. The essence of Hubbard's approximation was the neglect of correlations between electrons on different atomic sites, thus effectively replacing the infinite-range Coulomb interaction by an extremely short-range coupling. Despite its successes in making available a structure for analyzing the physical properties of Mott insulators,⁶ the Hubbard model also has presented several major difficulties.⁷⁻⁹ It is the purpose of this paper to rederive the Hubbard Hamiltonian, carefully examine some of its implications, and clear up some of the misconceptions about the model. We begin in Sec. II by deriving the Hubbard Hamiltonian from the general many-body Hamiltonian, explicitly leaving in the spin-dependent parameters. We show that the Hamiltonian is exact in the narrow-band limit, and relate the Hartree-Fock energies to

the atomic energy levels. Adopting an appropriate linearization procedure, we show that the model is also exact in the Hartree-Fock limit. In order to interpolate between these limits, a Green's-function formalism is introduced in Sec. III. For the narrow-band limit, a single-site, effective one-electron representation is introduced, and we show that it yields correct values for the chemical potential and total energy of the system. A major puzzle concerning the relationship between the number of electrons in the upper pseudoparticle band and the number of doubly occupied sites is resolved. We show that because the total energy depends only on the latter, transport parameters such as electrical conductivity and thermoelectric power can be calculated without the necessity of sophisticated many-body techniques. Section IV deals with the total energy of the system in the case of finite bandwidths. We show that a calculation of Herring,⁷ previously employed to conclude that the Hubbard model underestimates the total energy, is based on an incorrect premise. In fact, the Hubbard model yields the exact energy for the case investigated. We extend the calculation of the energy to finite temperature, and demonstrate that although the spin degeneracy is dependent on magnetic ordering, the energy and chemical potential are independent of such effects. However, in Sec. V, we show that the entropy of the system depends very much on the magnetic ordering, and that the presence or absence of the magnetic state changes the entropy by $Nk_B \ln 2$. All of the major results are summarized in Sec. VI.

II. HUBBARD HAMILTONIAN

The dynamics of electrons in a single, nondegenerate band are well described by the Hamiltonian

$$H = \sum_{\mathbf{k}} \sum_{\sigma} \epsilon_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\substack{\mathbf{k}, \mathbf{k}', \\ \mathbf{k}'', \mathbf{k}'''}} \sum_{\sigma, \sigma'} \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}''\mathbf{k}''' \rangle c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}'\sigma'}^{\dagger} c_{\mathbf{k}''\sigma} c_{\mathbf{k}'''\sigma'} - \sum_{\mathbf{k}, \mathbf{k}'} \sum_{\sigma} \left[\nu_{\mathbf{k}'\sigma} \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}\mathbf{k}' \rangle + \nu_{\mathbf{k}\sigma} \left(\langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}\mathbf{k}' \rangle - \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}'\mathbf{k} \rangle \right) \right] c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \quad (1)$$

where $c_{\mathbf{k}\sigma}^{\dagger}$ creates an electron in the Bloch state $|\mathbf{k}, \sigma\rangle$ with corresponding Hartree-Fock energy $\epsilon_{\mathbf{k}\sigma}$, $\nu_{\mathbf{k}\sigma}$ is the average occupation number of this Bloch state, and

$$\langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}''\mathbf{k}''' \rangle \equiv e^2 \int d\mathbf{r} d\mathbf{r}' \psi_{\mathbf{k}}^{\dagger}(\mathbf{r}) \psi_{\mathbf{k}'}^{\dagger}(\mathbf{r}') \times \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_{\mathbf{k}''}(\mathbf{r}) \psi_{\mathbf{k}'''}(\mathbf{r}').$$

At this point, Hubbard³ assumes that $\nu_{\mathbf{k}\sigma} = \nu_{\mathbf{k}}$, independent of spin, precluding the possibility of a magnetically ordered state. With this assumption, the term in square brackets in Eq. (1) becomes:

$$\left[\nu_{\mathbf{k}} \left(2 \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}\mathbf{k}' \rangle - \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}'\mathbf{k} \rangle \right) \right].$$

For the present, we want to maintain the possibility of magnetic ordering, so we shall retain the general Hamiltonian [Eq. (1)]. In order to simplify the equations, we define $E_{\text{int}, \mathbf{k}\sigma}^{\text{HF}}$,

$$E_{\text{int}, \mathbf{k}\sigma}^{\text{HF}} \equiv \frac{1}{2} \sum_{\mathbf{k}'} \left[\nu_{\mathbf{k}'\sigma} \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}\mathbf{k}' \rangle + \nu_{\mathbf{k}\sigma} \left(\langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}\mathbf{k}' \rangle - \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}'\mathbf{k} \rangle \right) \right]. \quad (2)$$

From this definition, we see that $\sum_{\mathbf{k}\sigma} E_{\text{int}, \mathbf{k}\sigma}^{\text{HF}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma}$ is the average intraband interaction energy, as calculated in the mean-field approximation. The total Hartree-Fock energy is obtained from the Hamiltonian $(H_{\text{eff}})_{\text{HF}}$, where

$$(H_{\text{eff}})_{\text{HF}} = \sum_{\mathbf{k}, \sigma} (\epsilon_{\mathbf{k}\sigma} - E_{\text{int}, \mathbf{k}\sigma}^{\text{HF}}) c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma}. \quad (3)$$

Equation (3) comes about because the Hartree-Fock energies,

$$\epsilon_{\mathbf{k}\sigma} = \epsilon_{\mathbf{k}\sigma}^0 + 2E_{\text{int}, \mathbf{k}\sigma}^{\text{HF}}, \quad (4)$$

where $\epsilon_{\mathbf{k}\sigma}^0$ represents that part of the energy of an electron in state $|\mathbf{k}, \sigma\rangle$ exclusive of its interactions with other electrons in the same band; i.e., $\epsilon_{\mathbf{k}\sigma}^0$ includes the electron's interaction with the core electrons (interband processes), its kinetic energy, and its interaction with the nuclei.

