VARIATIONAL APPROACH TO AN APPROXIMATE HAMILTONIAN FOR STRONGLY CORRELATED NARROW-BAND ELECTRONS - RELATION TO BAND CALCULATIONS AND THEORY OF EXCHANGE IN INSULATORS

Thesis for the Degree of Ph. D.
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ABSTRACT

VARIATIONAL APPROACH TO AN APPROXIMATE HAMILTONIAN FOR STRONGLY CORRELATED NARROW-BAND ELECTRONS - RELATION TO BAND CALCULATIONS AND THEORY OF EXCHANGE IN INSULATORS

By

Nilton Penha Silva

This paper contains a critique of one-electron band theory for narrow-band magnetic semiconductors, with the conclusion that the approaches in the literature are unsatisfactory from a conceptual point of view, the difficulty being connected with the question of what periodic potential, if any, is to be considered. We then present a new approach which is variational and consists of taking a trial Hamiltonian $\tilde{H}$, much simpler than the exact Hamiltonian, nevertheless containing two-electron terms as well as one-electron terms. Unlike one-electron theory, physical predictions are to be made only when the one-electron or band terms in $\tilde{H}$ are combined with important two-electron terms. Unlike previous theories (due to Hubbard, Anderson) which follow the

latter procedure recognizing the essential importance of certain two-particle terms, we choose the one-electron terms (the band-structure) variationally and simultaneously with a similar choice of the two-electron terms. This novel feature of our approach overcomes the difficulties in the previous theories, as shown by our initial investigations made within the narrow half-filled single-band problem. Two definitions of our trial Hamiltonian $\tilde{H}$ are considered; in one, $\tilde{H}$ is of the form of the Hubbard Hamiltonian, and in other, potential exchange terms are added.

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Nilton Penha Silva

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DEDICATION

In memory of my father.

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I. INTRODUCTION

This paper contains a critique of one-electron band theory for narrow-band magnetic semiconductors, e.g. NiO, $KMnF_3$, EuS, commonly spoken of as Mott insulators. The conclusion of this discussion is that the approaches[1-6] in the literature are unsatisfactory from a conceptual point of view. The difficulty we are discussing is not connected with the solution of a given one-electron periodic potential ("self-consistent" or not), but it is rather concerned with the question of what periodic potential, if any, should be considered. We go on to present an approach which is shown to have promise of being satisfactory (it overcomes all the objections raised in our critique).

We neglect phonon effects, focussing on the Schrödinger equation which describes the motion of the electrons in the Coulomb field of nuclei fixed in space. Nevertheless, this equation is not that of a single electron moving in a fixed potential, because of the Coulomb interaction between electrons - an electron "sees" the fixed nuclei and all the other electrons at their instantaneous positions: the Hamiltonian assumed is

$$H = \sum_i \left[\frac{P_i^2}{2m} + V(r_i)\right] + \frac{1}{2}\sum_{ij}{}' \frac{e^2}{r_{ij}} \qquad (1)$$

where V(r) is the potential due the nuclei. Hence the concept of a one-electron theory - a model where the electrons interact with some effective fixed potential V_{eff}, but not with each other - by no means obviously flows from the fundamental physics defined by (1). Nonetheless, this concept forms the basis of much of solid-state, molecular and atomic physics. A large portion of solid state work takes the nuclear positions to form the crystal structure. The resulting translational symmetry simplifies appreciably the one-electron problem (given the periodic potential), but does not bring the original problem (1) perceptibly closer to explicit solution.

Historically, some theoretical foundation was given to the one-electron theory in the variationally best one-electron approximation, the Hartree-Fock Approximation (HFA)[7,8,9]. However it was recognized early[10] that the common restricted version of this (plane wave solutions) was poor for the low-temperature properties of the electron gas, and presumably therefore for broad-band metals. The HFA is, again for non-zero temperature, also extremely poor and misleading for models of very narrow partially-filled-band insulators[11-15] such as the Mott insulators in which we are interested, even in its general (unrestricted) form.

The use of one-electron potentials other than the HF potential for the calculation of energy bands has been widespread. In the remaining paragraphs of this introductory section we will discuss methods which were not specifically

designed for narrow-band situations and which either have been applied to narrow-band materials in which we are interested or appear to have possibilities in this direction. In sections II and III, methods that were addressed explicitly to narrow band electrons will be considered in some detail. Finally in section IV we discuss our proposal as a contribution to the search for a satisfactory definition of one-electron states in Mott insulators; and in section V our approach is investigated for the half-filled-single-band problem.

Probably the most widely used potential for band calculations is Slater's "$\rho^{1/3}$ exchange"[1] or its well-known generalization known as the "Xα" method[16]. Slater's exchange was originally developed[1] as a simplifying approximation to the Hartree-Fock method. Namely the exchange terms were first averaged and the average exchange was further simplified by replacing the electron density ρ in the free-electron expression for the average exchange by $\rho(r)$, the electron density in the crystal. This leads to an exchange term $-A_o\rho(r)^{1/3}$ where A_o is a specific positive numerical constant. The Xα method consists of replacing A_o by a positive parameter A which is unspecified theoretically. The one-electron Hamiltonian G in this approach is the sum of three terms: the kinetic energy, the electrostatic potential energy due to an electron density $\rho(r)$ plus the nuclei, and $-A\rho(r)^{1/3}$. The final one-electron picture consists of one-electron states ψ_i, ε_i which satisfy $G\psi_i=\varepsilon_i\psi_i$ and the "self-consistency requirement" $\rho(r) = \sum_i |\psi_i(r)|^2$, the sum taken over occupied

states. Later it was argued that Slater's approximation[1] to the HFA would actually be better than the latter in certain respects, and in particular for energy band calculations[17]. Clearly the derivation of Slater's approximation as a method of improving on the HFA must be viewed as an arbitrary procedure, and the Xα method has to be seen as phenomenology.

Furthermore, the consequent uncertainty in the meaning of these procedures does not decrease as one proceeds from nearly-free-electron situations to cases of narrow bands[18] (because of the dependence on the free-electron case of the original argument[1]). In this connection we point out that these $\rho^{1/3}$ schemes are unsatisfactory on intuitive grounds in connection with an N-electron atomic (or ionic) calculation. For large distance r from the nucleus, $\rho(r)$ approaches zero exponentially; therefore the total potential in the Xα scheme does not approach the physically expected potential due to the (N-1)-electron ion (e.g. if the N-electron atom is neutral, the Xα scheme gives a total potential energy that is exponentially small at large r rather than the expected $-e^2/r$). We note that disagreement with the same physical expectation was the basis of Slater's criticism of the excited or unoccupied states in HF theory (see footnote 15), and that he claimed[17] a major improvement for his $\rho^{1/3}$ method in this connection. Clearly, a failure to properly predict the large-r behavior in atoms will introduce serious uncertainties into the prediction of band-structure effects in narrow bands.

A more fundamental approach based on the real physical problem of interest defined by (1) was taken by Kohn and coworkers[2] who developed a new variational principle and, making certain approximations appropriate to either slowly-varying $\rho(r)$ or to $\rho(r)$ with a large constant part, derived a one-electron potential similar to Slater's but with $A = \frac{2}{3} A_o$. However, the authors[2] noted that their theory could not make justifiable predictions "at the surface of atoms"; hence one would not expect band-structure effects in narrow bands to be discussed satisfactorily within this approach in accordance with the discussion of the previous paragraph.

Another approach to one-electron states in crystals which is not basically of a phenomenological nature is the field-theoretical approach described by Hedin and Lundqvist[3]. Here one-particle states (wave-functions $f_s(x)$ and corresponding energies ε_s; x stands for both space and spin coordinates) are precisely defined in principle in terms of the exact many-electron energy eigenstates, and it is shown that the one-electron Green's function (and therefore many physically observable quantities) can be determined in principle from these states. Unfortunately, this definition does not appear to be appropriate in its present form to the narrow-band regime, at least for obtaining a complete orthonormal set of one-electron functions, since these single-particle wave functions $f_s(x)$ are not linearly independent[3,19] for interacting electrons;

for our case of interest, where the interactions are very strong, criteria for the choice of an appropriate subset of the $f_s(x)$ (which further have to be normalized) do not exist[20].

The final band-theoretical method that was not originally presented in the context of narrow-band situations is the Wigner-Seitz potential[4]. This turns out to be related to certain results of our variational calculation, and will be discussed in section V.

Hubbard's derivation of the well-known Hubbard Hamiltonian H_H, which is presumed to be appropriate for narrow-band systems is discussed in section II. It is construed here as involving a one-electron band calculation in the sense that it involves a calculation of the one-electron operator appearing in H_H. Anderson's "ligand field theory", crucial to his theory of exchange in insulators, is a theory of one-electron states for the "non-magnetic lattice" which is supposed to have lattice translational symmetry and consequently these states are Bloch functions. We therefore consider this as a one-electron band theory. Both Hubbard's and Anderson's band theories are made in the Hartree-Fock approximation, Hubbard's in the restricted (non-magnetic), Anderson's in an unrestricted (magnetic) HF theory.

In view of the known failures[11-15] of the HFA as discussed above, we certainly must answer the obvious question, why even consider these HF band calculations

of Hubbard and Anderson? The answer is that the failures result from actually applying the HFA in the way it was derived, as a one-electron approximation, to deduce physical quantities (specific heat, susceptibility, etc.); whereas neither Hubbard nor Anderson use their HF band-calculation in this way. Rather, they use their one-electron operator in combination with important two-particle terms (intra-atomic repulsion in Hubbard's case, the same plus interatomic exchange in Anderson's case) which, for narrow bands, actually dominate the band-theoretic term. Hence our results of sections II and III, namely that these HF approaches are unsatisfactory within the context of the use made of them by their authors, do not follow obviously (as far as we can see) from previously known failures of the HF approximation.

It is convenient to discuss here the interesting work of Mattheiss[21]. At first sight he might appear to be following the philosophy of Slater's group since he[21] used Slater's $\rho^{1/3}$ exchange (un-spin-polarized) to calculate the band structure of $KNiF_3$. However, he didn't follow that philosophy[22] according to which one should compare the predictions of their one-electron theory with experiment and, if this results in failure, more refined one-electron approximations should be attempted. Instead Mattheiss correctly recognized the essential importance of following Anderson and Hubbard in introducing the large (intra-atomic) interaction terms along with his one-electron

term and considering the latter as a small perturbation, when dealing with these very narrow band situations[23]. However, Mattheiss' use of Slater's $\rho^{1/3}$ approximation for his one-electron terms is still arbitrary and unjustified, and part of the motivation for our approach (section IV) is to reduce, by theoretical means, the arbitrariness of this potential.

The gist of our variational approach presented in section IV is as follows. With Anderson and Hubbard, we recognize that in our narrow-band situations certain two-particle terms (including intra-atomic Coulomb interactions) are much larger than the interatomic single-particle terms essential to band structure, and cannot be approximated even crudely by effective single-particle terms for most of the common physical observables. Hence we do not consider applying a single-particle approximation to compare with experiment. Rather, physical predictions are to be made from a simplified "effective" Hamiltonian $\tilde{H}$ which includes certain types of two-electron terms. The one-electron terms in $\tilde{H}$ are called the band structure for the interacting system, and are chosen variationally simultaneously with a similar choice for the two-electron terms. It is in this simultaneous variational treatment of the one- and two-electron terms that we differ from Hubbard and Anderson, and it is this novel feature of our theory that overcomes the difficulties in their theories pointed out below, as shown in section V. Aspects of the present work have been reported earlier[24].

II. HUBBARD'S DERIVATION OF THE HUBBARD HAMILTONIAN; ITS FAILURE.

The Hubbard Hamiltonian was derived[5] in connection with the problem of narrow-band electrons. Its properties have been studied by a large number of authors[25]. It represents the simplest model of a crystal which contains the tendencies toward itinerant behavior and toward localization of the electrons. This Hamiltonian can be written as

$$H_H = \sum_{ij} \sum_{\sigma} b_{ij} \, c^{+}_{i\sigma} \, c_{j\sigma} + U \sum_{i} N_{i\uparrow} \, N_{i\downarrow} \qquad (2)$$

where {i} refers to sites; $c^{+}_{i\sigma}$ and $c_{i\sigma}$ respectively creates and destroys an electron with spin σ in the Wannier function $w_i(\underline{r})$ at site i; $N_{i\sigma} = c^{+}_{i\sigma} \, c_{i\sigma}$ the corresponding number operator; b_{ij} is a hopping or transfer integral; and finally U is the intra-site Coulomb interaction (U>0). The one-electron term causes the tendency toward itinerancy, while the two-electron (interaction) term causes localization.

One can study the properties of (2) in two different ways. In the first, one tries to calculate b_{ij} and U, according to the actual derivation of the Hamiltonian. The "band theory" part of such a derivation is the calculation of b_{ij} (the one-electron part of Hubbard Hamiltonian).

In the second, one regards b_{ij} and U as parameters and proceeds with the study of the properties of (2). It is in this latter, phenomenological, sense that most researchers have used the Hubbard Hamiltonian. In this sense (2) is not restricted to narrow-band electrons; it can be an approximation for any bandwidth, i.e., any b_{ij}/U, including bands that are wide compared to U. Our interest here is in the first view, namely we are concerned with the principles of the calculation of b_{ij} and U.

Let us outline briefly Hubbard's derivation of his Hamiltonian presented in reference 5. For clarity we will discuss this in the context of a single-s-band model. The Hamiltonian H in this model is[26]

$$H = \sum_{ij} \sum_{\sigma} h_{ij}\, c^{+}_{i\sigma}\, c_{j\sigma} + \frac{1}{2} \sum_{ijk\ell} \sum_{\sigma\sigma'} v_{ijk\ell}\, c^{+}_{i\sigma} c_{j\sigma'} c_{\ell\sigma'} c_{k\sigma} \qquad (3)$$

where h_{ij} is the matrix element of h - kinetic energy plus the Coulomb interaction of the electron with the ions - between $w_i(\underline{r})$ and $w_j(\underline{r})$; and

$$v_{ijk\ell} = \int d^3r_1\, d^3r_2\, w^{*}_i(\underline{r}_1) w^{*}_j(\underline{r}_2)\, \frac{e^2}{r_{12}}\, w_k(\underline{r}_1) w_\ell(\underline{r}_2) \quad . \qquad (4)$$

The Wannier functions $w_i(\underline{r})$ and the Bloch functions are related by

$$w_i(\underline{r}) = N_s^{-\frac{1}{2}} \sum_{\underline{k}} (\exp -i\underline{k}\cdot\underline{R}_i)\, \psi_{\underline{k}}(\underline{r}) \qquad (5)$$

where N_s is the number of sites, $\underline{R}_i$ is the position of site i, and $\sum_{\underline{k}}$ goes over a Brillouin zone. Then the Hamiltonian (3) can also be written as

$$H = \sum h_{\underline{k}} a_{\underline{k}\sigma} a_{\underline{k}\sigma} + \frac{1}{2} \sum v_{\underline{k}_1\underline{k}_2\underline{k}_3\underline{k}_4} a^{+}_{\underline{k}_1\sigma} a^{+}_{\underline{k}_2\sigma'} a_{\underline{k}_4\sigma'} a_{\underline{k}_3\sigma} \tag{6}$$

where

$$a^{+}_{\underline{k}\sigma} = N_s^{-\frac{1}{2}} \sum_i (\exp + i\underline{k}\cdot\underline{R}_i)\ c^{+}_{i\sigma} \tag{7}$$

is the Bloch function creation operator, and

$$h_{\underline{k}} = N_s^{-1} \sum_{ij} h_{ij} \exp -i\underline{k}\cdot\underline{R}_{ij} \quad , \tag{8}$$

$$v_{\underline{k}_1\underline{k}_2\underline{k}_3\underline{k}_4} = N_s^{-2} \sum v_{ijk\ell} \exp -i(\underline{k}_1\cdot\underline{R}_i + \underline{k}_2\cdot\underline{R}_j - \underline{k}_3\cdot\underline{R}_k - \underline{k}_4\cdot\underline{R}_\ell) \quad , \tag{9}$$

and

$$\underline{R}_{ij} = \underline{R}_i - \underline{R}_j \quad .$$

If one makes the standard non-magnetic HFA to H, one gets for the HF eigenvalues $\varepsilon^{HF}_{\underline{k}}$

$$\varepsilon^{HF}_{\underline{k}} = h_{\underline{k}} + \lambda_{\underline{k}} \quad , \tag{10}$$

with

$$\lambda_{\underline{k}} = \sum_{\underline{k}'} \nu_{k'} \ (2v_{\underline{k}'\ \underline{k}\ \underline{k}'\ \underline{k}} - v_{\underline{k}'\ \underline{k}\ \underline{k}\ \underline{k}'}) \quad , \tag{11}$$

where $\nu_{\underline{k}}$ is the average occupation number for state $\underline{k}$. Now, with (10), eq. (6) can be written

$$H = \sum (\varepsilon^{HF}_{\underline{k}} - \lambda_{\underline{k}})\ a^{+}_{\underline{k}\sigma} a_{\underline{k}\sigma} + \frac{1}{2} \sum v_{\underline{k}_1\underline{k}_2\underline{k}_3\underline{k}_4}\ a_{\underline{k}_1\sigma} a_{\underline{k}_2\sigma'} a_{\underline{k}_4\sigma'} a_{\underline{k}_3\sigma} \quad . \quad (12)$$

As Hubbard[5] noted, the presence of $\lambda_{\underline{k}}$ in (12) avoids counting the interactions of the electrons of the band twice, once explicitly in the Hamiltonian and also implicitly through $\varepsilon^{HF}_{\underline{k}}$.

