PHYSICAL REVIEW B VOLUME 9, NUMBER 4 15 FEBRUARY 1974

Low-density thermodynamics of the Hubbard chain

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(Received 15 October 1973)

All the three-electron wave functions and energy levels are obtained for the one-dimensional Hubbard model. The second and third virial coefficients for the system are calculated exactly. The virial expansion is converted into an electron density expansion which appears to converge much better than the virial series. The two-particle and three-particle contributions to the specific heat, entropy, intra-atomic correlation function, and magnetic susceptibility of the system are obtained and presented graphically.

I. INTRODUCTION

The Hubbard model is frequently used as an approximate description of electrons in solids. In its simplest form this model describes a single band of electrons which interact only when two electrons occupy the same lattice site. Although a great deal of effort has been devoted to the study of this model, it is still far from being understood.[1-5] Furthermore, it has not been proven that the Hubbard Hamiltonian is actually a reasonable model of any real solid. Despite the likely shortcomings of the Hubbard model, one might hope to gain insight into real physics from exact or approximate solutions of this simplified model, and it has been suggested that the Hubbard model may contain the essential physics necessary to explain magnetism or the metal-nonmetal transition.[6-12]

Much of this paper is concerned with the thermodynamic properties of the one-dimensional Hubbard model. This one-dimensional system is not entirely academic. Recent investigations of charge transfer salts based on tetracyanoquinodymethane (TCNQ)[13-15] and on other solids[16,17] show that these systems can be well approximated by one-dimensional models. One can also hope that some of the conclusions based on the study of this one-dimensional system will apply to other systems.

Previous theoretical work on the thermodynamics of the one-dimensional Hubbard model has taken a variety of forms. The ground-state energy was obtained by Lieb and Wu.[18] Takahashi[19] and Shiba[20] have calculated the susceptibility at $T=0$, and Ovchinnikov[21] and Coll[22] have computed elementary excitations. Exact results for nonzero temperature consist primarily of calculations for finite chains of six or less atoms.[23-25] Recently, Beni, Holstein, and Pincus[26] pointed out that the infinite-U one-dimensional Hubbard model can be easily solved.

An important theoretical reason for considering the one-dimensional Hubbard model is that the many-electron states can be obtained exactly.[18] As a step toward taking advantage of the simplicity of these states, all of the three-electron energy levels will be expressed in a form sufficiently simple to allow a calculation of the third virial coefficient of the one-dimensional Hubbard model. In principle, the virial series should be useful in understanding the thermodynamic properties of the Hubbard model. In practice, we find that the virial series converges slowly and a knowledge of the third term in the series is not particularly useful. To overcome this difficulty, an alternative series expansion for the free energy of the Hubbard model will be presented. The new series appears to be more rapidly convergent than the virial series, and is easier to use because it is a power series in the electron density rather than in the fugacity. Using this series we are able to calculate various thermodynamic properties of the one-dimensional Hubbard model up to third order in the density. Results of numerical calculations of the entropy, specific heat, susceptibility, and intra-atomic correlation functions will be presented.

II. HUBBARD MODEL

The one-dimensional Hubbard Hamiltonian is

$$H=\sum_{i=1}^{N}{}'(C_{i\sigma}^{\dagger}C_{i+1\sigma}+C_{i\sigma}^{\dagger}C_{i-1\sigma})+U\sum_{i=1}^{N}C_{i\uparrow}^{\dagger}C_{i\uparrow}C_{i\downarrow}^{\dagger}C_{i\downarrow}\ , \qquad (1)$$

where $C_{i\sigma}^{\dagger}$ $(C_{i\sigma})$ is the creation (annihilation) operator for an electron in a Wannier state with spin σ located at a site labeled i. Periodic boundary conditions mean that the site N is equivalent to the site 0. The creation operators acting on the vacuum state ϕ denote Slater-determinant wave functions. The creation and annihilation operators obey the usual fermion anticommutation relations. Single-electron eigenstates $(\psi_{k\sigma})$ of this Hamiltonian are the usual Bloch functions:

$$\psi_{k\sigma}=(1/\sqrt{N})\sum_{l=1}^{N}e^{ikl}C_{l\sigma}^{\dagger}\phi\ . \qquad (2)$$

The energy of this state is

$$\epsilon_k = 2\cos k \ . \tag{3}$$

The units used here imply that the total bandwidth is equal to four. To satisfy the periodic boundary conditions,

$$k = 2\pi n/N \ , \tag{4}$$

where n is an integer and k must lie in the first Brillouin zone.

The two-electron states are either spin triplets or spin singlets. The triplet states are unperturbed by the short-ranged interaction of the Hubbard model, and the two-electron energies are simply the sum of the single-electron energies with only Pauli-principle restrictions (the two electrons must have different momenta). The singlet states are either phase-shifted continuum states or bound states. The continuum singlet states have energies

$$\epsilon_{p_1p_2} = 2(\cos p_2 + \cos p_2) \ , \tag{5}$$

where p_1 and p_2 are phase-shifted momenta:

$$p_1 = k_1 + 2\delta_{p_1p_2}/N \ , \quad p_2 = k_2 - 2\delta_{p_1p_2}/N \ . \tag{6}$$

The phase shift is given by

$$\cot\delta_{p_1p_2} = (-2/U)(\sin p_1 - \sin p_2) \tag{7}$$

and the magnitude of $\delta_{p_1p_2}$ is less than $\frac{1}{2}\pi$. A one-to-one correspondence between the two electron interacting and noninteracting ($U=0$) states and energies is obtained by letting the phase shifts vanish.

For a fixed total momentum $q = p_1 + p_2$, the bound-state energies are greater than the band energies. These states correspond to the noninteracting state with $k_1 = k_2$ or $k_1 = k_2 + 2\pi/N$, and with the magnitude of k less than $\frac{1}{2}\pi$. For these values of the single-particle momenta, the phase shifts change discontinuously from $-\frac{1}{2}\pi$ to $\frac{1}{2}\pi$. A continuum state is lost and a bound state appears. The energy of the bound state with total momentum q is

$$\epsilon_q^B = [U^2 + (4\cos\tfrac{1}{2}q)^2]^{1/2} \ . \tag{8}$$

The three-electron states of the Hubbard model are spin quartets and spin doublets. The quartet states are unaffected by the interaction. The doublet states are either continuum states, or states composed of a bound-pair scattering from a continuum electron. The much more difficult problem of the many-electron continuum states of the one-dimensional Hubbard model has been solved by Lieb and Wu using methods of Yang and Gaudin.