The total Hamiltonian (1) then becomes

$$H = \sum_{\mathbf{k}, \sigma} (\epsilon_{\mathbf{k}\sigma} - 2E_{\text{int}, \mathbf{k}\sigma}^{\text{HF}}) c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\substack{\mathbf{k}, \mathbf{k}', \\ \mathbf{k}'', \mathbf{k}'''}} \sum_{\sigma, \sigma'} \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}''\mathbf{k}''' \rangle c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}'\sigma'}^{\dagger} c_{\mathbf{k}''\sigma} c_{\mathbf{k}'''\sigma'} - (H_{\text{eff}})_{\text{HF}} - \sum_{\mathbf{k}, \sigma} E_{\text{int}, \mathbf{k}\sigma}^{\text{HF}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\substack{\mathbf{k}, \mathbf{k}', \\ \mathbf{k}'', \mathbf{k}'''}} \sum_{\sigma, \sigma'} \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}''\mathbf{k}''' \rangle c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}'\sigma'}^{\dagger} c_{\mathbf{k}''\sigma} c_{\mathbf{k}'''\sigma'}. \quad (5)$$

The Hartree-Fock intraband interaction energy must be subtracted in Eq. (5) because the third term treats this interaction explicitly. In fact, using Eq. (4), the Hamiltonian (5) can be written

$$H = \sum_{\mathbf{k}, \sigma} \epsilon_{\mathbf{k}\sigma}^0 c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\substack{\mathbf{k}, \mathbf{k}', \\ \mathbf{k}'', \mathbf{k}'''}} \sum_{\sigma, \sigma'} \langle \mathbf{k}\mathbf{k}' | \frac{1}{\gamma} | \mathbf{k}''\mathbf{k}''' \rangle c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}'\sigma'}^{\dagger} c_{\mathbf{k}''\sigma} c_{\mathbf{k}'''\sigma'}. \quad (6)$$

Although Eq. (6) has the advantage that it explicitly separates the intraband interaction from the rest of the energy, the Hamiltonian (5) will prove more useful when dealing with the usual case, for which the Hartree-Fock problem has already been solved.

We can transform to the Wannier representation by introducing the Fourier transforms

$$\psi_{\mathbf{k}}(\mathbf{r}) = N^{-1/2} \sum_{\mathbf{i}} \exp(i\mathbf{k} \cdot \mathbf{R}_i) \phi(\mathbf{r} - \mathbf{R}_i),$$

$$c_{\mathbf{k}\sigma}^{\dagger} = N^{-1/2} \sum_{\mathbf{i}} \exp(i\mathbf{k} \cdot \mathbf{R}_i) c_{\mathbf{i}\sigma}^{\dagger},$$

$$T_{ij\sigma} \equiv N^{-1} \sum_{\mathbf{k}} \epsilon_{\mathbf{k}\sigma} \exp[i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)],$$

$$\nu_{ij\sigma} \equiv N^{-1} \sum_{\mathbf{k}} \nu_{\mathbf{k}\sigma} \exp[-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)],$$

where N is the total number of lattice sites. The total Hamiltonian then becomes

$$H = \sum_{i,j} \sum_{\sigma} T_{ij\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{1}{2} \sum_{i,j} \sum_{\sigma,\sigma'} \langle ij | \frac{1}{r} | kl \rangle c_{i\sigma}^{\dagger} c_{j\sigma'}^{\dagger} c_{i\sigma} c_{k\sigma'} - \sum_{i,j} \sum_{\sigma} \left[\nu_{ji-\sigma} \langle ij | \frac{1}{r} | kl \rangle + \nu_{ji\sigma} \left(\langle ij | \frac{1}{r} | kl \rangle - \langle ij | \frac{1}{r} | lk \rangle \right) \right] c_{i\sigma}^{\dagger} c_{k\sigma}, \quad (7)$$

where

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

The major approximation made by Hubbard³ is that all $\langle ij | (1/r) | kl \rangle$ can be neglected, except for $\langle ii | (1/r) | ii \rangle = U$. U is the Coulomb repulsion between two electrons on the same atomic site. With this approximation, the Hamiltonian (7) reduces to

$$H = \sum_{i,j} \sum_{\sigma} T_{ij\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U}{2} \sum_i \sum_{\sigma} (n_{i-\sigma} - 2\nu_{ii-\sigma}) n_{i\sigma}, \quad (8a)$$

or, alternatively

$$H = \sum_{\mathbf{F}} \sum_{\sigma} \epsilon_{\mathbf{F}\sigma} c_{\mathbf{F}\sigma}^{\dagger} c_{\mathbf{F}\sigma} + \frac{U}{2} \sum_i \sum_{\sigma} (n_{i-\sigma} - 2\nu_{ii-\sigma}) n_{i\sigma}, \quad (8b)$$

where $n_{i\sigma} \equiv c_{i\sigma}^{\dagger} c_{i\sigma}$. This equation should be compared to Hubbard's result [H, Eq. (10)]

$$H_H = \sum_{i,j} \sum_{\sigma} T_{ij\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U}{2} \sum_i \sum_{\sigma} (n_{i-\sigma} - 2\nu_{ii-\sigma}) n_{i\sigma} = \sum_{\mathbf{F}} \sum_{\sigma} \epsilon_{\mathbf{F}\sigma} c_{\mathbf{F}\sigma}^{\dagger} c_{\mathbf{F}\sigma} + \frac{U}{2} \sum_i \sum_{\sigma} (n_{i-\sigma} - 2\nu_{ii-\sigma}) n_{i\sigma}. \quad (9a)$$

The only difference between Eqs. (8) and (9) is the assumption in the latter that $\nu_{ii-\sigma} = \nu_{ii}$, independent of spin. However, by definition, $\nu_{ii\sigma} = N^{-1} \sum_{\mathbf{F}} \nu_{\mathbf{F}\sigma} = \langle n_{\sigma} \rangle$ for the Hartree-Fock calculation, where $\langle n_{\sigma} \rangle$ is the average value of n_{σ} over a canonical ensemble at temperature T . For $\nu_{ii\sigma}$ to be independent of spin, both $\langle n_{\sigma} \rangle$ and $\langle n_{-\sigma} \rangle$ must be equal to $\frac{1}{2}n$, where n is the average number of electrons per site. To apply the Hamiltonian (9), even to the cases $n_{\uparrow} \neq n_{\downarrow}$, we must remember to require $n_{\uparrow} = n_{\downarrow}$ in calculating the

Hartree-Fock energies, $\epsilon_{\mathbf{F}\sigma}$. In effect, this is exactly what Hubbard did; he simultaneously dropped the constant term, $-U \sum_i \sum_{\sigma} \nu_{ii} n_{i\sigma}$, and made the transformation $\epsilon_{\mathbf{F}\sigma} \rightarrow \epsilon_{\mathbf{F}\sigma}^0$ by using Eq. (4) with $2E_{\text{int},\mathbf{F}\sigma}^{\text{HF}} = U\nu_{ii}$. The resulting Hamiltonian is then:

$$H = \sum_{\mathbf{F},\sigma} \epsilon_{\mathbf{F}\sigma}^0 c_{\mathbf{F}\sigma}^{\dagger} c_{\mathbf{F}\sigma} + \frac{U}{2} \sum_i n_{i-\sigma} n_{i\sigma}, \quad (10)$$

where all of the intraband interaction energy is included explicitly in the second term. The $\epsilon_{\mathbf{F}\sigma}^0$ are the *noninteracting* energies, which are modified by the interaction $\frac{1}{2}U \sum_i n_{i-\sigma} n_{i\sigma}$. The Hamiltonian (8) is also exactly equal to Eq. (10), where the transformation is achieved in this case by writing $\epsilon_{\mathbf{F}\sigma} = \epsilon_{\mathbf{F}\sigma}^0 + U\nu_{ii-\sigma}$.