At this point it is convenient to write (12) in terms of Wannier-function creation and destruction operators, obtaining eq. (6) of reference 5:

$$H = \sum b_{ij}\ c^{+}_{i\sigma}\ c_{j\sigma} + \frac{1}{2} \sum v_{ijk\ell}\ c^{+}_{i\sigma}\ c^{+}_{j\sigma'}\ c_{\ell\sigma'}\ c_{k\sigma}$$

$$- \sum (2v_{ijk\ell} - v_{ij\ell k})\ \nu_{j\ell}\ c^{+}_{i\sigma}\ c_{k\sigma} \qquad (13)$$

where

$$b_{ij} = N_s^{-1} \sum_{\underline{k}} \varepsilon^{HF}_{\underline{k}} \exp i\underline{k}\cdot\underline{R}_{ij} \qquad (14)$$

and

$$\nu_{j\ell} = N_s^{-1} \sum_{\underline{k}} \nu_{\underline{k}} \exp i\underline{k}\cdot\underline{R}_{j\ell} \qquad (15)$$

(so $\nu_{jj} = 1/2$ for the half-filled band).

Having in mind that one is dealing with narrow-band electrons, we can imagine a picture where the Wannier functions are very much like the atomic s-functions and these form an atomic shell with a radius small compared

to the interatomic separation. Then Hubbard argues that the integral $U \equiv v_{iiii}$ should be much greater than $v_{ijk\ell}$, if i,j,k and ℓ are not all equal. In other words, the intrasite interaction U is much greater than all the intersite interactions. Neglecting then all intersite v's in the last two sums, the Hamiltonian (13) becomes the Hubbard Hamiltonian (2) plus constant terms, which are dropped. The neglect of the difference between the Coulomb interactions and their HFA (the second and third sum in (13), respectively) is, for macroscopic systems, better than neglecting the Coulomb interactions only, as we shall see. However we shall now show that this approach has an unacceptable flaw.

The explicit expression for Hubbard's transfer integral is

$$b_{ij} = h_{ij} + \sum_{k\ell} (2v_{ikj\ell} - v_{ik\ell j})\, \nu_{k\ell} \qquad (16)$$

obtained from Fourier transforming (10).

Consider first the very simple case of two sites and two electrons. In the usual situation where the bonding state ($\propto (w_1(r) + w_2(r))$) lies lowest, and the w_i are real, the expression (16) gives

$$b_{12} = h_{12} + v_{1121} + \frac{3}{2} v_{1221} - \frac{1}{2} v_{1212} \quad . \qquad (17)$$

All the quantities on the right side of (17) but the last one v_{1212} (inter-site Coulomb interaction) behave[27] like

exp $-\alpha R_{12}$ for large intersite separation R_{12} (α is a positive constant). But the quantity v_{1212} goes like $1/R_{12}$ for large intersite separation. Hence the low-lying singlet-triplet splitting $4b_{12}^2/U$, calculated from the Hubbard Hamiltonian, behaves as $1/R_{12}^2$ for large R_{12} , in drastic disagreement with the exponentially small behaviour of the singlet-triplet splitting obtained directly from the exact Hamiltonian (3). Explicit calculation of these splittings can be found in Appendix A1.

For an abritrary number of sites N_s , (16) can be written

$$b_{ij} = h_{ij} + \sum_k v_{ikjk} - v_{ijij}\, \nu_{ji}$$

$$+ 2\sum_{k\ell}{}' v_{ikj\ell}\, \nu_{k\ell} - \sum_{k\ell \neq ji} v_{ik\ell j}\, \nu_{k\ell} \,. \qquad (16\text{-a})$$

For macroscopic systems $N_s \to \infty$; although $\sum_k v_{ikjk}$ would diverge ($v_{ikjk} \tilde{=} \frac{1}{R_k}$ as $R_k \to \infty$) , these large-R_k terms are cancelled or screened by the interaction in h_{ij} of an electron with the nuclei, rendering the expression (16-a) convergent. From (16-a) the leading behavior for large $\underline{R}_{ij} = |\underline{R}_i - \underline{R}_j|$ is seen to be $b_{ij} \tilde{\sim} -v_{ijij}\nu_{ji}$. At zero T, at least for a variety of examples (e.g. a linear chain), ν_{ji} approaches zero as a power of R_{ij} and oscillates sinusoidally with a wavelength $\tilde{\sim}$ Fermi wavelength. So Hubbard's transfer integral oscillates and vanishes as a power of the intersite separation. This is again in serious disagreement with the expectation that it should be exponentially small:

perturbation theory[6,28,29] leads to a Heisenberg Hamiltonian

$$H_{Heis} = -\sum_{ij}{}' J_{ij}\, \underline{S}_i \cdot \underline{S}_j \qquad (18)$$

describing the low-lying states of H, where

$$J_{ij} = v_{ijji} - 2\, t_{ij}^2/(v_{iiii} - v_{ijij}) \qquad (19)$$

and

$$t_{ij} = h_{ij} + v_{iiji} + \sum_{\ell}^{(i,j)} v_{i\ell j\ell} \quad . \qquad (20)$$

The sum in (20) excludes the case ℓ=i and j. Since it can be shown[29] in the narrow-band case that $w_i(\underline{r})$ is exponentially small[30] for $|\underline{r} - \underline{R}_i| \to \infty$ [31], (20) gives t_{ij} and therefore J_{ij} being exponentially small for large $\underline{R}_{ij}$[32].

An even worse result would have been obtained if Hubbard had merely neglected the interatomic part of the Coulomb interaction (rather than the difference between it and its HF approximation). Then the transfer integral b_{ij} would have been simply h_{ij} , which <u>diverges</u> for an infinite crystal, fixed i and j , in accordance with the above discussion.

III. ANDERSON'S LIGAND FIELD THEORY; ITS UNACCEPTABILITY

In this section we examine the concept of the ligand field problem as discussed by Anderson and crucial to his theory of exchange in insulators[6]. This problem was defined[6] as that of determining "the exact one-electron states" for the crystal as a whole, excluding the effects of exchange interactions between the magnetic ions. These states are Bloch functions $|\underline{k}\rangle$ and their energies $\varepsilon_{\underline{k}}$; by their definition[6] they are to be "non-magnetic", i.e. each wave function is to be a product of a spatial and a spin function, with the spatial function and energy being independent of spin. From these states one is to construct "the exact Wannier functions" as in Eq. (5). Finally, one is to carry out perturbation theory for the full crystal many-electron problem considering interionic overlap to be small. This procedure leads, according to Anderson, to the low-lying energies of the system being predominantly the eigenvalues of the Heisenberg Hamiltonian (18) where the dominant contribution to the exchange "integral" J_{ij} is

$$J_{ij} = - 2|b_{ij}|^2/U + v_{ijji} \quad . \tag{21}$$

Here b_{ij} for $i \neq j$ is the transfer integral or hopping integral as calculated from the ligand field Hamiltonian H_{SC}:

$$b_{ij} \equiv (w_i|H_{SC}|w_j) \quad , \tag{22}$$

U is the change in energy needed, to zero order in overlap, to transfer an electron from w_i to w_j . The spins of w_i and w_j must be specified to define (22); Anderson did not specify these - we will discuss the various possibilities below. (We have simplified the notation to be appropriate for a single magnetic band, which is sufficient for our present purposes.) The first and second terms of (21) were called[6] "kinetic exchange" and "potential exchange", respectively. The states $|k>$, $\varepsilon_{\underline{k}}$ were defined[6] (in the "most formally exact" method) as eigenfunctions and energies of the Hartree-Fock operator H_{HF} in which the spins of all the magnetic ions are assumed parallel, i.e. in this most exact method $H_{SC} = H_{HF}$ and

$$H_{HF}|\underline{k}) = \varepsilon_{\underline{k}}|\underline{k}) \quad . \tag{23}$$

Anderson motivated this HF definition by saying that certain desirable properties are expected to follow (for example the non-magnetic electrons in the system, e.g. associated with F^- ions, can then be treated as core electrons whose wavefunctions will not change very much with magnetic excitations; again, the perturbation theory is rapidly convergent when use is made of "the exact

localized functions"). However these desirable properties were not shown[6] to occur. In fact, it has never been clear to us why a HF definition is at all appropriate: Since the w_i , which define the perturbation expansion, are to lead to excited-state properties (the excitations within the Heisenberg model, with energies per particle ranging over an interval $\simeq J_{ij}$), and since a complete set of one-electron states is necessary for perturbation theory (not just occupied states) the zero-T HF theory would not seem to have variational significance[33]. The non-zero-T HFA (even in the limit $T \to 0$), while variational, gives physically absurd predictions for very narrow band systems[12,14,34]. Nevertheless those absurdities were apparently not so obvious as to prevent many workers from being misled.

Recently, it was shown[29,35] that something is definitely wrong with Anderson's definition. We present here the simpler[29] of these arguments. Consider a two-site model having two electrons and two spatial orbitals w_1 and w_2, like H_2 in Slater's model[27] where w_1 and w_2 are real orthonormal linear combinations of the 1s-states centered at the two sites. The zero-T limit of the HF operator with occupied states $\psi_1 \ldots \psi_\ell$ is defined in general by its matrix elements in an orthonormal basis set $\phi_1, \phi_2, \ldots$ by

$$(\phi_i|H_{HF}(\psi_1 \ldots \psi_\ell)|\phi_j) \equiv (\phi_i|h|\phi_j) + \sum_{k=1}^{\ell} (\phi_i\psi_k|\hat{v}|\phi_j\psi_k) \qquad (24)$$

where

$$(\phi\psi|\hat{v}|\phi'\psi') \equiv (\phi\psi|v|\phi'\psi') - (\phi\psi|v|\psi'\phi') \qquad (25)$$

and

$$(\phi\psi|v|\phi'\psi') \equiv \int d^3r_1 d^3r_2 \; \phi^*(\underline{r}_1)\psi^*(\underline{r}_2)v(\underline{r}_{12})\phi'(\underline{r}_1)\psi'(\underline{r}_2) \quad (26)$$

The case of Anderson's definition (22) gives, from (24)

$$b_{12}^{\sigma}(\uparrow,\uparrow) \equiv (w_{i\sigma}|H_{HF}(w_{1\uparrow},w_{2\uparrow})|w_{2}\sigma) \quad (27)$$

$$= \begin{cases} h_{12} & \sigma = \downarrow \\ h_{12} + 2\, v_{1121} & \sigma = \downarrow \end{cases} \quad (28)$$

We used the symmetry and reality of w_1 and w_2 for the hydrogen molecule which implies $v_{1121} = v_{2212}$; also

$$h_{12} = \int w_1^*(\underline{r})\; h\; w_2(\underline{r})\; d^3r \quad , \quad (29)$$

where

$h = p^2/2m - e^2/|\underline{r} - \underline{R}_1| - e^2/|\underline{r} - \underline{R}_2|$, and $v(r_{12}) = e^2/r_{12}$.

The first difficulty presented by the result (28) is its strong dependence on the spin of the states between which the matrix element is taken: h_{12} and v_{1121} are of the same order (first) in the overlap between the atomic functions. Furthermore, the exact exchange integral J_{12} as shown in Appendix A1, is approximately

$$J_{12} = v_{1221} - 2t_{12}^2/(v_{1111} - v_{1212}) \quad (30)$$

for small overlap, where

$$t_{12} = h_{12} + v_{1121} \quad . \tag{31}$$

Expression (30) is like (21), but with b_{12} replaced by (31); thus it is different from <u>either</u> of the values given by Anderson's scheme[36]. Clearly then his theory is not defined precisely enough for his purposes, and neither of the choices (28) is correct within Anderson's picture, the error made (which is first order in the overlap) being of the same order as terms retained. Although unsatisfactory, we note that Anderson's result is far superior to Hubbard's. Fuchikami[35] came to a similar conclusion about the unsatisfactory nature of Anderson's definition[37].

Consider now the HF operator obtained by occupying antiparallel spin states. The corresponding transfer integral is

$$\begin{aligned} b_{12}^{\sigma}(\uparrow,\downarrow) &\equiv (w_{1\sigma}|H_{HF}(w_{1\uparrow},w_{2\downarrow})|w_{2\sigma}) \\ &= h_{12} + \sum_{i=1}^{2} (w_{1\sigma}w_{i\sigma_i}|\hat{v}|w_{2\sigma}w_{i\sigma_i}) \\ &= h_{12} + v_{1121} = t_{12} \ , \end{aligned} \tag{32}$$

independent of the spin σ . Hence the hopping integral calculated using the HF operator with occupied Wannier

functions having antiparallel spins leads to correct exchange splitting via (21). Fuchikami[35] apparently noticed the analogous point for her similar, but slightly more complicated two-site model.

However, contrary to Fuchikami[35], one cannot conclude from these special models that the HF operator for the antiferromagnetic state is correct in general (one can conclude only that using parallel spins is not always correct). In fact, in certain cases (e.g. MnO) it is impossible to have all the nearest-neighbor pairs be antiparallel. Thus it would be impossible in those cases to satisfy Anderson's requirement[6] that the exact one-electron states be solutions of a Schrödinger equation for the crystal as a whole simultaneously with this antiparallelism of all near-neighbor pairs.