The three-electron continuum state energies can be obtained from a simplified form of the Lieb-Wu equations (9)–(11).[18] The simplification is possible only when there are three electrons. Lieb and Wu considered only states characterized by real momenta (values for k), and did not derive expressions for wave functions or energy levels involving bound pairs. The states involving bound pairs have been discussed by McGuire and Yang[27] from an S-matrix point of view for a similar problem (the one-dimensional electron gas with delta-function interactions). We will obtain the bound three-electron states and energy levels for the one-dimensional Hubbard model in a form which satisfies the periodic boundary conditions.

The three-electron continuum states are characterized by three unequal momenta: p_1, p_2, and p_3. The doublet-state momenta are phase shifted away from their noninteracting values. In order to obtain the three-electron continuum phase shifts from the work of Lieb and Wu in simple form, we make the following variable substitutions:

$$N_a \rightarrow N \ ,$$

$$2\pi I_j/N_a \rightarrow k_j \ , \quad j = 1, 2, 3$$

$$k_j \rightarrow p_j \ , \qquad \Lambda_\beta \rightarrow \Lambda \ ,$$

$$\theta(2\sin k_j - 2\Lambda_\beta) \rightarrow 2\delta_j + \pi \ .$$

For three particles, the interacting states are described by the Lieb-Wu equations (9)–(11) with $M = 1$ and $J_\alpha = \frac{3}{2}$. After division by N, Eq. (9) becomes

$$p_j = k_j + 2\delta_j/N \ ; \tag{9}$$

Eq. (10) becomes

$$\delta_1 + \delta_2 + \delta_3 = 0 \ ; \tag{10}$$

and Eq. (11) becomes

$$\cot\delta_j = (-4/U)(\sin p_j - \Lambda) \ . \tag{11}$$

If k_1, k_2, and k_3 are all different, there are two solutions to the above equations denoted $\delta^\pm$. They correspond to two different solutions for $\Lambda (= \Lambda^\pm)$. The values for $\Lambda^\pm$ can be found using simple trigonometric identities:

$$\Lambda^\pm = \tfrac{1}{3}\left(\mathcal{S} \pm \{\mathcal{S}^2 + 3[(\tfrac{1}{4}U)^2 - \mathcal{P}]\}^{1/2}\right) \ , \tag{12}$$

$$\mathcal{S} = \sin p_1 + \sin p_2 + \sin p_3 \ , \tag{13}$$

and

$$\mathcal{P} = \sin p_1 \sin p_2 + \sin p_2 \sin p_3 + \sin p_3 \sin p_1 \ . \tag{14}$$

The phase shifts are determined up to a phase factor of $n\pi$. Rather than restricting the magnitude of the phase shifts to be less than $\frac{1}{2}\pi$, we make the following choice for the phase shifts: if

$$\sin k_1 \geq \sin k_2 \geq \sin k_3 \ , \tag{15}$$

then

$$-\tfrac{2}{3}\pi < \delta_1 \leqslant \tfrac{1}{3}\pi\ , \quad -\tfrac{1}{2}\pi < \delta_2 \leqslant \tfrac{1}{2}\pi\ , \ -\tfrac{1}{3}\pi < \delta_3 \leqslant \tfrac{2}{3}\pi\ . \tag{16}$$

This choice of phase shifts has the following properties:

(i) All the phase shifts are continuous functions of U, and they vanish as $U \to 0$; (ii) The sum of the phase shifts ($\delta_1^+ + \delta_2^+ + \delta_3^+$ or $\delta_1^- + \delta_2^- + \delta_3^-$) is zero; (iii) The two- and three-electron phase shifts are related as follows: $\delta_1^+ + \delta_1^- = \delta_{p_1 p_2} + \delta_{p_1 p_3} + O(1/N)$. Analogous equations apply for δ_2 and δ_3.

If two of the k's are equal (say k_1 and k_2), there is only one doublet solution and no quartet state. The phase shifts for this special case are specified by Eq. (10) and the following equations which are a special case of Eqs. (11)–(14):

$$\delta_2 = \delta_1 - \pi \,\mathrm{sgn}(\delta_1)$$

and

$$\cot\delta_1 = (-4/3U)\{[\sin p_1 - \sin p_3] \pm [(\sin p_1 - \sin p_3)^2 + 3(\tfrac{1}{4}U)^2]^{1/2}\}\ . \tag{17}$$

The sign of the square root is taken to be the negative of the sign of $(\sin p_1 - \sin p_3)$, and the magnitude of δ_1 is taken to be less than $\frac{1}{2}\pi$.

The three-particle states involving a bound pair can be obtained in a straightforward but tedious manner by fitting boundary conditions at the point of the electron-electron interaction. In terms of the creation and annihilation operators, these unnormalized states are

$$\psi^B_{q,p,\sigma} = \sum_l e^{iql} C^\dagger_{l\sigma} [A_1(l) + A_2(l)]\phi\ , \tag{18}$$

where $A_1(l)$ and $A_2(l)$ are

$$\begin{aligned} A_1(l) &= e^{-i\delta} \sum_{m=1}^{N} \sum_{n=-N/2}^{N/2} e^{i[(q-p)/2]n} e^{-\Gamma|n|} \\ &\quad \times e^{ipm} C^\dagger_{(l+n)\bar\sigma} C^\dagger_{(l+m)\bar\sigma}\ , \\ A_2(l) &= 2i \sin\delta \sum_{n<0} \sum_{m>0} e^{i[(q-p)/2](n+m)} \\ &\quad \times e^{-\Gamma(|n|+|m|)} C^\dagger_{(l+n)\bar\sigma} C^\dagger_{(l+m)\bar\sigma}\ . \end{aligned} \tag{19}$$

The quantity q represents the total momentum of the system. There is a phase shift associated with p, but none with q:

$$p = k + 2\delta/N\ , \tag{20}$$

$$\cot\delta = (-4/U)[\sin p - \cosh\Gamma \sin\tfrac{1}{2}(q-p)], \tag{21}$$

and the magnitude of δ is less than $\frac{1}{2}\pi$. The "width" $1/\Gamma$ of the bound state is given by

$$\sinh\Gamma = U/[4\cos\tfrac{1}{2}(q-p)] \tag{22}$$

and the total energy of the state is

$$\epsilon^B_{q,p} = 2\cos p + \{U^2 + [4\cos\tfrac{1}{2}(q-p)]^2\}^{1/2}\ . \tag{23}$$