In order to apply the Hartree-Fock method to the Hamiltonian (10), we must linearize the operator product $n_{i-\sigma} n_{i\sigma}$. This can be done by letting $n_{i\sigma} = \langle n_{i\sigma} \rangle + \tilde{n}_{i\sigma}$, where the operator $\tilde{n}_{i\sigma}$ represents the deviation of $n_{i\sigma}$ from the average value. Thus, $n_{i-\sigma} n_{i\sigma} = \langle n_{i-\sigma} \rangle \langle n_{i\sigma} \rangle + \langle n_{i-\sigma} \rangle \tilde{n}_{i\sigma} + \tilde{n}_{i-\sigma} \langle n_{i\sigma} \rangle$, where we have made the usual assumption that the deviations are small. Using the definition $\tilde{n}_{i\sigma} \equiv n_{i\sigma} - \langle n_{i\sigma} \rangle$, we get

$$n_{i-\sigma} n_{i\sigma} \rightarrow \langle n_{i-\sigma} \rangle n_{i\sigma} + \langle n_{i\sigma} \rangle n_{i-\sigma} - \langle n_{i-\sigma} \rangle \langle n_{i\sigma} \rangle = \langle n_{-\sigma} \rangle n_{i\sigma} + \langle n_{\sigma} \rangle n_{i-\sigma} - \langle n_{-\sigma} \rangle \langle n_{\sigma} \rangle, \quad (11)$$

where the final equality holds by virtue of the translational symmetry, $\langle n_{i\sigma} \rangle = \langle n_{\sigma} \rangle$. Substituting Eq. (11) into Eq. (10), we find

$$(H_{\text{eff}})_{\text{HF}} = \sum_{\mathbf{F},\sigma} \epsilon_{\mathbf{F}\sigma}^0 c_{\mathbf{F}\sigma}^{\dagger} c_{\mathbf{F}\sigma} + U \sum_{i,\sigma} \langle n_{-\sigma} \rangle n_{i\sigma} - NU \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle. \quad (12)$$

But since $U \sum_{i,\sigma} \langle n_{-\sigma} \rangle n_{i\sigma} = 2NU \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle$, Eq. (12) becomes:

$$(H_{\text{eff}})_{\text{HF}} = \sum_{\mathbf{F},\sigma} \epsilon_{\mathbf{F}\sigma}^0 c_{\mathbf{F}\sigma}^{\dagger} c_{\mathbf{F}\sigma} + NU \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle. \quad (13)$$

In fact, the Hamiltonian (13) is just what we expect from a Hartree-Fock description of electrons for which only intrasite interactions are important. In this case, $\sum_{\mathbf{F},\sigma} E_{\text{int},\mathbf{F}\sigma}^{\text{HF}} c_{\mathbf{F}\sigma}^{\dagger} c_{\mathbf{F}\sigma} = NU \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle$ and Eq. (13) is identical to the Hartree-Fock Hamiltonian (3).

We can also write Eq. (12) in the form

$$(H_{\text{eff}})_{\text{HF}} = \sum_{\vec{k}, \sigma} (\epsilon_{\vec{k}\sigma}^0 + U \langle n_{-\sigma} \rangle) c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} - NU \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle. \quad (14)$$

This expression differs from that derived by Hubbard [H, Eq. (15)] by the absence in the latter of the constant term, $-NU \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle$. The difference is due to the fact that Hubbard linearized the product $n_{i\sigma} n_{i-\sigma}$ in a manner designed to result in the proper criteria for ferromagnetism, whereas we are concerned here with the correct total energy.

Although the Hamiltonian (10) was originally proposed as the simplest method for generalizing the results of conventional band theory to the case in which electronic correlations are important, it has the additional advantage of reducing to the exact solutions in the two extreme cases, the narrow-band limit and the Hartree-Fock limit. To show this, we begin with the Hamiltonian (9b), which is applicable to solids without magnetic ordering. Since, in this case, $\langle n_{\sigma} \rangle = \langle n_{-\sigma} \rangle = \frac{1}{2}n$, the Hamiltonian can be simplified to

$$H = \sum_{\vec{k}, \sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - \frac{1}{2} N n^2 U, \quad (15)$$

where we have noted that $\sum_{i, \sigma} n_{i\sigma} = Nn$, the total number of electrons present.

First, we consider the narrow-band limit, in which all the Hartree-Fock energies $\epsilon_{\vec{k}}$ are the same, independent of \vec{k} . They can be evaluated by noting that when correlations are neglected, all possible configurations of the Nn electrons on the N sites are equally probable. In this case, the average interaction energy between a given electron and all the other electrons is $\frac{1}{2}nU$. Thus, if T_0 is the energy of the relevant atomic orbital, $\epsilon_{\vec{k}} = T_0 + \frac{1}{2}nU$. (In the important case of one electron per atom, i.e., $n=1$, this yields $\epsilon_{\vec{k}} = T_0 + \frac{1}{2}U$; thus, the Hartree-Fock energy lies halfway between the two quasiparticle bands at T_0 and $T_0 + U$, just as we might have expected.⁹ We shall return to the quasiparticle representation in Sec. III.) Since $\sum_{\vec{k}, \sigma} n_{\vec{k}\sigma} = Nn$, the Hamiltonian (15) in the narrow-band limit becomes

$$H_{\text{NB}} = NnT_0 + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (16)$$

where the interaction contribution to the Hartree-Fock term just cancels the constant term. Since the magnitude of $\sum_i n_{i\uparrow} n_{i\downarrow} = m$, the number of doubly occupied sites, the total energy in the narrow-band limit is

$$E_{\text{NB}} = NnT_0 + mU, \quad (17)$$

just what we would expect for strongly correlated, localized electrons.⁹

In the Hartree-Fock limit, we must linearize the correlation term in Eq. (15), $U \sum_i n_{i\uparrow} n_{i\downarrow}$. Using the same linearization procedure as in Eq. (11), we find

$$\begin{aligned} U \sum_i n_{i\uparrow} n_{i\downarrow} &\rightarrow U \sum_i (\langle n_{i\uparrow} \rangle n_{i\downarrow} + n_{i\uparrow} \langle n_{i\downarrow} \rangle - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle) \\ &\rightarrow U \sum_i \left(\frac{n}{2} n_{i\uparrow} + \frac{n}{2} n_{i\downarrow} - \frac{n^2}{4} \right) \\ &\rightarrow \frac{1}{4} N n^2 U, \end{aligned}$$

where again we have assumed translational invariance and no magnetic ordering. Thus, Eq. (15) becomes in the Hartree-Fock limit

$$H_{\text{HF}} = \sum_{\vec{k}, \sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} - \frac{1}{4} N n^2 U. \quad (18)$$