Furthermore, in any such HF scheme, the states do not satisfy, even approximately, Anderson's requirement of spin-independence. We can see this directly in terms of our simple two-site model. Consider the parallel-spin case. The HF equations are

$$(\Psi_\nu | H_{HF}(\Psi_1, \Psi_2) | \Psi_\mu) = \varepsilon_\nu \, \delta_{\nu\mu} \tag{33}$$

so if the eigenfunctions are written

$$\Psi_\nu = \sum_{i\sigma} A^\nu_{i\sigma} \, w_{i\sigma} \quad , \tag{34}$$

the coefficients $A^{\nu}_{i\sigma}$ are to satisfy

$$\sum_{j\sigma'} (w_{i\sigma}|H_{HF}(\Psi_1,\Psi_2)|w_{j\sigma'})\ A^{\nu}_{j\sigma'} = \varepsilon_{\nu}\ A^{\nu}_{i\sigma}\ . \tag{35}$$

It is easily verified from (24) that the matrix elements $(w_{i\sigma}|H_{HF}(w_{i\uparrow},w_{2\uparrow})|w_{j\sigma'})$ are zero if $\sigma = \sigma'$ and that

$$(w_{i\sigma}|H_{HF}(w_{1\uparrow},w_{2\uparrow})|w_{i\sigma}) = \begin{cases} h_{11} + v_{1212} - v_{1221}\ , & \sigma = \uparrow \\ h_{11} + v_{1111} + v_{1212}\ , & \sigma = \downarrow ; \end{cases} \tag{36}$$

thus with (28) we have all the matrix elements of $H_{HF}(w_{1\uparrow},w_{2\uparrow})$ in this model. The eigenstates of $H_{HF}(w_{1\uparrow},w_{2\uparrow})$ (in our limited model space) are

$$\Psi_{k\sigma} = 2^{-\frac{1}{2}}\ (w_1 + e^{ik}\ w_2)\ \alpha_{\sigma}\ ,\ k = 0,\pi\ , \tag{37}$$

(as easily seen from the symmetry), with energies, from (28) and (31):

$$\varepsilon_{k\sigma} = \begin{cases} h_{11} + v_{1212} - v_{1221} + e^{ik}\ h_{12} & \sigma = \uparrow \\ h_{11} + v_{1111} + v_{1212} + e^{ik}\ (h_{12} + 2\ v_{1121}) & \sigma = \downarrow \end{cases} . \tag{38}$$

Finally we see that (37), (38) provide a solution to the

HF equations (33) with occupied states

$$\Psi_1 = \Psi_{0\uparrow} \quad , \quad \Psi_2 = \Psi_{\pi\uparrow} \tag{39}$$

because from (24) and (37)

$$(\phi_i | H_{HF}(w_{1\uparrow}, w_{2\uparrow}) | \phi_j) = (\phi_i | H_{HF}(\Psi_{0\uparrow}, \Psi_{\pi\uparrow}) | \phi_j) \quad . \tag{40}$$

($H_{HF}(\psi_1 \ldots \psi_2)$ is invariant under a unitary transformation of the occupied orbitals, as is well-known). Thus

$$\varepsilon_{k\downarrow} - \varepsilon_{k\uparrow} = v_{1111} + v_{1221} + 2\, e^{ik}\, v_{1121} \quad . \tag{41}$$

Since (41) involves the intra-atomic Coulomb integral v_{1111}, the difference between up and down energies is very large, even for small overlap. Clearly the intra-atomic nature of this term implies that it will occur independently of the relative orientation of the occupied spins. Pictorially, the v_{iiii} occurs in $\varepsilon_{k\downarrow}$ because $w_{i\downarrow}$ is unoccupied; as is well-known (ref. 8, secs. 5-2, 6-2) the HF equation for an unoccupied state corresponds intuitively to the Schrödinger equation for an <u>added</u> electron. One might note that the wave-functions do not show this magnetic property in this model: the up and down wave-functions at site 1 are $w_{1\sigma} = w_1(\underline{r})\alpha_\sigma$ (the same spatial function for both spins). However, it is clear from the above

discussion that this non-magnetic property of wave-functions results only from the restricted nature of the basis set used to define our model; if for example one enlarged the basis set to include 2s states w_1', w_2' (giving 4 spatial orbitals), then the HF wave-functions $\psi^{\nu}_{k\sigma}$ will be of the form $\psi^{\nu}_{k\sigma} = \psi^{\nu}_{k\sigma}(\underline{r})\alpha_{\sigma}$ where $\nu = 1,2$ (corresponding to 1s and 2s), $k = 0,\pi$ again, but $\psi^{\nu}_{k\sigma}(\underline{r})$ will be expected to depend on σ even for zero overlap[38].

Finally we should address ourselves to the apparent conflict between the conclusions just reached about the unsatisfactory nature of Anderson's theory, and statements recently made supporting it[35,39,40]. Of these works we are principally concerned with those which consider the crystal as a whole. In fact there is no conflict with the work of Fuchikami[35], because a) her Wannier functions were determined using experimental output rather than by Anderson's HF method and b) she considered only 3d cation bands (without higher ones). Hence she did not deal with the aspect of Anderson's method that we have criticized. Her avoidance of this criticism is of course not without cost: she replaced a fundamental theoretical question, that of determining theoretically and therefore predicting the best Wannier functions, by a phenomenological procedure. We also note that a glaring defect in Fuchikami's calculation is the use of a value of U appreciably and apparently arbitrarily reduced (in quantitative terms) from the

carefully calculated value U_o . (The value of the exchange integral is very sensitive to this change since the kinetic exchange and potential exchange terms very nearly cancel if the U_o value is used.) The physical effect invoked as the cause of this reduction is real (it's called "electron rearrangement" by Fuchikami[35] and was referred to as a "correlation effect" by Hubbard et al.[41]). Such an effect can be included in a perturbation theory provided higher bands (e.g. 4s cation bands) are included in the basis set - in such a case the magnetic properties of the Wannier functions would show up in Fuchikami's HF method, as discussed earlier in this section.

Gondaira and Tanabe[40] seem to have followed Anderson's HF method; unfortunately they did not define their HF operator (in that the occupied spins were not defined) and therefore their consideration cannot be considered as a valid investigation of Anderson's approach. Finally the treatment of Anderson's approach by Huang Liu and Orbach[39] followed that of Fuchikami[35] and so is subject to the deficiencies of that method.

IV. VARIATIONAL APPROACH

Our initial approach consists of finding the variationally best Hamiltonian of the form

$$\tilde{H} = \sum b_{\nu i,\nu j}\, \tilde{c}^{+}_{\nu i\sigma}\, \tilde{c}_{\nu j\sigma} + \sum U_{\nu}\, \tilde{N}_{\nu i\uparrow}\, \tilde{N}_{\nu i\downarrow} \qquad (42)$$

where ν is a band index, i,j label atomic sites, $\tilde{c}^{+}_{\nu i\sigma}$ creates an electron in the Wannier function $\tilde{w}_{\nu i}$, with spin σ, $\tilde{N}_{\nu i\sigma} = \tilde{c}^{+}_{\nu i\sigma}\tilde{c}_{\nu i\sigma}$ and $b_{\nu i,\nu j}$, U_{ν} are the variational parameters. Further, $\tilde{w}_{\nu i}$ are taken as orthonormal linear combinations of a basis set of one-electron functions (which can be chosen arbitrarily), the coefficients being also variational parameters. In other words, we take the trial Hamiltonian essentially of the form finally assumed by Mattheiss[21] as a sum of a band structure Hamiltonian, namely the one-electron operator $\tilde{H}^{(1)}$ in (42), plus a Hubbard-type of interaction term (involving the U_{ν}). But instead of choosing the band structure Hamiltonian arbitrarily, and in a way conceptually associated with nearly-free electrons, we choose it variationally, treating it on the same footing as the U-terms.

To accomplish this we use the so-called variational principle of statistical mechanics[9], namely, that the trial

free energy at temperature T and chemical potential μ satisfies the inequality

$$F[\tilde{H}] \equiv \mathrm{tr}\ \tilde{\rho}(H-\tilde{H}) - \beta^{-1}\ \ell n\ \mathrm{tr}\ \exp-\beta(H - \mu N) \geq F[H] \qquad (43)$$

with

$$\tilde{\rho} \equiv \exp-\beta(\tilde{H} - \mu N)/\mathrm{tr}\ \exp-\beta(\tilde{H} - \mu N) \qquad (44)$$

for all Hermitean $\tilde{H}$. Here H is the Hamiltonian taken as exact and which is being approximated by $\tilde{H}$. By this principle, the best estimate of the free energy is the minimum of $F[\tilde{H}]$, and this is the criterion for determining the best parameters in $\tilde{H}$.

Clearly the resulting one-electron Hamiltonian $\tilde{H}^{(1)}$, namely the one-electron part of the "best" (42) is by definition variational, it is a property of the crystal as a whole and is non-magnetic. Further we will see that the "best" (42) gives the correct behavior for single narrow-band models provided the exact kinetic exchange,

$$K_{ij} \equiv -2t_{ij}^2/(v_{iiii} - v_{ijij}) \quad , \ (i\neq j) \qquad (45)$$

dominates the potential exchange v_{ijji}. Therefore for such models the (one-electron) eigenstates of the best $\tilde{H}^{(1)}$ could provide a definition of the ligand field states which represents a major improvement over the HF definition[6,35]. However the limitation to cases with dominant K_{ij} is unsatisfactory on general grounds (in fact there are cases where

this is expected to be violated[39]). Further for more than one narrow band (e.g. a "degenerate" band such as a 3d-band in NiO), the trial Hamiltonian (42) will be unsatisfactory on the additional ground that Hund's rule, essential to magnetism in insulators, would be violated[43].

These difficulties should be overcome by adding potential exchange type terms to (42); also generalizing the one-electron terms (with no additional serious increase in difficulty) we obtain as our trial Hamiltonian

$$\tilde{H} = \sum b_{\nu i,\mu j}\, \tilde{c}^{+}_{\nu i\sigma}\, \tilde{c}_{\mu j\sigma} + \sum U_{\nu}\, \tilde{N}_{\nu i\uparrow}\, \tilde{N}_{\nu i\downarrow}$$

$$- \frac{1}{2} \sum_{\nu i,\mu j}{}' \sum_{\sigma\sigma'} U_{\nu i,\mu j}\, \tilde{c}^{+}_{\nu i\sigma}\, \tilde{c}_{\nu i\sigma'}\, \tilde{c}^{+}_{\mu j\sigma'}\, \tilde{c}_{\mu j\sigma} \qquad (46)$$

where $U_{\nu i,\mu j}$ are additional variational parameters which physically appear as effective potential exchange matrix elements. It should be realized that the interaction terms in (46) are of a much simpler form than the (exact) Coulomb interactions.

To find the best H we must solve the stationarity equations $(\partial/\partial\lambda)F[\tilde{H}] = 0$ which may be written[42]

$$\mathrm{tr}\, \frac{\partial\tilde{\rho}}{\partial\lambda}\, (H - \tilde{H}) = 0 \qquad (47)$$

with fixed temperature T and chemical potential μ ; here λ stands for any one of the variational parameters. The derivative of the density matrix $\tilde{\rho}$, (44), with respect

to λ is of the form

$$\frac{\partial\tilde{\rho}}{\partial\lambda} = \tilde{Z}^{-1}(1 - \tilde{\rho}\ \mathrm{tr})\ \frac{\partial}{\partial\lambda}\ e^{-\beta(\tilde{H} - \mu N)} \quad ,$$

where

$$\tilde{Z} = \mathrm{tr}\ e^{-\beta(\tilde{H} - \mu N)} \tag{49}$$

and

$$\frac{\partial}{\partial\lambda}\ e^{-\beta(\tilde{H} - \mu N)} = \lim_{\delta\lambda\to 0}\ \frac{1}{\delta\lambda}\ [e^{-\beta(\tilde{H} + \delta\lambda\ \frac{\partial\tilde{H}}{\partial\lambda} - \mu N)} - e^{-\beta(\tilde{H} - \mu N)}] . \tag{50}$$

With the use of the expansion[44]

$$e^{A+B} = e^{A}[1+\int_0^1 dx_1\ B(x_1) + \int_0^1 dx_1 \int_0^{x_1} dx_2\ B(x_1)\ B(x_2)+\ldots] \tag{51}$$

(A and B are operators, and $B(x) \equiv e^{-xA}Be^{+xA}$) , the expression (48) becomes

$$\frac{\partial\tilde{\rho}}{\partial\lambda} = -\beta\ (1 - \tilde{\rho}\ \mathrm{tr})\ \rho \int_0^1 dx\ Q_\lambda(x) \tag{52}$$

where $Q_\lambda(x)$ is defined as

$$Q_\lambda(x) \equiv e^{x\beta(\tilde{H} - \mu N)}\ \frac{\partial\tilde{H}}{\partial\lambda}\ e^{-x\beta(\tilde{H} - \mu N)} . \tag{53}$$

Then it follows that the stationarity equation (47) becomes

$$\int_0^1 dx\ \langle Q_\lambda(x)\ (H - \tilde{H})\rangle - \langle H - \tilde{H}\rangle\langle\frac{\partial\tilde{H}}{\partial\lambda}\rangle = 0 . \tag{54}$$

We have used the following notation for the thermal average of an operator A:

$$\langle A \rangle \equiv \mathrm{tr}\ \tilde{\rho}\ A \quad . \tag{55}$$

The fact that $\tilde{H}$ and $\frac{\partial \tilde{H}}{\partial \lambda}$ do not commute with each other in general, makes (54) much more complicated to calculate than if they did.

We have so far investigated this approach only for the single-band problem, taken for simplicity of discussion to be an s-band. We further have limited ourselves to the narrow-band or small-overlap region. Our investigations are described in subsequent sections.

It is worthwhile mentioning that recently it has been shown[42] that a large class of approximations in statistical thermodynamics that are based on (43) yield expressions for the macroscopic quantities of the system that are consistent from both the statistical mechanical and thermodynamical points of view contrary to previous claims. A question in this regard arises because the variationally best parameters that appear in $\tilde{H}$ are generally T and μ dependent, unlike an exact microscopic Hamiltonian. That result was important in the considerations of the present paper. (It answers questions like, should the approximate entropy be calculated as $-\frac{\partial}{\partial T} F[\tilde{H}^{(b)}]$ or $-k\mathrm{tr}\ \tilde{\rho}^{(b)}\ \ell n\ \tilde{\rho}^{(b)}$, guaranteeing that they are the same. By $\tilde{H}^{(b)}$ and $\tilde{\rho}^{(b)}$ we mean the best $\tilde{H}$ and the respective density matrix according to (43)).

V. EXPLORATION OF THE VARIATIONAL APPROACH WITHIN THE SINGLE-BAND PROBLEM

The exact Hamiltonian for this problem is given by (3); and according to our approach the trial Hamiltonian should be:

$$\tilde{H} = \sum_{i,j\sigma} b_{ij}\, \tilde{c}^{+}_{i\sigma}\, \tilde{c}_{j\sigma} + U \sum_{i} \tilde{N}_{i\uparrow}\, \tilde{N}_{i\downarrow}$$

$$- \frac{1}{2} \sum_{ij}{}' \sum_{\sigma\sigma'} U_{ij}\, \tilde{c}^{+}_{i\sigma}\, \tilde{c}_{i\sigma'}\, \tilde{c}^{+}_{j\sigma'}\, \tilde{c}_{j\sigma} \quad . \qquad (56)$$

Although the Bloch functions $\psi_k(\underline{r})$ are physically invariant for a single band (aside from a phase factor exp i $\gamma_{\underline{k}}$) , the Wannier functions $w_i(\underline{r})$ which are to be constructed as

$$w_i(\underline{r}) = N_s^{-\frac{1}{2}} \sum_{\underline{k}} \exp i(-\underline{k}\cdot\underline{R}_i + \gamma_{\underline{k}})\ \psi_{\underline{k}}(\underline{r}) \qquad (56\text{-a})$$

are not invariant because of $\gamma_{\underline{k}}$. Then, in principle one should ask for the best w_i in the sense of (43), leading to an enormous number of variational parameters. However, it seems natural to demand the Wannier functions to have, in common with the atomic 1s functions a_i , the properties

of reality and invariance under inversion through $\underline{R}_i$; and also to go continuously to a_i as the interatomic separation goes to infinity. Then one proves (Appendix A2) that for the single band case $\gamma_{\underline{k}}$ is constant, leaving no physical arbitrariness in the choice of the Wannier functions, the variational parameters being only b_{ij}, U and U_{ij} . (We can then drop the tildes on the right side of (56).