The three-particle state in which the bound pair has momentum $(q - k - 2\delta/N)$ and the free particle has momentum $(k + 2\delta/N)$ corresponds to the $U = 0$ states in which the three electrons have momenta $\frac{1}{2}(q-k)$, $\frac{1}{2}(q-k)$, and k. If $\frac{1}{2}(q-k) = k$, there is still a bound state even though there is no free-electron state which corresponds to this state. On the other hand, there is a three-particle bound state which is eliminated when the phase shift δ changes discontinuously from $\frac{1}{2}\pi$ to $-\frac{1}{2}\pi$. This discontinuity occurs, according to Eq. 21, when

$$\sin p = \cosh\Gamma \sin\tfrac{1}{2}(q-p)\ . \tag{24}$$

To make a one-to-one correspondence between the $U = 0$ and $U \neq 0$ states, this eliminated interacting electron state must be associated with the noninteracting state forbidden by the Pauli principle. These two states approach each other continuously as $U \to 0$.

This completes our description of the three-electron solutions to the one-dimensional Hubbard model. These solutions will be used to obtain the virial coefficients to be described in Sec. III.

III. VIRIAL COEFFICIENTS

The grand partition function of a system of electrons can be expressed as a series expansion involving the one-particle, two-particle, etc., partition functions. Such an expansion is particularly useful in the limit of high temperatures and low densities.

The grand partition function Z of a system of electrons at temperature T may be written

$$Z = 1 + Z_1 e^{\nu} + Z_2 e^{2\nu} + Z_3 e^{3\nu} + \cdots\ , \tag{25}$$

where Z_n is the n-electron partition function, i.e.,

$$Z_n = \mathrm{Tr}\{e^{-\beta H_n}\} \tag{26}$$

with $\beta = 1/k_B T$, H_n is the Hamiltonian for n interacting electrons, and $\nu = \beta\mu$, where μ is the chemical potential.

The expansion for $\ln(Z)$ can be written

$$\ln(Z) = Z_1(e^{\nu} + b_2 e^{2\nu} + b_3 e^{3\nu} + b_4 e^{4\nu} + \cdots) \tag{27}$$

where the b_n are called the virial coefficients.[28] Using (25) to expand $\ln(Z)$, comparing with (27), and equating coefficients of equal powers of e^{ν}, we easily obtain

$$\begin{aligned} b_2 &= (Z_2 - \tfrac{1}{2} Z_1^2)/Z_1\ , \\ b_3 &= (Z_3 - Z_1 Z + \tfrac{1}{3} Z_1^3)/Z_1\ , \\ b_4 &= (Z_4 + Z_1^2 Z_2 - Z_1 Z_3 - \tfrac{1}{2} Z_2^2 - \tfrac{1}{4} Z_1^4)/Z_1\ . \end{aligned} \tag{28}$$

A numerical evaluation of the mth virial coefficient, b_m, requires the knowledge of the exact m-

electron eigenenergies. Some work has been done in the past on the calculation of the virial coefficients for a system of electrons interacting according to the Hubbard Hamiltonian.[29–31] Callaway[29] has obtained an exact expression for the second virial coefficient in this case. Callaway and Rajagopal[30] have approximately evaluated the third virial coefficient.

In this section we outline the *exact* calculation of the second and third virial coefficients for a system of electrons described by the one-dimensional Hubbard Hamiltonian. There are two contributions to the second virial coefficient b_2. First, there is a contribution from the two-electron bound states. Second, there is a term which results from the two-electron scattering states.[32]

The bound-state contribution $b_{2b}(U)$, where U is the potential, is given by

$$b_{2b}(U)-b_{2b}(0)=\sum_{q}\left\{e^{-\beta[(4\cos\frac{1}{2}q)^2+U^2]}-e^{-4\beta\cos\frac{1}{2}q}\right\}/Z_1\,, \tag{29}$$

where

$$Z_1=2\sum_{k}e^{-2\beta\cos k}\,, \tag{30}$$

with

$$-\pi\leqslant k,\quad q<\pi\,.$$

The continuum-state contribution $b_{2c}(U)$ can be calculated by expanding the partition function to first order in the phase shifts $\delta_{k_1k_2}$:

$$b_{2c}(U)-b_{2c}(0)=(2\beta/NZ_1)\sum_{k_1k_2}e^{-2\beta(\cos k_1+\cos k_2)}\times\delta_{k_1k_2}(\sin k_1-\sin k_2)\,. \tag{31}$$

The second virial coefficient $b_2(0)$ with the potential $U=0$ has the simple form

$$b_2(0)=-\sum_{k}e^{-4\beta\cos k}/Z_1\,. \tag{32}$$

The calculation of the third virial coefficient b_3 is a good deal more complicated than that of the second. In evaluating Z_3, the three-particle partition function, we have to consider the following contributions.

(i) The three-particle bound-state contribution, obtained by expanding these terms in the partition function to first order in $1/N$. For example, for the free electron (not bound),

$$e^{-2\beta\cos p}=e^{-2\beta\cos(k+2\delta/N)}$$

$$\simeq e^{-2\beta\cos k}(1+4\beta\sin k\,\delta/N)\,. \tag{33}$$

A similar expansion is used for the bound pair.

(ii) A correction to the above term which arises because a bound state is eliminated every time the phase shift changes discontinuously from $-\frac{1}{2}\pi$ to $\frac{1}{2}\pi$.