Eq. (18) yields just what we would expect from a Hartree-Fock description of electrons for which only intrasite interactions are important. The constant term $\frac{1}{4} N n^2 U$ just cancels the average interaction energy which is double-counted in the sum. (An alternative way of seeing this is to recall that, in the Hartree-Fock limit, the neglect of correlations results in $\frac{1}{4} n^2$ of the sites being doubly occupied on the average; this increases the energy by $\frac{1}{4} N n^2 U$, a term which represents the sum of the interactions. This term is counted twice when we sum the $\epsilon_{\vec{k}}$, so it must be subtracted off to obtain the correct total energy of the system.)

If the linearization procedure used in Eq. (11) is not used, an incorrect result is obtained for the total energy.

III. MANY-BODY AND SINGLE-SITE REPRESENTATIONS

In order to apply the Hubbard Hamiltonian to experimental results on real materials, it is important to evaluate physical parameters such as the chemical potential (i.e., the Fermi energy) and the number of doubly occupied sites in cases that are intermediate between the Hartree-Fock and narrow-band limits. It would also be extremely valuable if we could interpret the model in terms of an effective one-electron-like representation, particularly in view of the fact that real materials can possess both narrow and wide bands in the vicinity of the Fermi energy.⁹ Hubbard⁹ discussed an effective one-electron-like representation in his original paper, but a considerable amount of confusion has resulted, especially with respect to quantities such as the temperature dependence of the Fermi energy and the number of particles in the upper band. It is the purpose of this section to clarify the problem in a rigorous manner.

In order to interpolate between the Hartree-Fock and narrow-band limits, we introduce both real-time and imaginary-time (temperature-dependent) Green's functions. This formalism permits us to derive in a simple and unambiguous way a wealth of information about the correlated system. As is well known, the real-time Green's functions lead to the pseudoparticle spectrum of the system, whereas the imaginary-time Green's functions are directly related to the thermodynamic functions. For convenience, we eliminate the constant term in Eq. (15) by writing the Hartree-Fock energy $\epsilon_{\mathbf{F}}$ as $\epsilon_{\mathbf{F}} = \epsilon_{\mathbf{F}}^0 + \frac{1}{2}n^2U$, where $\epsilon_{\mathbf{F}}^0$ represents the noninteracting part of the electronic energy; $\frac{1}{2}n^2U$ is the electron-electron interaction energy. We have already discussed this procedure in Sec. II. Substituting into Eq. (15), we obtain

$$H = \sum_{\mathbf{F}, \sigma} \epsilon_{\mathbf{F}}^0 n_{\mathbf{F}\sigma} + U \sum_{\mathbf{F}} n_{\mathbf{F}} n_{\mathbf{F}},$$

which is just a rewriting of Eq. (10). Making use of the Fourier transforms, $T_{ij}^0 = N^{-1} \sum_{\mathbf{F}} \epsilon_{\mathbf{F}}^0 \exp[i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)]$ and $c_{j\sigma} = N^{-1/2} \sum_{\mathbf{F}} c_{\mathbf{F}\sigma} \exp(i\mathbf{k} \cdot \mathbf{R}_j)$, the Hubbard Hamiltonian becomes

$$H = \sum_{i,j} \sum_{\sigma} T_{ij}^0 c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{\mathbf{F}} n_{\mathbf{F}} n_{\mathbf{F}}.$$

For this Hamiltonian, we define the causal retarded and advanced Green's functions¹⁰

$$G_{r,a}(t, t') \equiv \mp i \Theta(\pm(t - t')) \langle \{ c_{i\sigma}(t), c_{j\sigma}^{\dagger}(t') \} \rangle \\ \equiv \langle \langle c_{i\sigma}(t); c_{j\sigma}^{\dagger}(t') \rangle \rangle_{r,a},$$

where $\{ , \}$ is the anticommutator and $\langle \rangle$ indicates the average over a grand-canonical ensemble at temperature T . We define, for real E , the Fourier transforms

$$\langle \langle c_{i\sigma}; c_{j\sigma}^{\dagger} \rangle \rangle_{E^{\pm}} \\ \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{iEt} \langle \langle c_{i\sigma}(t); c_{j\sigma}^{\dagger}(0) \rangle \rangle_{r,a}. \quad (19)$$

The analytic continuation of these functions into the complex energy plane will be denoted by $G_{ij}^{\sigma\sigma'}(E)$.

We introduce next the imaginary-time Green's function

$$g_{ij}^{\sigma\sigma'}(\tau, \tau') \equiv - \langle T_{\tau} [\check{c}_{i\sigma}(\tau) \check{c}_{j\sigma'}^{\dagger}(\tau')] \rangle, \quad (20)$$

where T_{τ} is the time-ordering operator; $\check{c}_{i\sigma}$ and $\check{c}_{j\sigma'}^{\dagger}$ are "imaginary-time" annihilation and creation operators defined by $\check{c}_{i\sigma}(\tau) \equiv e^{\hat{K}\tau} c_{i\sigma} e^{-\hat{K}\tau}$ and $\check{c}_{j\sigma'}^{\dagger} \equiv e^{\hat{K}\tau} c_{j\sigma'}^{\dagger} e^{-\hat{K}\tau}$. $\hat{K} = H - \mu \hat{N}$ is the grand-canonical Hamiltonian, μ is the chemical potential, and \hat{N} is the particle number operator. The Fourier transform of Eq. (20) is defined by

$$g(\tau) \equiv \frac{1}{k_B T} \sum_{i=0}^{\infty} e^{i\omega_i \tau} g(\omega_i),$$

where $\omega_i = \pi(2i+1)/k_B T$ is the fermion frequency. In the Bloch representation, where

$$G_{ij}(E) = \frac{1}{N} \sum_{\mathbf{F}} G(\mathbf{k}, E) e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}$$

and

$$g_{ij}(\omega_i) = \frac{1}{N} \sum_{\mathbf{F}} g(\mathbf{k}, \omega_i) e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}$$

we have

$$g(\mathbf{k}, \omega_i) = \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{2G(\mathbf{k}, \omega' - i\eta)}{i\omega_i - \omega'}, \quad (21)$$

with η an infinitesimal positive number.