Naturally the best parameters will be found to be functions of the various integrals in the exact Hamiltonian and of β and μ . In particular, the leading terms of the expression for b_{ii} and U are expected to be zero order in the overlap; similarly b_{ij} and U_{ij} (for $i \neq j$) are expected to be mainly of the first and second order in the overlap, respectively. One can see that this is very plausible: Suppose the exact Hamiltonian contains only the terms $\sum_i h_{ii}N_i + V \sum_i N_{i\uparrow}N_{i\downarrow} + \sum_{ij}{}' h_{ij} \sum_\sigma c^+_{i\sigma}c_{j\sigma} - (1/2) \sum_{ij}{}' v_{ijji}$ $\sum_{\sigma\sigma'} c^+_{i\sigma}c_{i\sigma'}c^+_{j\sigma'}c_{j\sigma}$, where $V \equiv v_{iiii}$. Then the minimum[9] of the trial free energy is attained for $b_{ii} = h_{ii}$, $U = V$, $h_{ij} = b_{ij}$ and $U_{ij} = v_{ijji}$, in which case min $F[\tilde{H}] = F[H]$. The quantities h_{ii} and V are clearly zero order in the overlap, and h_{ij},v_{ijji} for $i \neq j$ are first and second order in the overlap[45]. So that in the case of the full Hamiltonian (3), the parameters b_{ij} and U_{ij} ($i \neq j$) should be zero in the limit where the overlap goes to zero. In accordance with this expectation,

we will assume in the remainder of this paper that b_{ij} and $U_{ij} \to 0$ as the nearest overlap $\Delta \to 0$; more precisely, we shall assume that $b_{ij} = 0(\Delta)$ and $U_{ij} = 0(\Delta^2)$. The latter assumption will be shown to be a consistent one in each of the cases studied.

A. Zero-Bandwidth Hamiltonian; All Temperatures

To get some insight into more complicated cases we studied first the simple case in which we keep only terms to zeroeth order in overlap[13] in the exact Hamiltonian H (3); in other words, we consider the atomic limit or zero-bandwidth exact Hamiltonian:

$$H_o = \sum_i [h_{ll} N_i + V N_{i\uparrow} N_{i\downarrow} + \frac{1}{2} \sum_{j \neq i} v_{ijij} N_i N_j] \tag{57}$$

where $N_i = N_{i\uparrow} + N_{i\downarrow}$, $h_{ll} = h_{ii}$, and $V \equiv v_{iiii}$. In accordance with the discussion of the previous paragraph, the trial Hamiltonian is taken of the form

$$\tilde{H}_o = \sum_i [b_{ii} N_i + U N_{i\uparrow} N_{i\downarrow}] \equiv \sum_i \tilde{H}_i \quad . \tag{58}$$

This is also the atomic limit of the Hubbard Hamiltonian. The consistency of the assumption $b_{ij} = U_{ij} = 0$, $i \neq j$, will be seen in secs. B and C below.

Because (58) is function of number operators only, $\frac{\partial \tilde{H}_o}{\partial \lambda}$ commutes with $\tilde{H}_o$ and (54) becomes:

$$<\frac{\partial \tilde{H}_o}{\partial \lambda}(H_o - \tilde{H}_o)> - <H_o - \tilde{H}_o><\frac{\partial \tilde{H}_o}{\partial \lambda}> = 0 \qquad (59)$$

In particular for $\lambda = b_{11}$, making the restriction that b_{ii} is independent of i, as is h_{ii} by the lattice translational symmetry,

$$(V-U)\sum_j (<N_i N_{j\uparrow} N_{j\downarrow}> - <N_i><N_{j\uparrow} N_{j\downarrow}>)$$

$$+ (h_{11}-b_{11})\sum_j (<N_i N_j> - <N_i><N_j>)$$

$$+ \frac{1}{2}\sum_{j\ell}{}' v_{j\ell j\ell}(<N_i N_j N_\ell> - <N_i><N_j N_\ell>) = 0 \; ; \qquad (60)$$

similarly for $\lambda = U$

$$(V-U)\sum_j (<N_{i\uparrow} N_{i\downarrow} N_{j\uparrow} N_{j\downarrow}> - <N_{i\uparrow} N_{i\downarrow}><N_{j\uparrow} N_{j\downarrow}>)$$

$$+ (h_{11}-b_{11})\sum_j (<N_{i\uparrow} N_{i\downarrow} N_j> - <N_{i\uparrow} N_{i\downarrow}><N_j>)$$

$$+ \frac{1}{2}\sum_{j\ell}{}' v_{j\ell j\ell}(<N_{i\uparrow} N_{i\downarrow} N_j N_\ell> - <N_{i\uparrow} N_{i\downarrow}><N_j\, N_\ell>) = 0 \; . \qquad (61)$$

The traces in (60) and (61), according to (44) and (55) are to be taken over the eigenstates of $\tilde{H}_o$ (which are also eigenstates of $\tilde{H}_o - \mu N$). As pointed out by Kaplan[12],

a complete set of eigenstates of this operator is given by a set of Slater determinants obtained by occupying Wannier functions in all possible ways. Since $\tilde{H}_o - \mu N = \sum_i (\tilde{H}_i - \mu N_i)$, the density matrix

$$\tilde{\rho}_o = e^{-\beta(\tilde{H}_o - \mu N)} / \text{tr}\, e^{-\beta(\tilde{H}_o - \mu N)} \tag{62}$$

can be written as a product

$$\tilde{\rho}_o = \prod_i \tilde{\rho}_i \tag{63}$$

where

$$\tilde{\rho}_i = e^{-\beta(\tilde{H}_i - \mu N_i)} / \text{tr}\, e^{-\beta(\tilde{H}_i - \mu N_i)} . \tag{64}$$

Using (63) it is easy to formally evaluate (Appendix A3) the thermal averages in (60) and (61). Finally we obtain the following:

$$U = V \tag{65}$$

$$b_{11} = h_{11} + \tilde{n} \sum_{j \neq 1} v_{1j1j} , \tag{66}$$

where

$$\tilde{n} = 2(e^{-\beta(b_{11}-\mu)} + e^{-\beta(2b_{11}-2\mu+V)})/(1+2\, e^{-\beta(b_{11}-\mu)} + e^{-\beta(2b_{11}-2\mu+V)}) \tag{67}$$

is the average number of electrons per site in the trial Hamiltonian model. Equation (66) is, in fact, a self-consistent equation for b_{ll} , given the chemical potential and temperature. In particular there exists a special value of μ namely μ_o for a given T such that $\tilde{n} = 1$. This is of special interest because it is the zero-bandwidth limit of the half-filled band case to be discussed later in this paper. So in this case we have found, for all temperatures

$$b_{ll} = h_{ll} + \sum_{j \neq l} v_{ljlj} \quad . \tag{68}$$

From (67) and (68) we infer that the special value μ_o of the chemical potential should be

$$\mu_o = h_{ll} + \frac{V}{2} + \sum_{j \neq l} v_{ljlj} \tag{69}$$

independent of T.

Kaplan and Argyres, in appendix B of reference 13, showed that the ground state of the Hamiltonian (57) with the number of electrons equal to the number of sites, has one electron on each site, and the many-body ground state energy $E_g(N_s)$ is

$$E_g(N_s) = N_s h_{ll} + \frac{1}{2} \sum_{ij}{}' v_{ijij} \quad .$$

The ground state energies of the system described by (57)

when we add one electron to or remove one from the N_s electrons already there, are

$$E_g(N_s+1) = (N_s+1)h_{11} + \frac{1}{2}\sum_{i,j}{}' v_{ijij} + \sum_{k\neq 1} v_{1k1k} + V$$

$$E_g(N_s-1) = (N_s-1)h_{11} + \frac{1}{2}\sum_{ij}{}' v_{ijij} - \sum_{k\neq 1} v_{1k1k}$$

Then the chemical potential μ at zero T for H_o with N_s electrons is

$$\mu = \frac{1}{2}[E_g(N_s+1) - E_g(N_s-1)]$$

$$= h_{11} + \frac{V}{2} + \sum_{j\neq 1} v_{1j1j} \quad . \tag{70}$$

This result (70) although derived for zero-T should be valid for all temperatures. In fact we have derived through the expression

$$\text{tr } e^{-\beta(H_o-\mu N)}(N - N_s) = 0 \tag{71}$$

the chemical potential for two sites and rings of three, four and five sites, for any temperature:

two $\qquad \mu = h_{11} + \frac{V}{2} + v_{12}$

three $\qquad \mu = h_{11} + \frac{V}{2} + 2v_{12}$

four $\qquad \mu = h_{11} + \frac{V}{2} + 2v_{12} + v_{13}$

five $$\mu = h_{11} + \frac{V}{2} + 2v_{12} + 2v_{13} \ .$$

Here v_{12} and v_{13} are the first and second neighbor interactions v_{ijij} ; the result (70) is obviously a generalization of these.

Expressions (69) and (70) plus the argument of the previous paragraph suggest strongly that both Hamiltonians, the exact H_o and the best $\tilde{H}_o$ (which we will call $\tilde{H}_o^{(b)}$) are exactly half-filled band Hamiltonians.

From appendix A3 we see that the best value of the parameter U is found uniquely for any density of electrons $\tilde{n}$, except zero. The fact that the effective intrasite interaction U is strictly equal to the exact intrasite interaction V is reasonable for the grand canonical calculation. Our trial Hamiltonian $\tilde{H}_o$ does not contain any intersite effective interaction; hence one electron can, thermally or by other means, move to an excited state by going to any other previously singly-occupied site, with the same probability. And because of this lack of correlation between doubly-occupied and empty sites in $\tilde{H}_o$, we would expect that the interatomic interactions in H_o would enter our single interaction parameter U, in a canonical calculation (for fixed $N = N_s$, in our case), only through an average

$$\frac{1}{N_s - 1} \sum_{j \neq 1} v_{1j1j} \ ,$$

which goes to zero as N_s goes to infinity. ($v_{ijij} \to 0$ as $R_{ij} \to \infty$.) This expectation was found to be born out in straight-forward canonical calculations, for two sites and rings of four and six sites. The results are as follows:

$$\text{two} \qquad U = V - v_{12}$$

$$\text{four} \qquad U = V - \frac{1}{3}(2v_{12} + v_{13})$$

$$\text{six} \qquad U = V - \frac{1}{5}(2v_{12} + 2v_{13} + v_{14}) \cdot \quad (72)$$

This also checks the fact that the canonical ensemble approaches the grand-canonical ensemble when the number N_s increases to infinity.

When one studies the properties of the (phenomenological) Hubbard Hamiltonian, one in general neglects the term $b_{11} \equiv b_{ii}$, because there it only represents a shift in the chemical potential; that is, b_{11} becomes an unimportant constant. Here it is different; because of the presence of the difference $(H - \tilde{H})$ in the variational principle (43), b_{11} does not appear only in the combination $b_{11} - \mu$, there being terms containing b_{11} alone. We have seen already that, in fact, the best value of b_{11} given by (70) has been chosen by the variational principle to make $\tilde{H}_o^{(b)}$ have the same number of electrons as H_o. Its importance then has

already been shown . Another even more important reason to have b_{11} in our scheme is related to the consistency[42] between statistical mechanical and thermodynamical expressions for the macroscopic quantities of the system such as internal energy, entropy and average number of particles. It has been shown (in reference 42) that the presence of $b_{11}N$ terms in the trial Hamiltonian $\tilde{H}$ is necessary and sufficient to get the above consistency, b_{11} being a variational parameter.

The (approximate) entropy $S^{(b)}$ correspondent to $\tilde{H}_o^{(b)}$ can then be either calculated from $F[\tilde{H}_o^{(b)}]$ or from the (approximate) density matrix $\tilde{\rho}^{(b)}$:

$$S^{(b)} = - \frac{\partial}{\partial T} F[\tilde{H}_o^{(b)}] = -k \text{ tr } \tilde{\rho}^{(b)} \ln \tilde{\rho}^{(b)} . \quad (73)$$

The specific heat follows immediately, and we find it is independent of the Coulomb intersite interactions v_{kjkj} ; it is the same as calculated from a Hamiltonian which consists purely of intrasite interactions V:

$$C_v^{(b)}/kN_s = (\frac{\beta V}{4}/\cosh \frac{\beta V}{4})^2 \quad . \quad (74)$$

To evaluate the susceptibility, we have first to add the magnetic field term, namely $-h\sum_i M_i = -h\sum_i (N_{i\uparrow} - N_{i\downarrow})/2$, to both the exact Hamiltonian and trial Hamiltonian, and similarly, find the best parameters, as function of terms

of H_o, temperature, chemical potential and the magnetic field (h is equal to $g\mu_B$ times the magnetic field). In the half-filled band limit they turned out to be the same as those of (69) and (70), and consequently independent of the magnetic field. Again[42]

$$\langle M \rangle = - \frac{\partial}{\partial h} F[\tilde{H}_o^{(b)}] = \mathrm{tr}\ \tilde{\rho}^{(b)}\ M \qquad (75)$$

where $M = \frac{h}{2} \sum_i (N_{i\uparrow} - N_{i\downarrow})$ is the magnetization. The zero-field susceptibility (per site) is

$$\chi^{(b)} = \frac{\beta}{2} \left(e^{\frac{\beta V}{4}} / \cosh \frac{\beta V}{4}\right), \qquad (76)$$

and is also independent of the intersite interactions.

It would be interesting to compare thermodynamical properties of this $\tilde{H}_o^{(b)}$ with those of H_o for an arbitrary number of sites. Since one cannot calculate the exact free energy correspondent to the exact Hamiltonian H_o, in general, this cannot be accomplished. Recently, thermodynamical properties of a linear chain Hamiltonian consisting of intrasite and nearest neighbor Coulomb interactions, V and v_{12}, respectively, have been calculated by Tu and Kaplan[46]. They plot the specific heat C_v/kN and the inverse zero-field susceptibility $(\chi V/N\mu_B^2)^{-1}$ as function of kT/V, for different ratios of $\eta = v_{12}/V$. The ones for $\eta = 0$ correspond exactly to

our results here, and should be compared with the others for different η's . The susceptibility is practically insensitive to η when $0 \leq \eta < \frac{1}{2}$; the specific heat is also quite insensitive to change of η in the same interval although slightly more sensitive especially close to $\eta = \frac{1}{2}$. This value $\eta = \frac{1}{2}$ is a critical one as noted by Bari[47], because for $\eta > \frac{1}{2}$ the ground state of this Hamiltonian (containing V and v_{12} interactions only) consists of alternating empty and double occupied sites. Thus for $\eta > \frac{1}{2}$ the variational approximation $\tilde{H}_o^{(b)}$ is extremely poor since the approximate ground state contains singly-occupied sites ($U = V > 0$) ; however, as we have said, the variational approximation is quite good for rather large $\eta (\tilde{<} \frac{1}{2})$.

B. Narrow Half-Filled Band: The "Best" Hubbard Hamiltonian

In the narrow band region the overlap between the atomic functions is very small and all the terms in H, (3), which depend on the overlap are small compared to the others. For convenience we separate the exact Hamiltonian H in two parts:

$$H = H_o + H' \tag{77}$$

where H_o is the zero overlap part given by (57) and H' is defined by ($\sum'$ means a sum with all indices different)

$$H' = \sum_{\sigma} {\sum_{ij}}' [h_{ij} + v_{iiji}(N_{i\bar{\sigma}} + N_{j\bar{\sigma}}) + \sum_{k\neq i,j} v_{ikjk} N_k] c^{+}_{i\sigma} c_{j\sigma}$$

$$+ \frac{1}{2} \sum_{\sigma} {\sum_{ij}}' v_{ijji} [c^{+}_{i\bar{\sigma}} c_{j\bar{\sigma}} + c^{+}_{j\bar{\sigma}} c_{i\bar{\sigma}}) c^{+}_{i\sigma} c_{j\sigma} - N_{i\sigma} N_{j\sigma}]$$

$$+ \frac{1}{2} \sum_{\sigma} {\sum_{ijk}}' v_{iijk} (c^{+}_{i\bar{\sigma}} c_{k\bar{\sigma}} + c^{+}_{k\bar{\sigma}} c_{j\bar{\sigma}}) c^{+}_{i\sigma} c_{j\sigma} \qquad (78)$$

$$+ \frac{1}{2} \sum_{\sigma\sigma'} {\sum_{ijk\ell}}' v_{ijk\ell} c^{+}_{i\sigma} c^{+}_{j\sigma'} c_{\ell\sigma'} c_{k\sigma} \quad .$$

We begin our exploration of the narrow-band case with a trial Hamiltonian which is of the form of the Hubbard Hamiltonian (2). In other words we take the Hamiltonian (56) with $U_{ij} = 0$, and call it $\tilde{H}_H$:

$$\tilde{H}_H = \sum_i (b_{ll} N_i + U N_{i\uparrow} N_{i\downarrow}) + \sum_{\sigma} {\sum_{ij}}' b_{ij} c^{+}_{i\sigma} c_{j\sigma} \qquad (79)$$

which for convenience is written as

$$\tilde{H} = \tilde{H}_o + \tilde{T} \qquad (80)$$

where $\tilde{H}_o$ is (58) and $\tilde{T}$ is

$$\tilde{T} \equiv \sum_{\sigma} {\sum_{ij}}' b_{ij} c^{+}_{i\sigma} c_{j\sigma} \quad . \qquad (81)$$

As we argued before, the best $b_{ij} (i\neq j)$ are expected to be proportional to the overlap in the narrow band limit, so that when $H' \to 0$, $\tilde{T} \to 0$ too. We can then say that $\tilde{T}$ is "small" compared to H_o and expansion techniques can be used to solve the stationarity equations (54).