(iii) The continuum contribution to Z_3 and Z_1Z_2 terms in which k_1, k_2, and k_3 are all different. These terms denoted Z_3' and $(Z_1Z_2)'$ can be expressed in terms of phase shifts, but the calculation is considerably more complicated than the corresponding calculation of the second virial coefficient because of the cancellation of terms first order in $1/N$. To first order in $1/N$,

$$Z_3'=\frac{1}{6}\sum_{k_1,k_2,k_3}e^{-\beta[\epsilon_{k_1}+\epsilon_{k_2}+\epsilon_{k_3}]}\frac{4\beta}{N}[(\delta_1^++\delta_1^-)\sin k_1+(\delta_2^++\delta_2^-)\sin k_2+(\delta_3^++\delta_3^-)\sin k_3] \tag{34}$$

and

$$(Z_1Z_2)'=\frac{1}{6}\sum_{k_1k_2k_3}e^{-\beta[\epsilon_{k_1}+\epsilon_{k_2}+\epsilon_{k_3}]}\frac{4\beta}{N}[(\delta_{p_1p_2}+\delta_{p_1p_3})\sin k_1+(\delta_{p_2p_1}+\delta_{p_2p_3})\sin k_2+(\delta_{p_3p_1}+\delta_{p_3p_2})\sin k_3]\,. \tag{35}$$

The difference $Z_3'-(Z_1Z_2)'$ vanishes to first order in $1/N$ because

$$\delta_1^++\delta_1^-=\delta_{p_1p_2}+\delta_{p_1p_3}+O(1/N)\,.$$

Analogous equations apply for $\delta_2^\pm$ and $\delta_3^\pm$. This formula can be proven by taking the cotangent of each side and replacing p_i by k_i (a correction of order $1/N$). The choice of phase shifts described by Eqs. (15) and (16) means that there will be no difference of $\pm n\pi$ between the right- and left-hand sides of the above equation. Because there are N^3 terms in Z_3' and $(Z_1Z_2)'$, we must expand each term to order $(1/N)^2$ to find a nonzero contribution to b_3. The following is the correction to the phase shifts:

$$\delta_1^++\delta_1^--\delta_{p_1p_2}-\delta_{p_1p_3}=(1/N)[D_1^++D_1^--D_{12}-D_{13}] \tag{36}$$

and

$$D_1^\pm=-8\sin^2\delta_1[-\delta_1^\pm(\cos k_1/U)+\alpha_1^\pm+\alpha_2^\pm+\alpha_3^\pm]\,, \tag{37}$$

$$\alpha_i^\pm=\frac{\cos k_1}{3U}\left(1\pm\frac{3\sin k_1-\mathcal{S}}{2\{\mathcal{S}^2+3[(\frac{1}{4}U)^2-\mathcal{P}]\}^{1/2}}\right), \tag{38}$$

where $\mathcal{S}$ and $\mathcal{P}$ are defined in Eqs. (13) and (14). The two-particle corrections to the phase shifts are simpler:

$$D_{12} = 2\sin^2(\delta_{p_1p_2})(\cos k_1 - \cos k_2)/U . \qquad (39)$$

Other terms of order $1/N^2$ come from the expansion of $e^{-2\beta\cos p}$ to second order. These terms are of the form

$$(4\beta\delta^2 e^{-2\beta\cos p}/N^2)(\cos k + 2\beta\sin^2 k) . \qquad (40)$$

(iv) The three-particle continuum-state terms in which two of the three wave vectors are equal. In this case there is only one doublet state, and the expansion need be carried out only to first order in $1/N$.

The virial coefficients (b_2 and b_3) were calculated numerically on an IBM 360–65 computer. Each author independently programmed a calculation of the virial coefficients, and nearly identical results were obtained. The mesh size was chosen so as to ensure convergence of the integrals. Using our final mesh size, a straightforward evaluation of the three-dimensional integrals necessary to obtain b_3 would require evaluation of the integrands at about half a million points. Symmetry considerations drastically reduce the number of points in the integral, so that a calculation of both virial coefficients using double-precision accuracy took less than 30 sec of computer time.

The temperature dependence of the virial coefficients (b_2 and b_3) is shown in Fig. 1. The third virial coefficient is always larger in magnitude than the second even for small $\beta = 1/k_B T$. The ratio b_3/b_2 increases rapidly with β and as a result the virial series appears to converge very poorly unless e^{ν} is extremely small. The apparent poor convergence of the virial series motivated us to consider the density expansion for the Hubbard model which will be presented in Sec. IV.

IV. DENSITY EXPANSION

The virial expansion appears to converge slowly for the Hubbard model, and in practice the expansion is difficult to apply because of the necessity of finding the chemical potential as a function of temperature. The virial series can be used to generate another series in which the free energy is expressed as a power series in the electron density and the chemical potential need not be determined. This series is expanded about the $U=0$ limit of the Hubbard model, and it converges faster than the virial series even when U is large. In Sec. IV the convergence of this expansion will be demonstrated for the simple localized electron limit of the Hubbard model and in Sec. V the virial coefficients obtained earlier will be used to generate the new series up to third order in the density for the one-dimensional Hubbard model.

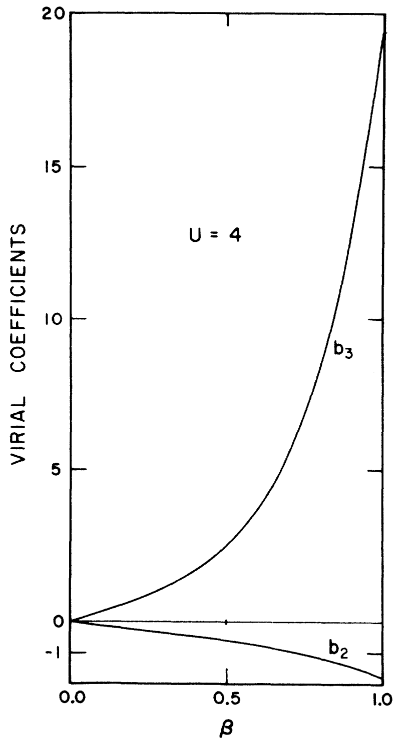

FIG. 1. Temperature ($\beta = 1/k_B T$) dependence of the interaction contribution to the second and third virial coefficients for $U=4$. Data for lower temperatures are not shown because b_3 becomes very large compared to b_2.

To obtain the density expansion we consider an artificial system with parametrized interactions which are adjusted to yield virial coefficients identical to the virial coefficients of the Hubbard model. We assume that if the two systems have identical virial coefficients they will have identical thermodynamic properties even, perhaps, if the virial series does not formally converge. The free energy in the artificial system can be simply and naturally expressed as a power series in the density. Since the artificial system is (supposedly) thermodynamically identical to the Hubbard model, the density power series for the artificial system is also valid for the Hubbard model. The term in this series proportional to ρ^m depends only on virial coefficients of order m or lower. This means that the density power series expansion for the free energy can be obtained up to order m if the first m virial coefficients are known.