In the narrow-band limit, $T_{ij}^0 = \delta_{ij} T_0$, and we can obtain G and g exactly using the equation of motion method described by Zubarev.¹⁰ We get

$$G_{ij}^{\sigma\sigma'}(E) = \frac{\delta_{\sigma\sigma'} \delta_{ij}}{2\pi} \left(\frac{1 - n_{-\sigma}}{E - T_0} + \frac{n_{-\sigma}}{E - T_0 - U} \right), \quad (22)$$

where $n_{-\sigma} = \langle n_{-\sigma} \rangle$ for a translationally invariant system. Also in the narrow-band limit, we have

$$g^{\sigma\sigma'}(\mathbf{k}, \omega_i) = \frac{\delta_{\sigma\sigma'}}{2\pi N} \left(\frac{1 - n_{-\sigma}}{i\omega_i + \mu - T_0} + \frac{n_{-\sigma}}{i\omega_i + \mu - T_0 - U} \right). \quad (23)$$

For nonzero bandwidth, following Hubbard,³ we find the approximate solution

$$G^{\sigma\sigma'}(\mathbf{k}, E) = \frac{\delta_{\sigma\sigma'}}{2\pi N} \frac{1}{E_{\mathbf{F}}^{(1)} - E_{\mathbf{F}}^{(2)}} \left(\frac{E_{\mathbf{F}}^{(1)} - T_0 - U(1 - n_{-\sigma})}{E - E_{\mathbf{F}}^{(1)}} - \frac{E_{\mathbf{F}}^{(2)} - T_0 - U(1 - n_{-\sigma})}{E - E_{\mathbf{F}}^{(2)}} \right), \quad (24a)$$

where $E_{\mathbf{F}}^{(1)} < E_{\mathbf{F}}^{(2)}$ are the roots of the equation

$$(E - \epsilon_{\mathbf{F}}^0)(E - T_0 - U) + n_{-\sigma} U(T_0 - \epsilon_{\mathbf{F}}^0) = 0. \quad (24b)$$

Although the approximate solution has several faults,⁷ it can still be used to obtain reliable information about the correlated electron system. Finally, the g function is obtained from Eq. (24):

$$g^{\sigma\sigma'}(\mathbf{k}, \omega_i) = \frac{\delta_{\sigma\sigma'}}{2\pi N} \frac{1}{E_{\mathbf{F}}^{(1)} - E_{\mathbf{F}}^{(2)}} \\ \times \left(\frac{E_{\mathbf{F}}^{(1)} - T_0 - U(1 - n_{-\sigma})}{i\omega_i - E_{\mathbf{F}}^{(1)} + \mu} - \frac{E_{\mathbf{F}}^{(2)} - T_0 - U(1 - n_{-\sigma})}{i\omega_i - E_{\mathbf{F}}^{(2)} + \mu} \right). \quad (25)$$

Thus, we have both the real-time [Eqs. (22) and (24)] and finite-temperature [Eqs. (23) and (25)]

Green's functions, for the narrow-band limit [Eqs. (22) and (23)] and for finite bandwidths [Eqs. (24) and (25)].

Perhaps the most important quantity that can be calculated with the above formalism is the chemical potential μ . The pseudoparticle density of states per atom in the atomic limit is given by

$$\begin{aligned}\rho(E) &= \frac{i}{N} \lim_{\eta \rightarrow 0^+} \sum_{j,\sigma} [G_{jj}^{\sigma\sigma}(E+i\eta) - G_{jj}^{\sigma\sigma}(E-i\eta)] \\ &= (2-n)\delta(E-T_0) + n\delta(E-T_0-U),\end{aligned}\quad (26)$$

where we have used Eq. (22) and the fact that $n_\sigma = n_{-\sigma} = \frac{1}{2}n$ for a nonmagnetic system. The chemical potential can then be evaluated from the equation

$$n = \int_{-\infty}^{\infty} dE \rho(E) \frac{1}{e^{(E-\mu)/k_B T} + 1}.$$

We obtain:

$$\mu = T_0 - k_B T \ln \left(\frac{(1-n) + [(1-n)^2 - n(n-2)e^{-U/k_B T}]^{1/2}}{n} \right).\quad (27)$$

The single-site representation⁹ is a scheme that makes use of the fact that any atomic site is either empty ($E=0$, nondegenerate), singly occupied ($E=T_0$, twofold degenerate), or doubly occupied ($E=2T_0+U$, nondegenerate). This can be looked at in terms of two one-electron-like levels, both at T_0 when empty but one moving to T_0+U when the other is occupied. The grand-partition function for a system of N independent sites can then be written down immediately as

$$\mathfrak{z} = (1 + 2e^{-(T_0-\mu)/k_B T} + e^{-(2T_0+U-2\mu)/k_B T})^N = \mathfrak{z}_S^N,\quad (28)$$

where \mathfrak{z}_S is the single-site grand partition function. Using $n = k_B T (\partial \ln \mathfrak{z} / \partial \mu)_T$, we can solve for the chemical potential in the single-site representation

$$\begin{aligned}\mu &= T_0 + U + k_B T \\ &\times \ln \left(\frac{(1-n) - [(1-n)^2 - n(n-2)e^{-U/k_B T}]^{1/2}}{n-2} \right).\end{aligned}\quad (29)$$

With simple algebraic manipulation, we find that the chemical potential defined in Eq. (29) is *identical* to that in Eq. (27), which was derived formally for the many-body system.