We propose to solve these stationarity equations for $\lambda=b_{11}$, U and $b_{ij}(i\neq j)$ in two limiting cases: 1) high temperatures, in the sense that $kT>>|b_{ij}|$ for all i and j; 2) low temperatures, in the sense that $kT<<$ nearest neighbor $|b_{ij}|$. In both cases $|b_{ij}|<<$ U .

B.1 High-Temperature Limit

It is convenient to define

$$\tilde{H}_o \equiv \tilde{H}_o - \mu N \tag{82}$$

and

$$\tilde{R} \equiv e^{\beta\tilde{H}_o} e^{-\beta(\tilde{H}_o+\tilde{T})}$$

such that

$$e^{-\beta(\tilde{H}_H-\mu N)} = e^{-\beta\tilde{H}_o}\tilde{R} \quad .$$

Consequently

$$\tilde{Z} = \tilde{Z}_o \langle\tilde{R}\rangle_o$$

$$\tilde{\rho} = \frac{1}{\langle\tilde{R}\rangle_o}\,\tilde{\rho}_o\,\tilde{R} \tag{86}$$

where

$$\tilde{Z}_o = \mathrm{tr}\, e^{-\beta\tilde{H}_o} \tag{87}$$

$$\tilde{\rho}_o = e^{-\beta\tilde{H}_o}/\tilde{Z}_o \tag{88}$$

and

$$\langle\ldots\rangle_o \equiv \mathrm{tr}\,\tilde{\rho}_o\,(\ldots) \quad . \tag{89}$$

With all these definitions the stationarity equations are written as

$$\langle\tilde{R}\rangle_o \int_o^1 dx \langle\tilde{R}Q_\lambda(x)\ (H - \tilde{H}_H)\rangle_o \qquad (90)$$

$$- \langle\tilde{R}(H - \tilde{H}_H)\rangle_o \langle\tilde{R}\ \frac{\partial\tilde{H}_H}{\partial\lambda}\rangle_o = 0 \quad .$$

According to (89) the thermal averages in (90) are to be evaluated with respect to the density matrix $\rho_o \propto \exp-\beta\tilde{H}_o$. We should point out that the equations (90) are still exact.

In this high temperature limit we expand $\exp \pm x\,\beta(\tilde{H}_o+\tilde{T})$ in powers of $\beta|b_{ij}|$ by using Eq. (51) and keeping only terms of first order in $\beta|b_{ij}|$:

$$e^{\pm x\beta(\tilde{H}_o+\tilde{T})} = e^{\pm x\beta\tilde{H}_o}\ [1 \pm \int_o^x ds\ \tilde{T}(\mp s)] \qquad (91)$$

where

$$\tilde{T}(s) \equiv e^{s\beta\tilde{H}_o}\ \tilde{T}\ e^{-s\beta\tilde{H}_o}$$

$$= \sum_\sigma \sum_{k\ell}{}' b_{k\ell}\ e^{s\beta U(N_{k\bar{\sigma}}-N_{\ell\bar{\sigma}})}\ c^+_{k\sigma}\ c_{\ell\sigma} \quad . \qquad (92)$$

We refer the reader to Appendix A4 for the proof of the last equality in (92).

Defining

$$g_{k\ell\bar{\sigma}}(s) \equiv e^{s\beta U(N_{k\bar{\sigma}} - N_{\ell\bar{\sigma}})} \qquad (93)$$

to simplify notation, we have

$$e^{\pm\beta(\tilde{H}_o+\tilde{T})} = e^{\pm\beta\tilde{H}_o}[1 \pm \beta \sum_{\sigma} \sum_{k\ell}' b_{k\ell} \int_o^x ds\, g_{k\ell\bar{\sigma}}(\mp s)\, c^+_{k\sigma}\, c_{\ell\sigma}] \quad . (94)$$

Similarly $\tilde{R}$ becomes

$$\tilde{R} = 1-\beta \int_o^1 ds\, \tilde{T}(s) = 1 -\beta \sum_{\sigma} \sum_{k\ell}' b_{k\ell} \int_o^1 ds\, g_{k\ell\bar{\sigma}}(s)\, c^+_{k\sigma}\, c_{\ell\sigma} \quad . (95)$$

Immediately we see $\langle \tilde{R} \rangle_o = 1$ because

$$\langle c^+_{k\sigma}\, c_{n\sigma} \rangle_o = 0 \text{ , for } k \neq n \quad . \qquad (96)$$

With (94), $Q_\lambda(x)$ defined in (53) becomes

$$Q_\lambda(x) = \Lambda_\lambda(x) + \beta \sum_{\sigma} \sum_{k\ell}' b_{k\ell} \int_o^x ds\, [g_{k\ell\bar{\sigma}}(-s)\, g_{k\ell\bar{\sigma}}(x)\, c^+_{k\sigma}\, c_{\ell\sigma}\, \Lambda_\lambda(x)$$

$$- \Lambda_\lambda(x)\, g_{k\ell\bar{\sigma}}(s)\, c^+_{k\sigma}\, c_{\ell\sigma}] \qquad (97)$$

where

$$\Lambda_\lambda(x) \equiv e^{x\beta\tilde{H}_o} \frac{\partial\tilde{H}}{\partial\lambda} e^{-x\beta\tilde{H}_o} \quad . \qquad (98)$$

In accordance with previous discussion we assume the best parameters $b_{ij}(i \neq j)$ to be proportional to the overlap between atomic functions i and j; we then calculate (90) neglecting terms which are higher than first order in the overlap. In so doing we easily find that for $\lambda = b_{11}$ and $\lambda = U$ the stationarity equations (90) become identical to (60) and (61) respectively; we already have the solutions for those equations:

$$U = V \tag{99}$$

$$b_{11} = h_{11} + \sum_{j\neq 1} v_{1j1j} \quad . \tag{100}$$

This last one holds only in the half-filled band regime.

For $\lambda = b_{ij} (i \neq j)$ eq. (90) becomes

$$\int_o^1 dx \sum_\sigma \langle g_{ij\bar{\sigma}}(x)\ c^+_{i\sigma}\ c_{j\sigma}\ (H - \tilde{H}_H)\rangle_o \ +$$

$$+ \beta \sum_{\sigma\sigma'} {\sum_{k\ell}}' b_{k\ell} \int_o^1 dx \Big\{ \int_o^x ds \langle [g_{k\ell\bar{\sigma}'}(-s)\ g_{k\ell\bar{\sigma}'}(x)\ c^+_{k\sigma'} c_{\ell\sigma'} g_{ij\bar{\sigma}}(x) c^+_{i\sigma} c_{j\sigma}$$

$$- g_{ij\bar{\sigma}}(x)\ c^+_{i\sigma}\ c_{j\sigma}\ g_{k\ell\bar{\sigma}'}(s)\ c^+_{k\sigma'}\ c_{\ell\sigma'}] (H - \tilde{H}_H)\rangle_o - \tag{101}$$

$$- \int_o^1 ds \langle g_{k\ell\bar{\sigma}'}(s)\ c^+_{k\sigma'}\ c_{\ell\sigma'}\ g_{ij\bar{\sigma}}(x)\ c^+_{i\sigma}\ c_{j\sigma}\ (H - \tilde{H}_H)\rangle_o \ +$$

$$+ \langle g_{k\ell\bar{\sigma}'}(x)\ c^+_{k\sigma'}\ c_{\ell\sigma'}\ c^+_{i\sigma}\ c_{j\sigma}\rangle_o \langle H - \tilde{H}_H\rangle_o \Big\} = 0 \ .$$

We then proceed as in Appendix A5 to solve (101) for b_{ij}; we find

$$b_{ij} = [1 - \frac{v_{ijij}}{V} f(\beta V)]^{-1}\ t_{ij} \tag{102}$$

where t_{ij} is given in (20), and $f(\beta V)$ is

$$f(\beta V) = \frac{1 - (1 + \beta V) e^{-\beta V}}{1 + \beta V\ e^{-\frac{1}{2}\beta V} - e^{-\beta V}} \ ; \tag{103}$$

$f(\beta V) \to 1(0)$ as $\beta V \to \infty(0)$. We see that Eq. (102) is consistent with our assumption $b_{ij} = 0(\Delta)$. Then, particularly if $kT \ll V$ the expression for b_{ij} will reduce to

$$b_{ij} = (1 - \frac{v_{ijij}}{V})^{-1} t_{ij} \quad . \tag{104}$$

The fact that the best U turned out to be equal to V is again very reasonable, because $kT \gg |b_{ij}|$ for any pair i and j means that the electron can go from site to any other singly-occupied site with equal probability; then the same discussion of section V.A on this matter applies here. The value of b_{ll} is also understandable: as can be shown, it again makes both Hamiltonians H and $\tilde{H}_H^{(b)}$ (the best $\tilde{H}_H$) have the same number of electrons to first order in b_{ij} (in the half-filled band case).

B.2 Low-Temperature Limit

In order to calculate the quantities appearing in the stationarity equations (54), we must first discuss the eigenstates of $\tilde{H}_H$. When the number of electrons N is equal to the number of sites N_s, the ground states of H_o with $U>0$ have one electron on each site, and no doubly-occupied or empty sites, the degeneracy being 2^N. Adding small b_{ij} terms to it will remove the degeneracy; second order degenerate perturbation theory[6,29,48] (for the energy) shows the resulting energy levels are the same as those of a Heisenberg Hamiltonian (except for a constant) with the exchange integral $\tilde{J}_{ij} = -2b_{ij}^2/U$.

One can divide the complete set of eigenfunctions of $\tilde{H}_o$ in two sub-sets: G - the ground states; and E - the excited states. Consider the following:

$$\tilde{H}_o|\tilde{n}_o\rangle = \tilde{\varepsilon}_o|\tilde{n}_o\rangle \quad , \quad \tilde{\varepsilon}_o = N_s b_{11}$$

$$\tilde{H}_H|\tilde{n}\rangle = \tilde{E}_n|\tilde{n}\rangle \tag{105}$$

where $|\tilde{n}_o\rangle$ is in G, and $\tilde{E}_n$ and $|\tilde{n}\rangle$ are the eigenvalues and eigenfunctions of $\tilde{H}_H$, resulting from the removal of the degeneracy of the ground state of $\tilde{H}_o$. These contain the low-lying eigenstates.

If one defines idempotent operators P and Q such that

$$P\Psi \in G \tag{106}$$

and

$$Q\Psi \in E$$

for all wavefunctions Ψ so $P + Q = 1$, then one can write the eigenfunctions $|\tilde{n}\rangle$ as [29]

$$|\tilde{n}\rangle = \tilde{C}_n \left[1 - Q \frac{1}{\tilde{H}_H - \tilde{E}_n} Q \tilde{T}\right] P \tilde{n}_o\rangle \quad , \tag{107}$$

where $\tilde{C}_n$ is the normalization constant, which can be considered real. One then can make the following expansion[29]

$$Q\frac{1}{\tilde{H}_H - \tilde{E}_n}Q = Q\frac{1}{\tilde{H}_o - \tilde{\varepsilon}_o}Q \sum_{k=0}^{\infty} (-)^k \left[Q\frac{1}{\tilde{H}_o - \tilde{\varepsilon}_o}Q \left(\tilde{T} - \Delta\tilde{E}_n\right)Q\right]^k \quad , \tag{108}$$

where $\Delta\tilde{E}_n = \tilde{E}_n - \varepsilon_o$. By keeping only the first term (k=0) in the series (108), one obtains the approximate eigenfunctions of $\tilde{H}_H$, in formal second order degenerate perturbation theory:[29]

$$|\tilde{n}> = \tilde{C}_n \left[1 - Q \frac{1}{\tilde{H}_o - \tilde{\varepsilon}_o} Q\tilde{T}\right] P|\tilde{n}_o> \quad . \tag{109}$$

In the class of the operators Q , one can distinguish the operators $Q^{(\nu)}$, with $\nu = 1, 2, 3, \ldots$ which project functions onto the ν^{th} excited states of the unperturbed Hamiltonian $\tilde{H}_o$, the energy of these states being $N_s b_{11} + \nu U$. Since our perturbation term $\tilde{T}$, (81) , involves a hopping $c^+_{i\sigma} c_{j\sigma}$ from site j to another i , it is clear that the operator Q in (109) is in fact a $Q^{(1)}$ operator. For clarity, it is convenient to rewrite (109) with this new information:

$$|\tilde{n}> = \tilde{C}_n \left[1 - Q^{(1)} \frac{1}{\tilde{H}_o - \tilde{\varepsilon}_o} Q^{(1)} \tilde{T}\right] P|\tilde{n}_o> \quad . \tag{110}$$

The orthonormalization condition $<\tilde{m}|\tilde{n}> = \delta_{nm}$ gives

$$\tilde{C}_n^2 = \left[1 + \frac{1}{U^2} <\tilde{n}_o|P\tilde{T}Q^{(1)}\tilde{T}P|\tilde{n}_o>\right]^{-1} = \left[1 + \sum_{ij}{}' \frac{b_{ij}^2}{U^2} A_n^{ij}\right]^{-1} \tag{111}$$

with

$$\frac{1}{U} <\tilde{m}_o|P\tilde{T}Q^{(1)}\tilde{T}P|\tilde{n}_o> = \sum_{ij}{}' \frac{b_{ij}^2}{U} A_n^{ij} \delta_{nm} \quad , \tag{112}$$

where

$$A_n^{ij} \equiv \sum_{\sigma\sigma'} {}' \langle \tilde{n}_o | \, c_{i\sigma}^+ \, c_{j\sigma} \, c_{j\sigma'}^+ \, c_{i\sigma'} \, | \tilde{n}_o \rangle \quad . \tag{113}$$

Here we have considered $b_{ij} = b_{ji} = b_{ij}^*$.

It is clear from (112) that $|\tilde{n}_o\rangle$ and $\sum_{ij}' \frac{b_{ij}^2}{U} A_n^{ij}$ are, respectively, eigenfunctions and eigenvalues of the operator $\tilde{H}_{eff}$

$$\tilde{H}_{eff} = \frac{1}{U} P\tilde{T}Q^{(1)}\tilde{T}P \tag{114}$$

which, in Appendix A6 is shown to be identical to the Heisenberg Hamiltonian, with $J_{ij} = -2b_{ij}^2/U$, except for constant terms.