We cannot rigorously prove the validity of this power series expansion since there is no proof of convergence of the virial series for the Hubbard model. Clearly, we should not expect convergence below any phase transition temperature. However, since we are actually only able to obtain terms to third order, the mathematical problem of convergence is rather academic. The transformation of the virial series into a power series in the density is usually done by assuming that the fugacity can be expanded as a power series in the density. The description here is somewhat different but leads to the standard results. The introduction of the artificial system gives an intuitive picture of the meaning of the power series, and makes the derivation of the susceptibility relatively simple.

The artificial fermion system has single-electron energies equal to the single-electron energies of the Hubbard model. The interactions are assumed to be infinitely long range and momentum and spin independent, so that the thermodynamics can be simply calculated. The energy of two-electron states for this system is

$$E_{k_1 k_2} = \epsilon_{k_1} + \epsilon_{k_2} + [E_2(\beta)/N] , \tag{41}$$

where $E_2(\beta)$ is an effective temperature-dependent pairwise-additive interaction, which is determined by equating the second virial coefficient of the artificial system $\tilde{b}_2$ to the same quantity for the Hubbard model. Neglecting terms of order $1/N$ and smaller, this virial coefficient is

$$\tilde{b}_2 = -\tfrac{1}{2} - \beta Z_1 E_2(\beta) . \tag{42}$$

Equating $\tilde{b}_2$ to b_2 yields

$$E_2(\beta) = -(\tfrac{1}{2} + b_2)/\beta Z_1 . \tag{43}$$

Because $E_2(\beta)$ was assumed to represent pair interactions, the energy of an n-electron state with $\tfrac{1}{2}n(n-1)$ distinct electron pairs is

$$E_{k_1, k_2 \cdots k_n} = \sum_{i=1}^{n} \epsilon_{k_i} + \frac{n(n-1)}{2N} E_2(\beta) . \tag{44}$$

The free energy per atom of this artificial system can be easily calculated because the interactions are so simple, and for large n it is

$$F(\beta) = F^{(0)}(\beta) + \tfrac{1}{2}\rho E_2(\beta) , \tag{45}$$

where $F^{0}(\beta)$ is the free energy of the noninteracting Hubbard model and ρ is the electron density.

The artificial system with only pair interactions can reproduce only the second virial coefficient of the Hubbard model. In order to duplicate all the virial coefficients, additional parametrized interactions involving more than two particles must be included in the artificial system. The energy of an n-electron state is then

$$\begin{aligned} E_{k_1 \cdots k_n} &= \sum_{i=1}^{n} \epsilon_{k_i} + \frac{n(n-1)}{2N} E_2(\beta) \\ &\quad + \frac{n(n-1)(n-2)}{6N^2} E_3(\beta) + \cdots \\ &= \sum_{i=1}^{n} \epsilon_{k_i} + \sum_{j=2}^{n} \binom{n}{j} \frac{E_j(\beta)}{N^{(j-1)}} , \end{aligned} \tag{46}$$

where $\binom{n}{j}$ is a binomial coefficient. Each interaction energy $E_m(\beta)$ is uniquely determined by the Hubbard-model virial coefficients of order less than or equal to m. The term $E_3(\beta)$, for example, which represents a three-particle interaction in the artificial system is given by

$$E_3(\beta) = \frac{-6[b_3(U) - b_3(U=0)] - 2[b_2^2(U) - b_2^2(U=0)]}{\beta (Z_1/N)^2} . \tag{47}$$

The free energy of the model system can still be simply calculated, and for large n this free energy is naturally expressed as a power series in the density:

$$\begin{aligned} F(\beta) &= F^{0}(\beta) + \tfrac{1}{2}\rho^2 E_2(\beta) + \tfrac{1}{6}\rho^3 E_3(\beta) \\ &\quad + \cdots + (\rho^n/n!) E_n(\beta) + \cdots . \end{aligned} \tag{48}$$

In order to demonstrate the density expansion and its convergence properties we first consider a particularly simple case; the Hubbard model in the localized-electron limit (hopping equal to zero) and one electron per atom. This is a good test because it is probably the most unfavorable case for the convergence of the density expansion. This is because the density is large and the expansion is about the itinerant- rather than the localized-electron limit.

For this simple case the first three virial coefficients can be easily calculated. They are

$$\begin{aligned} b_2 &= -\tfrac{1}{2} - \tfrac{1}{2}(1 - e^{-\beta U}) , \\ b_3 &= \tfrac{1}{3} + (1 - e^{-\beta U}) , \\ b_4 &= -\tfrac{1}{4} - \tfrac{3}{2}(1 - e^{-\beta U}) - \tfrac{1}{4}(1 - e^{-\beta U})^2 , \end{aligned} \tag{49}$$

and the chemical potential is $\tfrac{1}{2}U$. The virial series for this system does not converge, and the first three terms in the series give a very poor approximation to the thermodynamics of the system.

The effective interaction energies $E_m(\beta)$ are obtained from the virial coefficients, and they are

$$\begin{aligned} E_2(\beta) &= (1/2\beta)(1 - e^{-\beta U}) , \\ E_3(\beta) &= (3/4\beta)(1 - e^{-\beta U})^2 , \\ E_4(\beta) &= -(3/4\beta)(1 - e^{-\beta U})^2 + (5/2\beta)(1 - e^{-\beta U})^3 , \end{aligned} \tag{50}$$

and for an electron density ρ equal to one, the series expansion for the free energy is

$$\begin{aligned} F &= (-1/\beta)\ln(4) + (1/4\beta)[(1 - e^{-\beta U}) + \tfrac{3}{8}(1 - e^{-\beta U})^2 \\ &\quad + \tfrac{5}{12}(1 - e^{-\beta U})^3 + \cdots] . \end{aligned} \tag{51}$$

The exact free energy for this simple case is

$$F = \tfrac{1}{2}U - (1/\beta)\ln(2 + 2e^{\beta U/2}) . \tag{52}$$

In Fig. 2, we have compared the exact specific heat obtained from free energy given in Eq. (52) with the series approximations of the specific heat accurate to second, third, and fourth order in the density. Clearly the approximations are qualitatively reasonable for small βU, but are far from perfect. This is not surprising since a low-density