Another important quantity is the number of electrons in the upper band. In the single-site scheme, the "second" electron on a site has energy T_0+U , so that the number of electrons in the

upper band (at $E=T_0+U$) is equal to the number of doubly occupied sites m , where

$$m = \frac{N e^{-(2T_0+U-2\mu)/k_B T}}{\mathfrak{z}_S} = \frac{Nn}{2(1 + e^{(T_0+U-\mu)/k_B T})}.\quad (30)$$

On the other hand, we can calculate the number of electrons in the upper pseudo-particle band N_u :

$$\begin{aligned}N_u &= N \int_{-\infty}^{\infty} dE \rho_u(E) \frac{1}{1 + e^{(E-\mu)/k_B T}} \\ &= \frac{Nn}{1 + e^{(T_0+U-\mu)/k_B T}},\end{aligned}\quad (31)$$

where $\rho_u(E)$ is the pseudoparticle density of states per atom in the upper band [from Eq. (26)]. Comparing Eqs. (30) and (31), we discover that the number of electrons in the upper pseudoparticle band is *twice* the number in the upper band of the single-site representation! The resolution of this apparent paradox lies in the fact that the respective "upper bands" are really very different quantities. In the single-site picture, the number of available states in the upper band is a temperature-dependent quantity that exists only by virtue of filled states in the lower band. Within the Green's-function formalism, the upper band is created only after the interaction between electrons is switched on. The spectrum is a function of U , $\epsilon_{\mathbf{k}}$, and n . (In fact, there is a finite probability for an electron on a singly occupied site to be in the upper pseudoparticle band at $T > 0$.) Physically, the reason for the difference is that *either* the spin-up or the spin-down electron on doubly occupied sites can be considered to have energy T_0+U , and thus be in the upper band; in the single-site representation, only one of these electrons can actually be placed in the upper band or else the total energy will be overestimated. As we shall see shortly, all the thermodynamic quantities depend not on the number of electrons in the upper band, but on the number of doubly occupied sites. We shall demonstrate that this latter quantity is the same in both pictures.

First, we note from the form of the Hamiltonian (16), that the number of doubly occupied sites $m (= N \langle n_{\uparrow} n_{\downarrow} \rangle)$ is exactly $\langle V \rangle / U$, where $\langle V \rangle$ is the thermal average of the interaction energy. This energy is given by

$$\begin{aligned}\langle V \rangle &= \frac{N\Omega_0}{(2\pi)^3} k_B T \lim_{\eta \rightarrow 0^+} \sum_{\mathbf{k}} \sum_i e^{i\omega_i \eta \frac{1}{2}} (i\omega_i - \epsilon_{\mathbf{k}}^0 + \mu) \\ &\quad \times \text{Tr} \mathfrak{g}(\vec{\mathbf{k}}, \omega_i),\end{aligned}\quad (32)$$

where Ω_0 is the system volume, $\mathfrak{g}(\vec{\mathbf{k}}, \omega_i)$ is defined in Eq. (23), and $\epsilon_{\mathbf{k}}^0 = T_0$ in the atomic limit. Making these substitutions,

$$\begin{aligned} \langle V \rangle &= Nk_B T \lim_{\eta \rightarrow 0^+} N \sum_i e^{i\omega_i \eta} \frac{1}{2} (i\omega_i - T_0 + \mu) \left[\frac{2}{N} \left(\frac{1 - \frac{1}{2}n}{i\omega_i - T_0 + \mu} + \frac{\frac{1}{2}n}{i\omega_i - T_0 - U + \mu} \right) \right] \\ &= \frac{NnU}{2(1 + e^{(T_0 + U - \mu)/k_B T})}. \end{aligned} \quad (33)$$

Then

$$m = Nn/2(1 + e^{(T_0 + U - \mu)/k_B T}). \quad (34)$$

Comparing with Eq. (30), we see that the number of doubly occupied sites is indeed the same as calculated in the single-site representation. A useful by-product of the form of the Hamiltonian (16), is that the four-operator average $\langle c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{i\downarrow} c_{i\uparrow} \rangle$ can be calculated by recognizing its relationship to the interaction energy, as described previously. Thus, physical properties involving four-operator correlation functions (e.g., conductivity and thermoelectric power) can be evaluated *without* recourse to two-particle Green's functions, as is ordinarily necessary for other Hamiltonians. In addition, since we have shown that $\langle n_{i\uparrow} n_{i\downarrow} \rangle$ is the same for the single-site and many-body representations (in the narrow-band limit), physical properties (e.g., the energy, which simply equals $NnT_0 + mU$) can be calculated in whichever one that is most convenient. This provides an enormous simplification, since the single-site representation circumvents the sophisticated techniques of many-body theory, and can easily be made compatible with the conventional one-electron bands which are ordinarily present near the Fermi level of Mott insulators.¹¹

IV. TOTAL ENERGY OF THE SYSTEM

For a real system, with finite bandwidth, the total energy has been the subject of much confusion. Herring⁷ calculated the total energy in the strong-correlation limit and obtained a result which appeared to be much too small. He thereby concluded that the Hubbard model underestimates the total energy. In this section, we show that, in fact, the Hubbard model gives the exact answer in this case.

Consider the case of a square band:

$$\rho(E) = \begin{cases} 2N/\Delta & (|E| < \frac{1}{2}\Delta) \\ 0 & (|E| > \frac{1}{2}\Delta) \end{cases}, \quad (35)$$

where $\rho(E)$ is the total density of states, in the absence of correlations and we have chosen $T_0 = 0$ for convenience. The Fermi energy ϵ_F of the ground state can be obtained from the relation

$$Nn = \int_{-\infty}^{\epsilon_F} dE \rho'(E), \quad (36a)$$

where

$$\rho'(E) = \rho(g(E, n)) = \frac{E(E - U)}{E - U(1 - \frac{1}{2}n)}. \quad (36b)$$

We consider the case for which $n \leq 1$, so that we are concerned only with the lower band. Solving Eq. (36) for ϵ_F , we find

$$\epsilon_F = \frac{1}{2}\Delta n + \frac{1}{2}\{U - \frac{1}{2}\Delta - [(U + \frac{1}{2}\Delta)^2 - U\Delta n]^{1/2}\}. \quad (37)$$

This result is in agreement with Herring.⁷ However, Herring evaluates the total energy from the relation

$$E = N \int_0^n \epsilon_F dn. \quad (38)$$

For the case $n=1$, $U = \infty$, Eq. (38) yields the result,

$$E = -\frac{1}{8}N\Delta.$$

Since the exact energy is $E=0$, Herring concludes that the Hubbard model underestimates the total energy of the system.