It follows from (105) and (110) that

$$\tilde{E}_n = - \sum_{ij}' \frac{b_{ij}^2}{U} A_n^{ij} + N_s \, b_{11} \, . \tag{115}$$

These are then equal to Heisenberg Hamiltonian eigenvalues, except for a constant. (By constant here we mean independent of $|\tilde{n}_o\rangle$) . To simplify the calculation we are about to make, let us consider only nearest neighbor hopping $b_{ij}=b_{12}$. Then (115) becomes

$$\tilde{E}_n = -\frac{b_{12}^2}{U} A_n + N_s \, b_{11} \, . \tag{116}$$

where

$$A_n = 2 \sum_{<ij>} A_n^{ij} \quad , \tag{117}$$

$\sum_{<ij>}$ denoting sum over nearest-neighbor pairs.

For an arbitrary number of sites one does not know how to calculate the eigenvalues and eigenfunctions of the Heisenberg Hamiltonian, which means, in our language here, that we don't know how to evaluate A_n and $|\tilde{n}_o>$ for an arbitrary N_s. Nevertheless as we will show, our calculation of the best parameters can be accomplished without knowing explicitly $|\tilde{n}_o>$ and A_n.

Since we are interested here in temperatures which are low compared to U and $|b_{12}|$, we perform the traces in the stationarity equations (54), only over the low-lying eigenstates of $\tilde{H}_H$. We then get

$$\sum_{n,\ell} e^{\beta\frac{b_{12}^2}{U}(A_n+A_\ell)} \left\{ <\tilde{n}|\frac{\partial\tilde{H}_H}{\partial\lambda}|\tilde{n}> \left[\frac{b_{12}^2}{U}(A_n - A_\ell) - <\tilde{\ell}|H|\tilde{\ell}>\right] + \int_o^1 dx <\tilde{n}|Q_\lambda(x)\ H|\tilde{n}>\right\} = 0 \quad . \tag{118}$$

Because of the restriction on the traces, $b_{11}N$ appears only as a constant term ($=b_{11}N_s$); thus b_{11} cannot be determined variationally within the present approximation; consequently we drop it out of the calculation. (But see section B.3).

The last term in (118), containing the integral is found to be

$$\int_o^1 dx\ <\tilde{n}|Q_\lambda(x)H|\tilde{n}> = \sum_m \frac{e^{-\beta\frac{b_{12}^2}{U}(A_n-A_m)}-1}{-\beta\frac{b_{12}^2}{U}(A_n-A_m)} <\tilde{n}|\frac{\partial\tilde{H}_H}{\partial\lambda}|\tilde{m}><\tilde{m}|H|\tilde{n}>$$

$$+ kT \sum_\phi (\tilde{E}_\phi - \frac{b_{12}^2}{U}A_n) <\tilde{n}|\frac{\partial H_H}{\partial\lambda}|\tilde{\phi}><\tilde{\phi}|H|\tilde{n}> \quad , \tag{119}$$

where $|\tilde{m}\rangle$ and $|\tilde{\phi}\rangle$ are eigenstates of $\tilde{H}_H$ which originate from G and E, respectively. Then we proceed and calculate the several matrix elements in (118) and (119). We started with the matrix element of the exact Hamiltonian H between the eigenfunctions of the trial Hamiltonian $\tilde{H}_H$. In accordance with our previous discussion we assume that b_{12} is $0(\Delta)$, and since we are doing this perturbation theory which is second order in $\tilde{T}$, we neglect terms in this matrix element which are of higher order than Δ^2.

Dropping the P operators which appear in (110), because $P|\tilde{n}_o\rangle = |\tilde{n}_o\rangle$, and defining, for nearest neighbor i and j only

$$v_{12} \equiv v_{ijij}\ ,\ t_{12} \equiv t_{ij} \text{ and } X_{12} \equiv v_{ijji} \tag{120}$$

we have, using (110)[49],

$$\langle\tilde{m}|H|\tilde{n}\rangle = \tilde{C}_n\tilde{C}_m\ [\langle\tilde{m}_o|H|\tilde{n}_o\rangle - \frac{2}{U}\langle\tilde{m}_o|HQ^{(1)}\tilde{T}|\tilde{n}_o\rangle +$$

$$+ \frac{1}{U^2}\langle\tilde{m}_o|\tilde{T}\ Q^{(1)}H\ Q^{(1)}\ \tilde{T}|\tilde{n}_o\rangle] \tag{121}$$

$$= \delta_{nm}\ [\frac{1}{2}\sum_{k\ell}{}' v_{k\ell k\ell} - \frac{1}{2}X_{12} + Y\ A_n]\ , \tag{122}$$

where, for convenience we defined

$$Y \equiv \frac{b_{12}^2}{U^2}\ (V-v_{12}) - \frac{2b_{12}t_{12}}{U} + \frac{1}{2}\ X_{12}\ . \tag{123}$$

Details of the above calculation are found in Appendix A7.

Before proceeding with the calculations it is worth rewriting (118), taking in account (119) and (122):

$$\sum_{n,\ell} e^{\beta \frac{b_{12}^2}{U}(A_n+A_\ell)} \left[\langle\tilde{n}|\frac{\partial\tilde{H}_H}{\partial\lambda}|\tilde{n}\rangle \left(\frac{b_{12}^2}{U}+Y\right)(A_n-A_\ell) + \right.$$

$$\left. + kT \sum_{\phi} (\tilde{E}_\phi - \frac{b_{12}^2}{U} A_n)^{-1} \langle\tilde{n}|\frac{\partial\tilde{H}_H}{\partial\lambda}|\tilde{\phi}\rangle\langle\tilde{\phi}|H|\tilde{n}\rangle\right] = 0 \quad (124)$$

Notice that the constant terms of (122) (specially the long range Coulomb interaction terms $\sum_{k,\ell} v_{k\ell k\ell}$) have been cancelled out. Since now we know that $(\frac{b_{12}^2}{U}+Y)$ is second order in Δ, we just have to evaluate $\langle\tilde{n}|\frac{\partial\tilde{H}_H}{\partial\lambda}|\tilde{n}\rangle$ to the lowest order in Δ. Straightforwardly we find

$$\langle\tilde{n}|\frac{\partial\tilde{H}_H}{\partial U}|\tilde{n}\rangle = \frac{1}{U^2}\sum_i \langle\tilde{n}_o|\tilde{T}\, Q^{(1)}\, N_{i\uparrow}N_{i\downarrow}\, Q^{(1)}\, \tilde{T}|\tilde{n}_o\rangle = \frac{b_{12}^2}{U^2} A_n \quad (125)$$

and

$$\langle\tilde{n}|\frac{\partial\tilde{H}_H}{\partial b_{12}}|\tilde{n}\rangle = -\frac{2}{U}\sum_{<ij>}\sum_\sigma \langle\tilde{n}_o|c_{i\sigma}^+ c_{j\sigma}\, Q^{(1)}\, \tilde{T}|\tilde{n}_o\rangle = -\frac{2b_{12}}{U} A_n. \quad (126)$$

The second set of terms inside the square bracket in (124) has an overall factor kT assumed to be higher order than Δ. Then we only have to calculate these terms up to order of Δ^2. With (110) we can rewrite it as

$$\sum_{\phi} (\tilde{E}_\phi - \frac{b_{12}^2}{U} A_n)^{-1} \langle\tilde{n}|\frac{\partial\tilde{H}_H}{\partial\lambda}|\tilde{\phi}\rangle\langle\tilde{\phi}|H|\tilde{n}\rangle \quad (127)$$

$$= \sum_{\phi} (\tilde{E}_\phi - \frac{b_{12}^2}{U} A_n)^{-1} \tilde{C}_n^2 \langle\tilde{n}_o|(1-\frac{1}{U}\tilde{T}\, Q^{(1)})\, \frac{\partial\tilde{H}_H}{\partial\lambda}|\tilde{\phi}\rangle\langle\tilde{\phi}|H(1-\frac{1}{U}\, Q^{(1)}\tilde{T})|\tilde{n}_o\rangle .$$

A careful examination of (127) shows that within the second order in Δ, the only eigenfunctions $|\tilde{\phi}\rangle$ that enter in the calculation are the ones resulting from the removal of the degeneracy of the first excited state of $\tilde{H}_o$, with the same number of electrons N_s, which lies higher by U. If we then express $|\tilde{\phi}\rangle$ in terms of $|\tilde{\phi}_o\rangle$, as we did in (110) for $|\tilde{n}\rangle$ and $|\tilde{n}_o\rangle$, we have

$$|\tilde{\phi}\rangle = \tilde{C}_\phi \left[1 - (P + Q^{(2)}) \frac{1}{\tilde{H}_o - \tilde{\varepsilon}_1} (P + Q^{(2)})\tilde{T}\right]Q^{(1)}|\tilde{\phi}_o\rangle$$

$$= \tilde{C}_\phi (1 - S\,\tilde{T}\,Q^{(1)})|\tilde{\phi}\rangle \qquad (128)$$

where

$$S \equiv P \frac{1}{\tilde{H}_o - \tilde{\varepsilon}_1} P + Q^{(2)} \frac{1}{\tilde{H}_o - \tilde{\varepsilon}_1} Q^{(2)} . \qquad (129)$$

The normalization constant $\tilde{C}_\phi$ and energy $\tilde{E}_\phi$ are found to be

$$\tilde{C}_\phi^2 = \left[1 + \frac{b_{12}^2}{U^2}(B_\phi + B'_\phi)\right]^{-1} \qquad (130)$$

$$\tilde{E}_\phi = U + \frac{b_{12}^2}{U}(B_\phi - 2B'_\phi) \qquad (131)$$

where

$$B_\phi \equiv 2\sum_{\langle i,j\rangle} \sum_{\sigma\sigma'} \langle\tilde{\phi}_o|c_{i\sigma}^+ c_{j\sigma}\, P\, c_{j\sigma'}^+ c_{i\sigma'}|\tilde{\phi}_o\rangle \qquad (132)$$

$$B'_{\phi} \equiv 2\sum_{<i,j>} \sum_{\sigma\sigma'} <\tilde{\phi}_o|c^+_{i\sigma}\, c_{j\sigma}\, Q^{(2)}\, c^+_{j\sigma'}\, c_{i\sigma'}|\tilde{\phi}_o>$$

Then we proceed as in Appendix A8, and get the final form of the stationarity equations (124)

$$\sum_{n,\ell} e^{\beta \frac{b_{12}^2}{U}(A_n+A_\ell)} \left\{ \frac{b_{12}^2}{U} A_n(A_n-A_\ell)\left(\frac{b_{12}^2}{U} + Y\right) + \right.$$

$$\left. + kT \frac{b_{12}}{U^2} A_n \left[\frac{b_{12}}{U}(V-v_{12}) - t_{12}\right]\right\} = 0 = \frac{\partial F[\tilde{H}]}{\partial U}$$

and

$$\sum_{n,\ell} e^{\beta \frac{b_{12}^2}{U}(A_n+A_\ell)} \left\{ \frac{b_{12}}{U} A_n(A_n-A_\ell)\left(\frac{b_{12}^2}{U} + Y\right) \right.$$

$$\left. + kT \frac{1}{U} A_n \left[\frac{b_{12}}{U}(V-v_{12}) - t_{12}\right]\right\} = 0 = \frac{\partial F[\tilde{H}]}{\partial b_{12}} . \qquad (133)$$

From these two equations it follows easily that

$$\frac{b_{12}^2}{U} + Y = 0$$

$$\frac{b_{12}}{U}(V-v_{12}) - t_{12} = 0 ; \qquad (133')$$

(the A_m, defined in (117) and (113), are not needed!).

Recalling the definition of Y in (123) we find from (133') that the best parameters b_{12} and U are:

$$b_{12} = t_{12}\left(1 + \frac{X_{12}}{K_{12}}\right) \qquad (134)$$

$$U = (V-v_{12})\ (1 + \frac{X_{12}}{K_{12}}) \tag{135}$$

where

$$K_{12} = -\frac{2t_{12}^2}{V-v_{12}}$$

is the exact nearest neighbor kinetic exchange; K_{ij} was defined in Eq. (45). $U = \infty$ is seen to be a solution of (133'), which on physical grounds can be seen to lead to higher free energy.

It can be seen from (110) that $|\tilde{n}>$ is a linear combination of singly-occupied-site functions $|\tilde{n}_o>$ and functions $\sum_{<ij>} \sum_{\sigma} c_{i\sigma}^{+} c_{j\sigma} |\tilde{n}_o>$ which have one doubly-occupied and one empty site and all the other sites are singly-occupied; the ratio of this mixture is easily seen to be b_{12}/U . If a similar perturbation theory is done on the exact Hamiltonian H , the same sort of mixture in the wavefunctions is found, the ratio of the mixture being equal to $t_{12}/(V - v_{12})$. Our results (134) and (135) for the best parameters show that the minimal principle (43) matched the wavefunctions of both the exact and trial Hamiltonians, since

$$b_{12}/U = t_{12}/(V - v_{12}) \quad . \tag{136}$$

Another important feature of our results (134) and (135) is that the low-lying eigenvalues of both Hamiltonians have been matched; in other words the appropriate Heisenberg exchange integrals are the same (despite the lack of U_{ij} in $\tilde{H}$):

$$-\frac{2b_{12}^2}{U} = -\frac{2t_{12}^2}{(\bar{V}-v_{12})} + v_{1221} = K_{12} + X_{12} \quad . \qquad (137)$$

Hence we have accomplished Anderson's objective of defining a non-magnetic one-electron Hamiltonian whose transfer integral leads via the kinetic exchange to the correct low-lying exchange splittings when $|K_{12}| >> X_{12}$.

However, the above approach fails to give a physically acceptable approximation to the properties of H when $X_{12} > |K_{12}|$.[50] This is seen as follows. We assumed, in the course of making our calculation, that $U >> |b_{12}| >> kT$, leading to (134) and (135); but when $X_{12} > |K_{12}|$, (135) gives $U<0$, which is inconsistent with our initial assumption. The only alternatives to that assumption are $0<U \sim |b_{12}|$, $0<U<<|b_{12}|$, or $U<0$. It can be seen that any of these assumptions would lead to a very poor approximation to H .

In section V.C we discuss an improved model for the special simple case of two sites.

B.3 Two Sites; All Temperatures

The results so far derived for narrow-band systems show that the best Hamiltonian of the form (79) is temperature dependent, the low temperature one being appreciably different from the high temperature one. Unfortunately, we are not able to find how to connect the best low temperature parameters with the best high temperature ones, because the expansion techniques we have used do not hold for this intermediate region of temperatures. However, since our results (in the grand canonical ensemble) are independent of the number of sites, we decided to study numerically the simple case of two sites only, for all temperatures, with the hope of extrapolating the intermediate temperature results for an arbitrary number of sites. This also could provide a check on the analytical expressions for the best parameters.

The exact single-band Hamiltonian (3) specialized for this two-site case is explicitly:

$$
\begin{aligned}
H = {} & h_{11}(N_1 + N_2) + V(N_{1\uparrow}N_{1\downarrow} + N_{2\uparrow}N_{2\downarrow}) + v_{12}N_1N_2 \\
& + \sum_{\sigma} [h_{12} + v'_{12}\ (N_{1\bar{\sigma}} + N_{2\bar{\sigma}})]\,(c^{+}_{1\sigma}c_{2\sigma} + c^{+}_{2\sigma}\ c_{1\sigma}) \\
& + X_{12} \sum_{\sigma} [\tfrac{1}{2}\ (c^{+}_{1\bar{\sigma}}\ c_{2\bar{\sigma}} + c^{+}_{2\bar{\sigma}}\ c_{1\bar{\sigma}})(c^{+}_{1\sigma}\ c_{2\sigma} + c^{+}_{2\sigma}\ c_{1\sigma}) \\
& \qquad - N_{1\sigma}\ N_{2\sigma}] \qquad (138)
\end{aligned}
$$

where some new symbols are introduced:

$$v'_{12} \equiv v_{1121} \tag{139}$$

$$X_{12} \equiv v_{1221} \quad .$$

The eigenstates of (138) are easily found and they are displayed in Table 1. The eigenstates of the Hubbard Hamiltonian for two sites can immediately be drawn from that same figure just by replacing h_{11} by b_{11} , V by U , h_{12} by b_{12} and setting $v_{12} = v'_{12} = X_{12} = 0$. The eigenfunctions are the same except for two singlets.