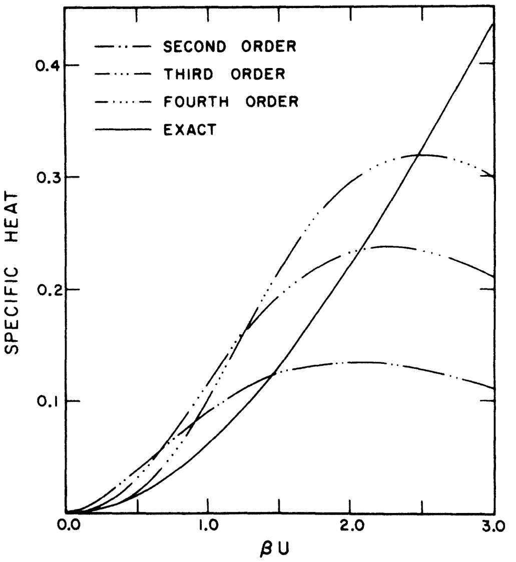

FIG. 2. Specific heat of the Hubbard model in the localized-electron limit with one electron per atom. Exact results are compared with approximations accurate to second, third, and fourth order in the density.

expansion has been applied to a high-density system. Note that contributions to the specific heat from the higher-order terms proportional to ρ^3 and ρ^4 can be either positive or negative, depending on the value of βU.

Finally, we would like to point out a general property of the series expansion: that terms proportional to ρ^{2n} and ρ^{2n-1} are proportional to β^{n-1} for small β. This means that the density power series should converge both for high temperature and low density. This convergence property of the density expansion can be seen from perturbation theory. The partition function of the Hubbard model could, in principle, be determined from a traditional perturbation expansion about the $U=0$ limit of the Hubbard model. An nth-order term in this series would be proportional to $(\beta U)^n$ times the expectation value of a string of $2n$ interaction representation number operators. These expectation values include terms proportional to various powers of the density—but only powers less than or equal to $2n$ since that is the number of number operators. Equivalently, by a rearrangement of terms, any term in the partition function proportional to the mth power of the density must also be proportional to an integral power of β $(=n')$ greater than or equal to $\frac{1}{2}m$. Then, if the free energy $[-(1/\beta)\ln(Z)]$, is expressed as a power series in ρ, the term proportional to ρ^m must vanish at least as fast as $\beta^{(n'-1)}$ as β goes to zero. This implies that

$$\lim_{\beta\to 0}(E_{2n}(\beta)/\beta^n)\to C_{2n}\ ,$$

$$\lim_{\beta\to 0}(E_{2n-1}/\beta^n)\to C_{2n-1}\ . \qquad (53)$$

The constants C_n could, in principle, be obtained from a power-series expansion at $\mathrm{Tr}\{e^{-\beta H}\}$, but in practice it is tedious to go to a very high order.

V. RESULTS

A sampling of the results obtainable from the density expansion of the free energy of the one-dimensional Hubbard model is presented graphically in this section. Because of the oversimplicity of the Hubbard model, comparisons of experimental data with these results should be treated with some skepticism, and only a limited number of data are presented here. We feel that the primary utility of the results presented here is to give a qualitative picture of electron interaction effects from a high-temperature, low-density point of view. The results are presented for $U=4$ and $U=8$ because these interaction strengths characterize, roughly speaking, the "intermediate-coupling" regime where perturbation treatments are least useful.

The interaction corrections to the specific heat (curves C_2 and C_3) are presented in Fig. 3. The total specific heat is obtained by adding the specific heat of the noninteracting system ($U=0$) to $\rho^2 C_2 + \rho^3 C_3$ + higher-order terms in the density. Since

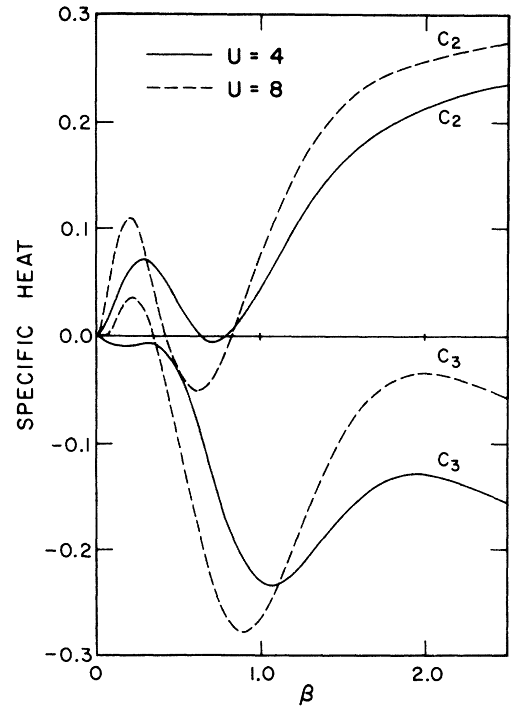

FIG. 3. Interaction contributions to the specific heat proportional to ρ^2 and ρ^3 denoted C_2 and C_3 respectively. Curves are shown for $U=4$ and $U=8$. The electron density is ρ.

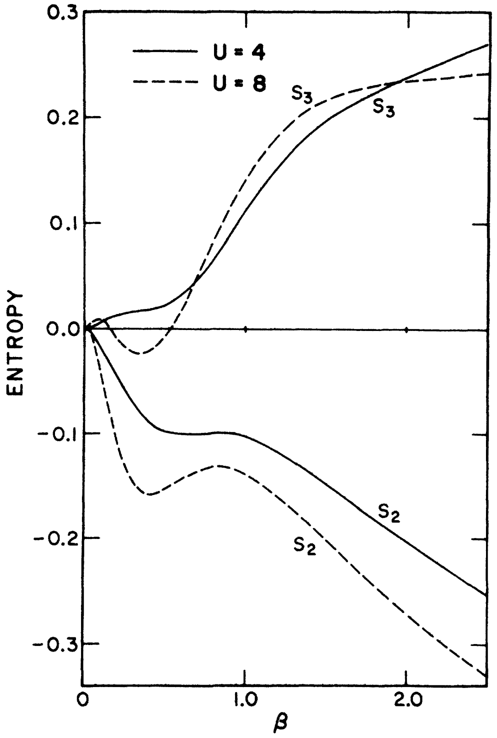

FIG. 4. Interaction contribution to the entropy proportional to ρ^2 and ρ^3, for $U=4$ and $U=8$.