We shall now show that the Hubbard model, in fact, yields the exact result for the total energy. The error in the previous calculation arises because Eq. (38) is inapplicable in this case, due to the band-narrowing effects of electronic correlations. This can be made evident by first looking at the density of states in the lower band. From Eq. (36b), we find for the strong-correlation limit ($U = \infty$)

$$\rho'(E) = \begin{cases} N/\Delta & [|E| < \frac{1}{4}(2-n)\Delta] \\ 0 & [|E| > \frac{1}{4}(2-n)\Delta] \end{cases}. \quad (39)$$

In this same limit,

$$\epsilon_F = -\frac{1}{2}\Delta + \frac{3}{4}n\Delta. \quad (40)$$

These results are shown in Fig. 1. The solid lines indicate the band edges E_{\min} and E_{\max} and the dashed line marks the Fermi level. The sketch makes clear why Herring underestimates E/N by $\frac{1}{8}\Delta$. The difference between the true energy and that calculated above is just the "area" of the triangle bordered by E_{\min} and a horizontal line at $E = -\frac{1}{2}\Delta$. The correct expression for the total energy is thus:

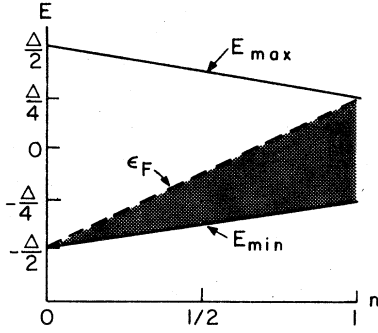


FIG. 1. Behavior of band edges and Fermi energy as functions of n , for a square density of states, with $U = \infty$. The shaded area indicates the occupied states at $T=0$.

$$E = N \int_0^n \mu \, dn = N \int_0^n \left(\epsilon_F + n \frac{\partial E_{\min}}{\partial n} \right) dn, \quad (41)$$

where we integrate to $n=1$. As we see, the Fermi energy ϵ_F does not equal the chemical potential μ , as is often the case, but is instead given by $\mu = \epsilon_F + n \partial E_{\min} / \partial n$.

The physical interpretation of Eq. (41) is that as we add each electron with energy ϵ_F , we simultaneously increase the energy of *all* the electrons in the band, by $\partial E_{\min} / \partial n$, due to the band-narrowing effects of the additional correlations. Equation (41) yields

$$E = 0,$$

the exact answer.

We are now interested in generalizing this approach to finite temperatures. For the case $n=1$:

$$E = \frac{N \Omega_0 k_B T}{(2\pi)^3} \int d\vec{k} \sum_l e^{i\omega_l n \frac{1}{2}} (i\omega_l + \epsilon_F^0 + \mu) \times \text{Tr} \mathcal{G}^{\sigma\sigma'}(\vec{k}, \omega_l), \quad (42)$$

where \mathcal{G} is the finite-temperature Green's function Eq. (25) and the trace is taken over spin indices. Substituting Eq. (25) into Eq. (42) and performing the sum over l , we obtain:

$$E = \frac{\Omega_0}{(2\pi)^3} \int d\vec{k} \frac{1}{E_{\vec{k}}^{(1)} - E_{\vec{k}}^{(2)}} \times \left(\frac{[E_{\vec{k}}^{(1)} - T_0 - U(1-n/2)](\epsilon_F^0 + E_{\vec{k}}^{(1)})}{1 + e^{(E_{\vec{k}}^{(1)} - \mu)/k_B T}} - \frac{[E_{\vec{k}}^{(2)} - T_0 - U(1-n/2)](\epsilon_F^0 + E_{\vec{k}}^{(2)})}{1 + e^{(E_{\vec{k}}^{(2)} - \mu)/k_B T}} \right)$$

where $E_{\vec{k}}^{(1)}$, $E_{\vec{k}}^{(2)}$ are given by the roots of Eq. (24b), with $n_{\sigma} = n_{-\sigma} = \frac{1}{2}n$. We again specialize to a square density of states as given by Eq. (35), but reinstate the atomic energy level explicitly,

which shifts the energy scale by T_0 . Making the variable change $[2\Omega_0/(2\pi)^3] d^3k \rightarrow (2/\Delta) dE$, we get $E_{\vec{k}}^{(1)} = \frac{1}{2}(E + T_0)$ and $E_{\vec{k}}^{(2)} = \frac{1}{2}(E + T_0 + U)$. [We have assumed $(\Delta/U)^2 \ll 1$. The decoupling scheme used by Hubbard³ was chosen to be valid in this limit and leads to unphysical behavior in the opposite limit. A later paper by Hubbard⁵ corrects this defect. Errors in the following calculation will vanish in the limit of interest, $U \rightarrow \infty$.] We now have

$$E = \frac{-N}{4U\Delta} \int_{T_0 - \Delta/2}^{T_0 + \Delta/2} dE \times \left(\frac{(E - T_0 - U)(3E + T_0)}{1 + e^{(E - T_0 - U)/k_B T}} - \frac{(E - T_0 + U)(3E + T_0 + 2U)}{1 + e^{(E - T_0 + U)/k_B T}} \right).$$

Letting $x = E - T_0$, we get

$$E = \frac{-N}{4U\Delta} \int_{-\Delta/2}^{\Delta/2} dx \times \left(\frac{(x - U)(3x + 4T_0)}{1 + e^{(x - U)/k_B T}} - \frac{(x + U)(3x + 4T_0 + 2U)}{1 + e^{(x + U)/k_B T}} \right). \quad (43)$$

Even at reasonably high temperatures, $U \gtrsim 0.5$ eV, it is still true that $e^{U/2k_B T} \gg 1$. Since $\Delta^2 \ll U^2$, we can make the approximations $(1 + e^{(x - U)/2k_B T})^{-1} \simeq 1 - e^{(x - U)/2k_B T}$ and $(1 + e^{(x + U)/2k_B T})^{-1} \simeq e^{-(x + U)/2k_B T}$. After substituting these expressions into Eq. (43), we can integrate to obtain the total energy. If, in addition, we ignore terms of order one compared with $U/k_B T$, we obtain

$$E = N \left[T_0 + \left(\frac{\sinh(\Delta/4k_B T)}{\Delta/4k_B T} \right) \frac{U}{2} e^{-U/2k_B T} - \left(\frac{\cosh(\Delta/4k_B T)}{\Delta/4k_B T} \right) \Delta e^{-U/2k_B T} \right]. \quad (44)$$

Note that for $\Delta=0$, $E = N(T_0 + \frac{1}{2}Ue^{-U/2k_B T})$, as it should. In the limit $\Delta/U \rightarrow 0$,

$$E \rightarrow N \left[T_0 + \left(\frac{\sinh(\Delta/4k_B T)}{\Delta/4k_B T} \right) \frac{U}{2} e^{-U/2k_B T} \right].$$

As $U \rightarrow \infty$, $E \rightarrow NT_0$. As discussed previously, this is the expected result.

V. ENTROPY AND OTHER THERMODYNAMIC CONSIDERATIONS

One of the major applications of the Hubbard model is as a quantitative means of analyzing Mott transitions. However, any study of phase transitions requires a knowledge of the free energies of the system. Consequently, we next

turn to a discussion of the entropy. Very little previous work has been carried out on the entropy of a strongly correlated system. In this regard, it is clear that the possibility of magnetic ordering is of fundamental importance, and we must consider magnetic states explicitly.