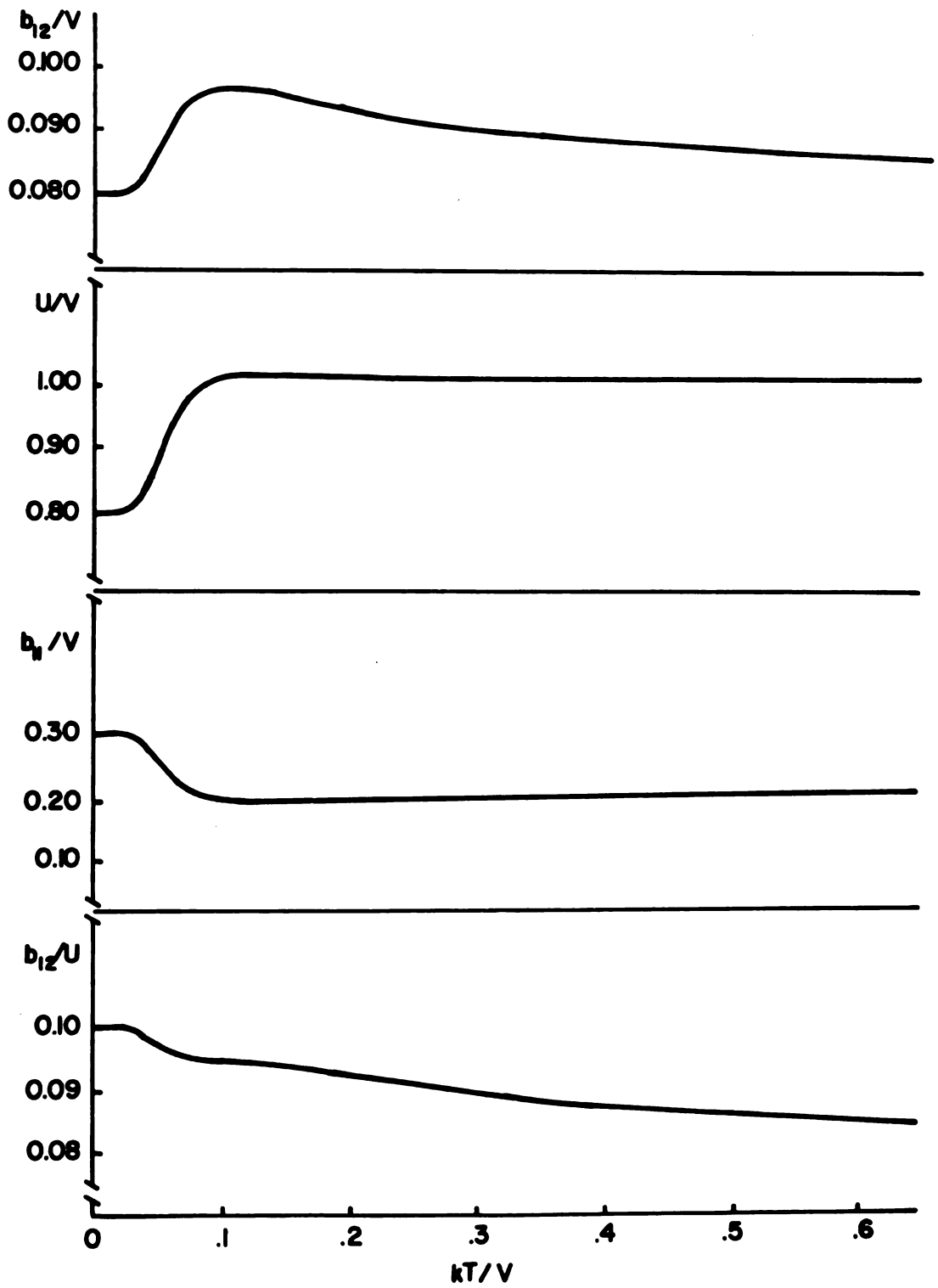
The variational procedure consists of calculating the trial free energy $F[\tilde{H}]$ (left side of (43)), carrying the traces over the eigenstates of the Hubbard Hamiltonian (exactly) and minimizing $F[\tilde{H}]$ as a function of b_{11}, b_{12}, U for given sets of h_{11}, V, V_{12}, v'_{12}, X_{12}, h_{12}, μ and T . Figure 1 shows the output of one of the calculations as function of the temperature. The input parameters were chosen to simulate a small overlap situation. The numerical calculation not only checked the analytical results but also showed how to connect between low and high-T results. Presumably, for a larger number of sites, the behavior is similar. We noticed that for smaller overlap the flatness of the low-T region extends to higher $kT/|K_{12}|$ (still $kT<<|t_{12}|$).

For very low temperatures the free energy is insensitive to a change in b_{11} , which agrees with our previous discussion

(sec. V.B.2). However, if we make the numerical calculation coming from higher temperatures to lower ones we notice that the best b_{11} tends toward a limiting value which is that required to give the same number of electrons for both Hamiltonians.

We concluded before that the minimal principle (43), in establishing the best trial Hamiltonian $\tilde{H}_H$ tries to match up the eigenfunctions and the low-lying splitting in both H and $\tilde{H}_H^{(b)}$. These conclusions were established for the low-T regime. Here these results have been confirmed numerically. In fact, examining Table 1, it is easy to see that, for small overlap, C (the coefficient which mixes doubly-occupied with singly-occupied states in the singlets) is the same for both H and $\tilde{H}_H^{(b)}$, with the results (134) and (135), namely $b_{12}/U = t_{12}/(V-v_{12})$; the eigenfunctions are then the same. It is even easier to see that the low-lying splittings are equal, in the small overlap regime; just compare (A1.11) with (A1.12), using (134) and (135).

Figure 1. The values of b_{12}, U and b_{11} for the "best" half-filled Hubbard Hamiltonian are shown as functionsof kT, in units of V. Also is shown the ratio b_{12}/U. The parameters in the exact Hamiltonian were, in units of V: $v_{12} = 0.2$, $h_{12} = 0.05$, $v'_{12} = 0.03$, (so $t_{12} = 0.08$), $h_{11} = X_{12} = 0$.


b_{12}/V
0.100
0.090
0.080
U/V
1.00
0.90
0.80
b_{11}/V
0.30
0.20
0.10
b_{12}/U
0.10
0.09
0.08
0
.1
.2
.3
.4
.5
.6
kT/V

C. Narrow Half-Filled Band; The "Best" Modified Hubbard Hamiltonian (With Potential Exchange)

As we showed in section V.B.2 our initial approach with the trial Hamiltonian being the Hubbard Hamiltonian is successful in one sense and a failure in other. It is successful in accomplishing Anderson's objective of defining a non-magnetic Hamiltonian which leads through the kinetic exchange to the correct exact low-lying exchange splittings. But it fails in the sense that it cannot give the correct physics of the exact Hamiltonian when the potential exchange exceeds the magnitude of the exact kinetic exchange, this suggesting that adding an effective potential exchange to our trial Hamiltonian might resolve this difficulty. We therefore propose studying the full (56) as our trial single band Hamiltonian. We have begun an investigation of this for the simple case of two sites.

C.1 Two Sites; Low-Temperature Limit

The Hamiltonian (56), which we now call $\tilde{H}_{HX}$ specialized to the two-site case is

$$\tilde{H}_{HX} = b_{11}(N_1 + N_2) + U(N_{1\uparrow}N_{1\downarrow} + N_{2\uparrow}N_{2\downarrow}) +$$

$$+ b_{12} \sum_{\sigma} (c^{+}_{1\sigma} c_{2\sigma} + c^{+}_{2\sigma} c_{1\sigma}) +$$

$$+ U_{12} \sum_{\sigma} (c^{+}_{1\sigma} c_{2\sigma} c^{+}_{2\bar{\sigma}} c_{1\bar{\sigma}} - N_{1\sigma}N_{2\sigma}) \qquad (140)$$

(still rather simpler than the corresponding "exact" Hamiltonian (138)). Its eigenstates are easily obtained from Table 1 by replacing V, h_{11}, h_{12}, X_{12} by U, b_{11}, b_{12} and U_{12} and setting $v_{12} = v'_{12} = 0$, except for the singlets which are shown separately in Table 2. This exception occurs because of the lack of terms $(c^{+}_{1\bar{\sigma}} c_{2\bar{\sigma}} c^{+}_{1\sigma} c_{2\sigma} +$ $c^{+}_{2\bar{\sigma}} c_{1\bar{\sigma}} c^{+}_{2\sigma} c_{1\sigma})$ in $\tilde{H}_{HX}$.

Again, we have to solve the stationarity equations (54), these for one more variational parameter taken as $U_{12} = U_{21} = U^{*}_{12}$. So far we have studied this problem in the low temperature region only, so it will be discussed only in this regime of temperature. If we make the restriction on the traces that we did for the previous low temperature calculation (for an arbitrary number of sites), namely taking the traces only over the eigenfunctions originating from G , we will not be able to determine variationally as before, the parameter b_{11}; further, we will not be able to find uniquely the other parameters because the inclusion of the effective potential parameter U_{12} destroys the independence of the stationarity equations. We then felt it was necessary to

extend the space in which the traces are to be calculated, to include the states for which $N = N_s \pm 1$ (originated from E). In other words, for this particular case of two sites, the traces are taken over the lowest singlet, the three triplets ($N = N_s = 2$) the four states for which $N = N_s - 1 = 1$ and the four states for which $N = N_s + 1 = 3$. The $\tilde{H}_{HX} - \mu N$ eigenvalues corresponding to these eight states lie above the ground level by roughly $U/2$.

In evaluating the traces in the stationarity equations we have expanded $\tilde{E}'^{\pm}$ (singlet eigenvalues of $\tilde{H}_{HX}$) in the following way:

$$\tilde{E}'^{-} = \frac{1}{2}\left[(U + U_{12}) - ((U - U_{12})^2 + 16\, b_{12}^2)^{\frac{1}{2}}\right] \cong U_{12} - \frac{4b_{12}^2}{U}$$

$$\tilde{E}'^{+} = \frac{1}{2}\left[(U + U_{12}) + ((U - U_{12})^2 + 16\, b_{12}^2)^{\frac{1}{2}}\right] = U + \frac{4b_{12}^2}{U} \quad . \tag{141}$$

The quantity U_{12}, as we pointed out before is expected to be second order in the overlap.

After a long but straightforward calculation we end up with the following form for the equations $\partial F[\tilde{H}_{HX}]/\partial\lambda$ where $\lambda = b_{11}$, U_{12}, U and b_{12}, respectively:

$$(2v_{12} - 2b_{11} + 2h_{11} + U_{12} - X_{12} - U + V)\cosh \beta b_{12} - 2v'_{12} \sinh \beta b_{12} = 0 \tag{142}$$

and

$$3e^{-2\beta\tilde{J}}\,L + 2\,e^{-\frac{1}{2}\beta\bar{U}}\Big\{e^{-2\beta\tilde{J}}\,[(2(U-V) + b_{11}-v_{12}-h_{11} + 3L +$$

$$+ U_{12} - X_{12})\quad \cosh \beta b_{12} - (3b_{12} - 3t_{12} - v'_{12}) \sinh \beta b_{12}]$$

$$+[(b_{11}-v_{12}-h_{12}+X_{12}-U_{12}) \cosh \beta b_{12}+(b_{12}-t_{12}+v'_{12}) \sinh \beta b_{12}]\Big\} = 0$$

(143)

and

$$e^{-2\beta\tilde{J}}\,\frac{3b_{12}^2}{U^2}\,L + e^{-2\beta\tilde{J}}(3 + e^{-2\beta\tilde{J}})\,\frac{kT}{U^2}\,b_{12}\,M +$$

$$+e^{-\frac{1}{2}\beta\bar{U}}\Big\{e^{-2\beta\tilde{J}}\,[(\frac{4b_{12}^2}{U^2}\,(U-V+U_{12}-X_{12}) - L(1-\frac{8b_{12}^2}{U^2}) +$$

$$+ (v_{12}-b_{11}+h_{11}-U+V) + \frac{kT}{U^2}\,8b_{12}\,M)\quad \cosh \beta b_{12} +$$

$$+\quad ((b_{12}-t_{12})(1 - \frac{8b_{12}^2}{U^2}) - v'_{12})\quad \sinh \beta b_{12}]\quad +$$

$$+3[(v_{12}-b_{11}-U+V)\quad \cosh \beta b_{12} + (b_{12}-t_{12}-v'_{12})\quad \sinh \beta b_{12}]\Big\} = 0$$

(144)

and

$$e^{-2\beta\tilde{J}}\,\frac{6b_{12}^2}{U}\;L + e^{-2\beta\tilde{J}}\,(3 + e^{-2\beta\tilde{J}})\,\frac{2kT}{U}\,M \;+$$

$$+e^{-\frac{1}{2}\beta\bar{U}}\;\Big\{e^{-2\beta\tilde{J}}\Big[-\,(2(b_{12}-t_{12}) + \frac{8kT}{U}\,M + \frac{8b_{12}}{U}\,(U-V+U_{12}-X_{12})$$

$$+\;\frac{16b_{12}}{U}\,L)\;\cosh\beta b_{12} + (16\,\frac{b_{12}}{U}(b_{12}-t_{12})+(U-V+U_{12}-X_{12}))\sinh\beta b_{12}\Big]$$

$$+3[-2(b_{12}-t_{12})\cosh\beta b_{12} + (U-V+U_{12}-X_{12})\sinh\beta b_{12}]\Big\} \;= 0\,, \qquad (145)$$

where we have defined

$$\bar{U} \equiv U + U_{12} \qquad (146)$$

$$L \equiv \frac{4b_{12}}{U}[b_{12}-2t_{12}+\frac{b_{12}}{U}(V-v_{12})]-2(U_{12}-X_{12}) \qquad (147)$$

$$M \equiv \frac{b_{12}}{U}\,(V-v_{12}) - t_{12} \qquad (148)$$

$$\tilde{J} \equiv \frac{2b_{12}^2}{U} + U_{12} \qquad (149)$$

In the above equations we have replaced $b_{11} - \mu$ by $(-U + U_{12})/2$ which fixes the number of electrons in the system equal to two.

In this regime $kT << |b_{12}|$; then we replace $\sinh \beta b_{12}$ by $s \cosh \beta b_{12}$, where s is the sign of b_{12}. The percentage error made with this replacement is of the order

of $\exp -2\beta|b_{12}|$ which gets drastically smaller when kT gets lower and lower. With this replacement we obtain from (142) an expression for $U_{12} - X_{12}$ in terms of the other quantities appearing there. We found it convenient to insert that expression into (143) - (145) wherever $U_{12} - X_{12}$ appears explicitly. Then keeping, inside the curly bracket, terms which are zero and first order in the overlap we see that the system of equations (142) - (145) reduces to a much simpler one

$$U-V + b_{11}-h_{11}-v_{12} - s(b_{12}-t_{12}-v'_{12}) = 0 \tag{150}$$

$$\frac{2b_{12}}{U}\left[b_{12} - 2t_{12} + \frac{b_{12}}{U}(V-v_{12})\right] - U_{12} + X_{12} = 0 \tag{151}$$

$$\frac{b_{12}}{U}(V-v_{12}) = t_{12} \tag{152}$$

$$2v_{12} - 2b_{11} + 2h_{11} - U + V - 2sv'_{12} + U_{12} - X_{12} = 0 \,. \tag{153}$$

It is convenient to note that Eq. (152) implies that b_{12} has the same sign as t_{12} (since $U>0$) .