C_3 is multiplied by one additional power of ρ, the density expansion appears to be converging for small ρ, but when $\rho = 1$ the third-order correction is about as large as the second-order term. The anomaly in C_2 for small β occurs when the temperature is sufficiently large to produce a large number of high-energy bound states. The high-temperature behavior of C_3 is complicated. At lower temperatures, the second-order correction to the specific heat constitutes an enhancement, while the third-order correction decreases the specific heat.

The interaction corrections to the entropy proportional to ρ^2 and ρ^3 are shown in Fig. 4. The high-temperature anomalies can be seen again in the entropies. At lower temperatures the second-order entropy correction is negative, but the third-order correction is positive.

The intra-atomic correlation terms are shown in Figs. 5 and 6. The correlation function is obtained by differentiating the free energy with respect to U. Unlike the cases of the specific heat and the entropy, no additional terms need be added to the results in Figs. 5 and 6. Instead,

$$\langle n_\uparrow n_\downarrow \rangle = \rho^2 \langle n_\uparrow n_\downarrow \rangle_2 + \rho^3 \langle n_\uparrow n_\downarrow \rangle_3 + \cdots ; \qquad (54)$$

as β goes to zero, the second-order contribution to the correlation function approaches the uncorrelated

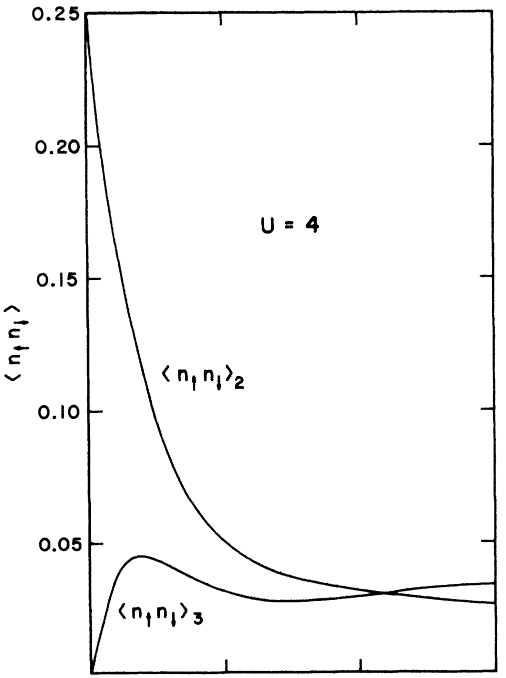

FIG. 5. Intra-atomic correlations proportional to ρ^2 and ρ^3 for $U=4$. Curves remain roughly constant for larger β.

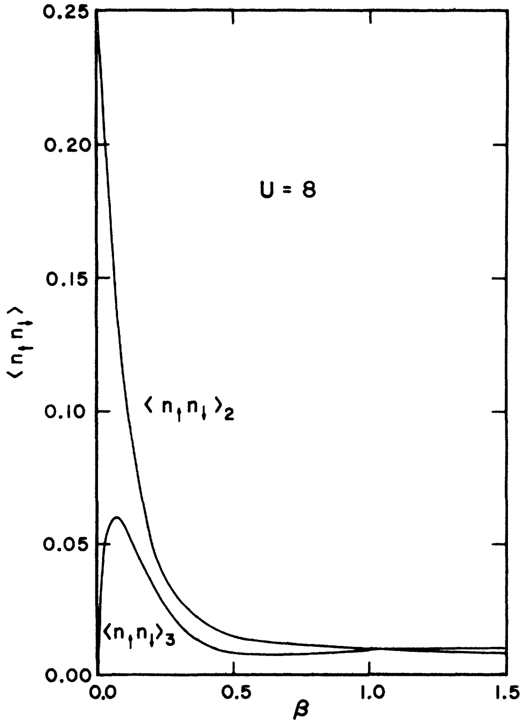

FIG. 6. The intra-atomic correlations proportional to ρ^2 and ρ^3 for $U=8$. Again the curves approach a constant value as β increases.

limit, $\frac{1}{4}\rho^2$. As the temperature is decreased, correlations reduce the second-order contribution to $\langle n_\uparrow n_\downarrow \rangle$, but the third-order contribution increases with β for small β. At lower temperatures the correlations tend to approach a constant.

A great deal of theoretical work has been devoted to investigations of the magnetic properties of the Hubbard model. We will use a low-density expansion of the one-dimensional Hubbard model to obtain expressions for the first two corrections to the inverse susceptibility. All the previous results could be obtained simply by appropriate differentiation of the free-energy terms in the expansion, but in order to obtain the susceptibility a slightly different expansion must be considered.

The susceptibility can be calculated from a knowledge of the free energy as a function of magnetization m. This quantity $F(\beta, m)$ is obtained by artificially constraining the magnetization. Minimization of the free energy with respect to m yields the true free energy and the equilibrium magnetization. The quantity $F(\beta, m)$ can be expanded in a series similar to the density expansion discussed earlier. By equating the second virial coefficient of the Hubbard model to the second virial coefficient of the artificial system with the same magnetization, the term $\frac{1}{2}\rho^2 E_2(\beta)$ becomes

$$2\rho_\uparrow \rho_\downarrow E(\beta) = \tfrac{1}{2}(\rho^2 - m^2)E_2(\beta) \;, \tag{55}$$

where ρ_σ is the density of electrons with spin σ. The form of this term is a consequence of the fact that only electrons with antiparallel spins interact. Similarly, the third-order term becomes

$$\tfrac{1}{6}\rho(\rho^2 - m^2)E_3(\beta) \;. \tag{56}$$

Higher-order terms have more complicated magnetization dependences and are not simply proportional to $(\rho^2 - m^2)$. The susceptibility is found by adding an external field term $-Bm$ to $F(B, m)$. The free energy of the Hubbard model is then

$$F(\beta, m) = F_0(\beta, m) + \tfrac{1}{2}(\rho^2 - m^2)E_2(\beta) + \tfrac{1}{6}\rho(\rho^2 - m^2)E_3(\beta) + \cdots - Bm \;, \tag{57}$$

where $F_0(\beta, m)$ is the free energy of the noninteracting Hubbard model. Setting the derivative of F with respect to m equal to zero, and writing $\partial F_0/\partial m$ as $2m\partial F_0/\partial m^2$ we obtain the susceptibility:

$$\chi = \frac{m}{B} = \left[\frac{1}{2\partial F_0/\partial m^2}\right]\left[1 - \left(E_2 + \frac{\rho E_3}{3}\right)\left(\frac{1}{\partial F_0/\partial m^2}\right)\right]^{-1} . \tag{58}$$

Denoting the susceptibility of the noninteracting Hubbard model as χ_0, χ becomes

$$\chi = \chi_0[1 - (E_2 + \tfrac{1}{3}E_3\rho)\chi_0]^{-1} \;. \tag{59}$$

Here $(E_2 + \frac{1}{3}E_3\rho)$ can be interpreted as the effective interaction of the Stoner theory of ferromagnetism which enhances the susceptibility. Equation (51) can be written

$$\chi^{-1} = \chi_0^{-1} - (E_2 + \tfrac{1}{3}E_3\rho + \cdots) \;. \tag{60}$$

This result appears to differ from the result of Ref. 30 because we have calculated χ^{-1} rather than χ, and our χ_0 which is the susceptibility of the noninteracting Hubbard model differs from the χ_0 defined by Callaway and Rajagopal.