For the case of $n=1$, the chemical potential is independent of temperature; thus

$$\left(\frac{\partial S}{\partial \beta}\right)_{\mu, \Omega_0} = k_B \beta \left(\frac{\partial E}{\partial \beta}\right)_{\mu, \Omega_0},$$

where $\beta = 1/k_B T$. Integrating this relation, we find

$$S(\beta) = S(\infty) + k_B \beta E|_{\infty} - k_B \int_{\infty}^{\beta} d\beta E. \quad (45)$$

Using $E = N[T_0 + U/2(1 + e^{\beta U/2})]$, we can easily evaluate Eq. (45) in the narrow-band limit:

$$S(\beta) = S(\infty) + Nk_B \ln(2 \cosh \frac{1}{4}\beta U) - \frac{1}{4} Nk_B \beta U \tanh \frac{1}{4}\beta U. \quad (46)$$

With $F = E - S/k_B \beta$ and $\Omega = F - \mu N$, where Ω is the thermodynamic potential, we have

$$\Omega(\beta) = -(N/\beta) \ln[e^{S(\infty)/Nk_B} (1 + e^{\beta U/2})]. \quad (47)$$

Finally, since $\Omega = -(1/\beta) \ln \mathfrak{z}$, we obtain

$$\mathfrak{z}(\beta) = e^{S(\infty)/k_B} (1 + e^{\beta U/2})^N. \quad (48)$$

In the single-site representation discussed previously [see Eq. (28)], $\mathfrak{z} = [2(1 + e^{\beta U/2})]^N$, which implies $S(\beta=0) = k_B \ln 2^N$. Thus, in this picture, the ground state is 2^N -fold degenerate, with either spin equally probable for the electron on each site. [We restrict ourselves to $\langle n_i \rangle = \langle n_i \rangle$, but for $N \gg 1$, $N! / [(\frac{1}{2}N)!]^2 \approx 2^N$.] This is just what we would expect for independent atomic sites. In the original model of Hubbard,³ only states with full translational symmetry, i.e., $\langle n_{i\sigma} \rangle = n_{\sigma}$, were considered. This restriction eliminates antiferromagnetically ordered states. However, as long as Δ/U is finite, the ground state in the strong-correlation region is antiferromagnetic at low temperatures. Thus, Eqs. (45)–(48) are valid only for $T > T_N \sim \Delta^2/U$, where T_N is the Néel temperature. $S(\beta=\infty)$ is then the “zero-temperature limit” of the entropy in the higher-temperature nonmagnetic phase, rather than a real physical quantity.

For arbitrary bandwidth, we must use the many-body formalism. This analysis (for $n=1$) reduces in the narrow-bandwidth limit to the result found previously for independent sites, i.e., ground-state degeneracy $= 2^N$. When the hopping energy T_{ij} in the Hamiltonian (8) has off-diagonal terms, the intersite interaction lifts the degeneracy of the 2^N atomic ground states. The ground-

state wave function then involves configurations in which pairs of electronic wave functions can overlap at the site locations; i.e., the energy decrease due to delocalization more than balances the increased Coulomb repulsion. As we increase T_{ij} , more up and down spins are “paired,” and the spin entropy is reduced. Indeed, weakly correlated electrons ($T_{ij} \gg U$), lie in a half-filled band which can be occupied only in one unique way, with every \vec{k} state below the Fermi level doubly occupied. These results suggest that an interesting problem to study is the behavior of the ground-state entropy as correlations in a half-filled band are progressively increased from zero (metal, with zero entropy) to infinite strength (Mott insulator, with $S = k_B \ln 2^N$). But the main point we wish to emphasize here is that many important thermodynamic quantities (e.g., μ and E) depend only on derivatives of $\ln \mathfrak{z}$, which do *not* involve the ground-state degeneracy.

VI. SUMMARY

We have rederived the Hubbard Hamiltonian, explicitly maintaining the possibility of magnetically ordered states. An effective Hartree-Fock Hamiltonian has been obtained from the Hubbard Hamiltonian and we have demonstrated that the appropriate linearization procedure yields the correct total energy in the Hartree-Fock limit. We have also shown that the Hubbard Hamiltonian is exact in the narrow-band limit, and have thereby related the Hartree-Fock and atomic energies. Using real-time and imaginary-time Green’s functions, we have been able to interpolate between the Hartree-Fock and narrow-bandwidth limits. This procedure has been used to clear up a long-standing puzzle concerning the fact that the number of electrons in the upper pseudoparticle band is twice the number of doubly occupied sites. The single-site approximation and its effective one-electron-like representation has been introduced and justified in the narrow-band limit. We have shown that physical properties such as electrical conductivity and thermoelectric power, involving four-operator correlation functions can be evaluated correctly in the single-site representation, without recourse to two-particle Green’s functions. This is an extremely important result, since the single-site representation can then be used in conjunction with conventional band theory, which adequately describes the wider bands that are ordinarily present in Mott insulators. The total energy of the system has been evaluated at both zero temperature and finite temperature. It has been shown that a criticism of the Hubbard model based on the conclusion that it underesti-

mates the total energy is itself erroneous, and that the Hubbard model gives the exact total energy in the special case considered. Finally, we have shown that the energy at finite temperature can be calculated without regard to the presence or absence of magnetic ordering, but that this choice is critical to a determination of the entropy.

ACKNOWLEDGMENTS

Research was supported by the NSF under NSF-MRL Grant No. DMR 72-03027A05 and Fundação de Amparo à Pesquisa do Estado de São Paulo, SP, Brasil, Contract No. 77/0549.

*Present address: T. J. Watson Research Center, IBM, Yorktown Heights, N.Y. 10598.

†Permanent address: Instituto de Física-Unicamp, 13100 Campinas, SP Brasil.

‡Department of Electrical Engineering and Computer Science.

¹N. F. Mott, Proc. Phys. Soc. (Lond.) A 62, 416 (1949).

²N. F. Mott, Philos. Mag. 6, 287 (1961).

³J. Hubbard, Proc. R. Soc. A 276, 238 (1963), hereinafter referred to as H.

⁴J. Hubbard, Proc. R. Soc. A 277, 237 (1964).

⁵J. Hubbard, Proc. R. Soc. A 281, 401 (1964).

⁶D. Adler, Semiconductors and Insulators 3, 367 (1978).

⁷C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. 4.

⁸D. Adler, Solid State Phys. 21, 29 (1968).

⁹D. Adler, J. Solid State Chem. 12, 332 (1975).

¹⁰D. N. Zubarev, Soviet Phys.-Usp. 3, 320 (1960).

¹¹D. Adler and J. Feinleib, Phys. Rev. B 2, 3112 (1970).