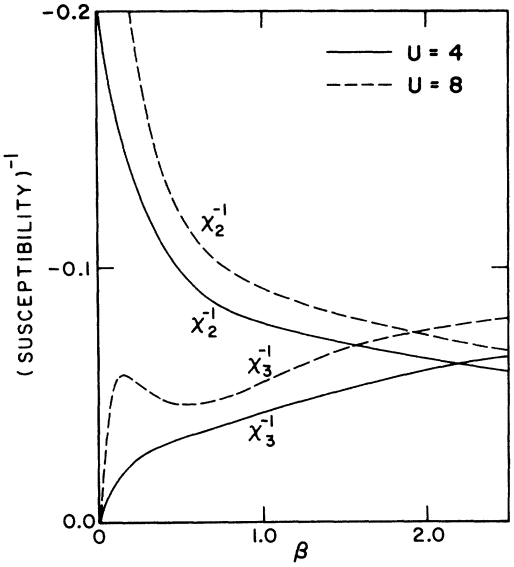

FIG. 7. Interaction contributions to the inverse susceptibility (enhancement factor) proportional to square and cube of the electron density ρ. The zero-order susceptibility is that of the noninteracting Hubbard model.

The interaction corrections to χ^{-1} are shown in Fig. 7. E_2 is denoted χ_2^{-1}, and $\frac{1}{3}E_3$ is denoted as χ_3^{-1}. Both terms enhance the susceptibility. The two-particle susceptibility enhancement decreases with increasing β, and the three-particle enhancement generally increases with increasing β.

Clearly, the calculation of the third virial coefficient and the associated density expansion is only a small step toward the understanding of the Hubbard model. It is possible that a virial analysis could be carried out to higher order, but a considerably more sophisticated treatment of the eigenenergies would be necessary.

ACKNOWLEDGMENTS

We wish to thank Dr. Joseph Callaway and Dr. A. K. Rajagopal for a number of helpful discussions and ideas which made the completion of this work possible.

[1] J. des Cloizeaux, J. Phys. Radium 20, 606 (1959); J. Phys. Radium. 20, 751 (1959).

[2] J. Hubbard, Proc. R. Soc. A 276, 238 (1963); Proc. R. Soc. A 281, 401 (1964).

[3] M. C. Gutzwiller, Phys. Rev. Lett. 10, 159 (1963).

[4] J. Kanamori, Prog. Theor. Phys. 30, 275 (1963).

[5] A. B. Harris and R. V. Lange, Phys. Rev. 157, 295 (1967).

[6] M. Cyrot, Phys. Rev. Lett. 25, 871 (1970).

[7] T. Kaplan and R. Bari, J. Appl. Phys. 41, 815 (1970).

[8] J. C. Kimball and J. R. Schrieffer, in *Magnetism in Alloys*, edited by P. A. Beck and J. T. Waber (American Institute of Mining, Metallurgical, and Petroleum Engineers, Boston, 1972), p. 21.

[9] Y. Nagaoka, Solid State Commun. 3, 409 (1965).

[10] J. Callaway, Phys. Rev. 170, 576 (1968).

[11] D. M. Edwards, J. Appl. Phys. 39, 481 (1968).

[12] L. M. Roth, Phys. Rev. B 2, 3702 (1970); Phys. Rev. 186, 428 (1969).

[13] I. F. Shchegolev, Phys. Status Solidi 12, 9 (1972).

[14] A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B 5, 952 (1972).

[15] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973).

[16] R. J. Birgeneau, R. Dingle, M. T. Hutchings, G. Shirane, and S. L. Holt, Phys. Rev. Lett. 26, 718 (1971).

[17] R. N. Rogers, F. Carboni, and P. M. Richards, Phys. Rev. Lett. 19, 1016 (1967).

[18] E. H. Lieb and F. Y. Wu, Phys. Rev. Lett. 20, 1445 (1968).

[19] M. Takahashi, Prog. Theor. Phys. 42, 1098 (1969); Prog. Theor. Phys. 43, 1619 (1970).

[20] H. Shiba, Phys. Rev. B 6, 930 (1972).

[21] A. A. Ovchinnikov, Zh. Eksp. Teor. Fiz. 57, 2137 (1969) [Sov. Phys.-JETP 30, 1160 (1970)].

[22] C. Coll (unpublished).

[23] H. S. Shiba and P. Pincus, Phys. Rev. B 5, 1966 (1972).

[24] K. H. Heinig and X. X. Monecke, Phys. Status Solidi B 49, K139 (1972); Phys. Status Solidi B 49, K141 (1972).

[25] D. Cabib and T. A. Kaplan, Phys. Rev. B 7, 2199 (1973).

[26] G. Beni, T. Holstein, and P. Pincus, Phys. Rev. B 8, 312 (1973).

[27] J. B. McGuire, J. Math. Phys. 5, 622 (1965); J. Math. Phys. 6, 432 (1965); C. N. Yang, Phys. Rev. Lett. 19, 1312 (1967); Phys. Rev. 168, 1920 (1968).

(Wiley, New York, 1963), Chap. 14.

[29] J. Callaway, Phys. Rev. B 5, 106 (1972).

[30] J. Callaway and A. K. Rajagopal, Phys. Rev. B 3, 1763 (1971).

[31] J. Callaway and D. M. Edwards, Phys. Rev. 136, A1333 (1964).

[32] F. Beth and G. H. Uhlenbeck, Physica (Utr.) 3, 729 (1936); Physica (Utr.) 4, 915 (1937).