Solving then the above system of equations we get

$$U = V + \frac{2v_{12}}{V-v_{12}}|t_{12}| - \frac{v_{12}}{V-v_{12}}K_{12} \tag{154}$$

$$b_{12} = \frac{V}{V-v_{12}}t_{12} - s\frac{v_{12}}{V-v_{12}}K_{12} \tag{155}$$

$$U_{12} = X_{12} - \frac{v_{12}}{V-v_{12}} K_{12} \tag{156}$$

$$b_{11} = h_{11} + v_{12} - s\, v'_{12} - \frac{v_{12}}{V-v_{12}} |t_{12}| \tag{157}$$

to second order. These results hold for any ratio $X_{12}/|K_{12}|$.

Because of the complexity of the equations (142) - (145), we have not been able to estimate analytically the order of magnitude of the error made in determining the best parameters. Presumably it is smaller than second order in the overlap. We made a numerical calculation which agrees with the values found above. Although for each best parameter the leading order would be satisfactory, we have to know them up to second order in overlap, in order to solve for U_{12} (which is essentially second order in the overlap). See for instance, equation (142) or (153). We note the consistency of our original assumptions, U, b_{11}, b_{12}, U_{12} are respectively zeroeth, zeroeth, first and second order.

With the results (154) - (157), it can be seen that the wavefunctions of the exact and trial Hamiltonians have again been matched (compare C and $\tilde{C}'$ in Tables 1 and 2, respectively, in the limit of small overlap). Also the low-lying splittings have been made identical to second order in overlap; in other words, the Heisenberg exchange $\tilde{J}_{HX}$ appropriate to $\tilde{H}_{HX}$ is equal to J_H appropriate to H

$$\tilde{J}_{HX} = -2b_{12}^2/U + U_{12} = K_{12} + X_{12} = J_H \tag{158}$$

To check it see (A1.13), (A1.11) and (154) - (157).

The chemical potential necessary to fix the number of electrons in the best $\tilde{H}_{HX}$ equal to two is, according to (A1.10), equal to

$$\mu = h_{11} + \frac{V}{2} + v_{12} - \frac{X_{12}}{2} - sv'_{12} \quad . \tag{159}$$

In Appendix A1 we calculate the chemical potential to make the exact Hamiltonian H have two electrons; and for

$$kT << ||t_{12}| - |v'_{12}|| \ , \ |t_{12}| > |v'_{12}| \tag{160}$$

the expression (159) above is the correct one to second order. For the other situation, namely

$$kT << ||t_{12}| - |v'_{12}|| \ , \ |t_{12}| < |v'_{12}| \tag{161}$$

the exact chemical potential is not the same as in (159), differing from that in terms which are first order in the overlap. The former case where $|t_{12}| > |v'_{12}|$ is the more realistic one at least for the hydrogen molecule.

Also for the conditions (160), the separation in $E - \mu N$ between the ground state of the system (a singlet) and the lowest of the $(N_s \pm 1)$ levels has been matched perfectly (to second order): This separation δ_{HX} for $\tilde{H}_{HX}^{(b)}$ is $\frac{U}{2} - \frac{3}{2} U_{12} - |b_{12}| + \frac{4b_{12}^2}{U}$ as seen from the

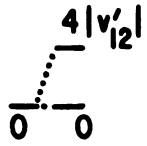
right hand column of Table 1; the corresponding separation for H, under the condition (160) is $\delta = \frac{V}{2} - \frac{3}{2} X_{12} - |t_{12}| + \frac{4t_{12}^2}{V-v_{12}}$. From (154) - (157) it can be seen that to second order,

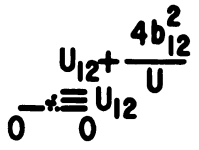
$$\delta_{HX} = \delta \quad . \tag{162}$$

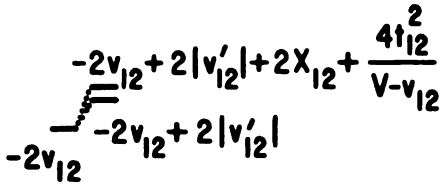
It is interesting to notice that the lowest of the $(N_s \pm 1)$ levels is made up of bonding states, for $t_{12} < 0$, or antibonding states, for $t_{12} > 0$; since the sign of b_{12} is the same of t_{12}, correspondly the same happens with the Hamiltonian $\tilde{H}_{HX}^{(b)}$. Now with (161) the degeneracy of this level is between bonding states for $(N_s \pm 1)$ and antibonding for $(N_s \mp 1)$, depending on the sign of v'_{12} and t_{12}; whereas in the $\tilde{H}_{HX}^{(b)}$ the situation is the same as above (there being no degeneracy between bonding and antibonding states). This would appear to be a reason why the results are better for (160) than for (161).

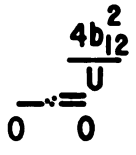
But in any case the leading term in the expression for the best U (namely $U = V$) matches the position of the $(N_s \pm 1)$ levels with respect to the ground state, to zero order in overlap. Further, the position of the highest levels, namely those with N_s and $(N_s \pm 2)$particles (all of which are degenerate for $\tilde{H}_{HX}-\mu N$) matches the average position of the respective levels in the exact model. See Figure 2 to clarify these points.

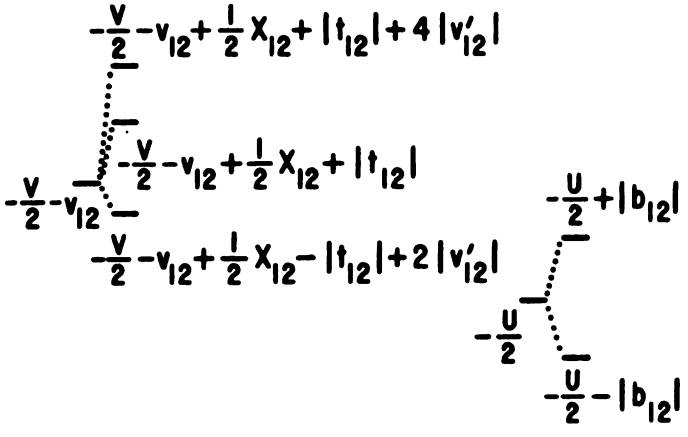
Figure 2. The eigenvalues of i) $H - \mu N$, ii) $\tilde{H}_H - \mu N$ and iii) $\tilde{H}_{HX} - \mu N$ in the zero and small overlap limits for the half-filled-band grand canonical ensemble. In case i) it is assumed that $t_{12} < 0$, $v'_{12} < 0$ and $|t_{12}| > |v'_{12}|$ and $kT << ||t_{12}| - |v'_{12}||$. The levels in ii) and iii) were drawn roughly as in the best $\tilde{H}_H$ and $\tilde{H}_{HX}$.

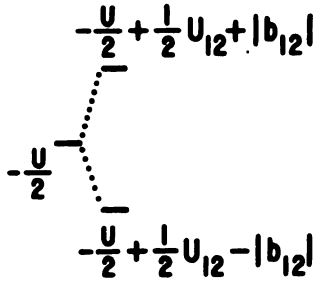

$4|v'_{12}|$
0
0

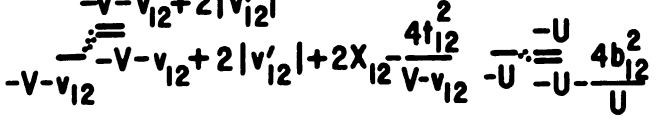

$U_{12}+\frac{4b_{12}^2}{U}$
U_{12}
0
0

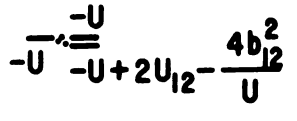

$-2v_{12}+2|v'_{12}|+2X_{12}+\frac{4t_{12}^2}{V-v_{12}}$
$-2v_{12}+2|v'_{12}|$
$-2v_{12}$


$\frac{4b_{12}^2}{U}$
0
0


$-\frac{V}{2}-v_{12}+\frac{1}{2}X_{12}+|t_{12}|+4|v'_{12}|$
$-\frac{V}{2}-v_{12}+\frac{1}{2}X_{12}+|t_{12}|$
$-\frac{V}{2}-v_{12}$
$-\frac{V}{2}-v_{12}+\frac{1}{2}X_{12}-|t_{12}|+2|v'_{12}|$
$-\frac{U}{2}+|b_{12}|$
$-\frac{U}{2}$
$-\frac{U}{2}-|b_{12}|$


$-\frac{U}{2}+\frac{1}{2}U_{12}+|b_{12}|$
$-\frac{U}{2}$
$-\frac{U}{2}+\frac{1}{2}U_{12}-|b_{12}|$


$-V-v_{12}+2|v'_{12}|$
$-V-v_{12}$
$-V-v_{12}+2|v'_{12}|+2X_{12}-\frac{4t_{12}^2}{V-v_{12}}$
$-U$
$-U-\frac{4b_{12}^2}{U}$


$-U$
$-U$
$-U+2U_{12}-\frac{4b_{12}^2}{U}$

C.2 Effective One-Electron Potential

It is interesting to try to find an effective one-electron potential W(r) such that

$$\langle w_i | K + W | w_j \rangle = b_{ij} \tag{163}$$

where $K \equiv p^2/2m$ is the kinetic energy operator. The most interesting case is in connection with our best Hamiltonian $\tilde{H}_{HX}$ containing the effective potential exchange. Since we have so far found this Hamiltonian only for two sites our discussion here will be only on the effective potential for this case.

The diagonal element of (163) namely $b_{11}=h_{11} + v_{1212}$, to the leading order in the overlap can be reproduced if one uses for W the Wigner-Seitz potential W_{ws}. This is defined as the potential "seen" by an electron in a Wigner-Seitz cell. For two sites, the Wigner-Seitz cell associated with an ion is the half-space from the mid-point of the site axis, including that ion. In this case, W_{ws} is the potential due to the singly positive ion in the cell that the electron finds itself, plus the potential due to the other atom. We can write then that

$$\langle w_i | W_{ws} | w_k \rangle = \sum_j \int_{\text{cell } j} d^3r \; w_i(\underline{r}) \left[-\frac{e^2}{|\underline{r}-\underline{R}_j|} + e^2 \sum_{\ell \neq j} \left(\int \frac{w_\ell^2(\underline{r}')\, d^3r'}{|\underline{r}'-\underline{r}|} - \frac{1}{|\underline{r}-\underline{R}_\ell|} \right) \right] w_k(\underline{r}) \quad . \tag{164}$$

With (164), the diagonal element of (163) is

$$\langle w_1|K + W_{ws}|w_1\rangle = \int_{\text{all space}} d^3r\, w_1(\underline{r})\left(K - \frac{e^2}{|\underline{r}-\underline{R}_1|} - \frac{e^2}{|\underline{r}-\underline{R}_2|}\right)w_1(\underline{r})$$

$$+ \int_{\text{cell 1}} d^3r\, w_1^2(\underline{r}) \int_{\text{all space}} \frac{w_2^2(\underline{r}')d^3r'}{|\underline{r}-\underline{r}'|} \qquad (165)$$

$$+ \int_{\text{cell 2}} d^3r\, w_1^2(\underline{r}) \int_{\text{all space}} d^3r' \frac{w_1^2(\underline{r}')}{|\underline{r}-\underline{r}'|}$$

which to zero-order in the overlap becomes

$$\langle w_1|K - \frac{e^2}{|\underline{r}-\underline{R}_1|} - \frac{e^2}{|\underline{r}-\underline{R}_2|}|w_1\rangle + \int d^3r \int d^3r' \frac{w_1^2(\underline{r})w_2^2(\underline{r}')}{|\underline{r}-\underline{r}'|} =$$

$$= h_{11} + v_{1212} = b_{11} \quad . \qquad (166)$$

If the Wigner-Seitz potential is used to calculate the off-diagonal element of (163) it does not reproduce our best b_{12} given by (155):

$$\langle w_1|K + W_{ws}|w_2\rangle = K_{12} + \theta_{12} \qquad (167)$$

where

$$K_{12} \equiv \langle w_1|K|w_2\rangle \qquad (168)$$

and

$$\theta_{12} \equiv \langle w_1 | W_{ws} | w_2 \rangle =$$

$$= - \int_{\text{cell 1}} d^3r\, w_1(\underline{r}) w_2(\underline{r}) \frac{e^2}{|\underline{r}-\underline{R}_1|} - \int_{\text{cell 2}} d^3r\, w_1(\underline{r}) w_2(\underline{r}) \frac{e^2}{|\underline{r}-\underline{R}_2|}$$

$$- \int_{\text{cell 1}} d^3r\, w_1(\underline{r}) w_2(\underline{r}) \left[\frac{e^2}{|\underline{r}-\underline{R}_2|} - e^2 \int_{\text{all space}} d^3r' \frac{w_2^2(\underline{r}')}{|\underline{r}-\underline{r}'|}\right.$$

$$\left. - \int_{\text{cell 2}} d^3r\, w_1(\underline{r}) w_2(\underline{r}) \left[\frac{e^2}{|\underline{r}-\underline{R}_1|} - e^2 \int_{\text{all space}} \frac{w_1^2(\underline{r}') d^3r'}{|\underline{r}-\underline{r}'|}\right]\right. \quad (169)$$

which to the lowest order in overlap is

$$\theta_{12} = - \int_{\text{cell 1}} d^3r\, w_1(\underline{r}) w_2(\underline{r}) \frac{e^2}{|\underline{r}-\underline{R}_1|} - \int_{\text{cell 2}} d^3r\, w_1(\underline{r}) w_2(\underline{r}) \frac{e^2}{|\underline{r}-\underline{R}_2|}. \quad (170)$$

Our best transfer integral b_{12}, to lowest order in the overlap, is

$$b_{12} = \frac{V}{V-v_{12}} \; t_{12} = \frac{V}{V-v_{12}} \{K_{12} - \langle w_1 | \frac{e^2}{|r-R_1|} | w_2 \rangle\}$$

$$= K_{12} + \gamma_{12} \quad (171)$$

where

$$\gamma_{12} = \frac{1}{V-v_{12}} \{v_{12} K_{12} - V \langle w_1 | \frac{e^2}{|\underline{r}-\underline{R}_1|} | w_2 \rangle\} \quad (172)$$

So the difference between (167) and (171) is $\theta_{12}-\gamma_{12}$ which is equal to

$$\langle w_1|W_{ws} - W|w_2\rangle = \frac{v_{12}}{V-v_{12}} \left[2 \int_{\text{cell 1}} w_1(\underline{r})w_2(\underline{r})\frac{e^2}{|\underline{r}-\underline{R}_1|} d^3r - K_{12}\right]$$

$$+ \frac{V}{V-v_{12}} \left[\int_{\text{cell 2}} w_1(\underline{r})w_2(\underline{r}) \frac{e^2}{|\underline{r}-\underline{R}_1|} d^3r\right.$$

$$\left. - \int_{\text{cell 2}} w_1(\underline{r})w_2(\underline{r}) \frac{e^2 d^3r}{|\underline{r}-\underline{R}_2|}\right]$$

which does not appear to be zero in general. In fact it seems to be of first order in the overlap, and therefore it is not expected to be negligible, although we have not made a numerical estimate.

That an improvement over the Wigner-Seitz potential is needed can be seen intuitively when one realizes that for small overlap most of the hopping integral comes from the region where the electron position $\underline{r}$ is in between the ions. For the WS potential, the "other" electron discontinuously jumps from one ion to the other as the electron of interest (at $\underline{r}$) crosses the midpoint (which seems unreasonable). The quantity t_{12} is easily seen from eq. (31) to be the matrix element between w_1 and w_2 of K and the potential due to the nuclei plus one electron distributed equally over the two ions (in w_1^2 and w_2^2), a much more reasonable picture. However, the factor

$V/(V - v_{12})$ increases the difficulty of finding explicitly the corresponding potential W (which we have not been able to do), this W appearing to be a complicated one and a function of the kinetic energy.

VI. SUMMARY AND DISCUSSION

A new approach to the problem of narrow-band magnetic semiconductors has been presented and investigated in the context of the half-filled single band problem. The approach consists of using the minimal principle of statistical mechanics for the free energy, to find a "best" Hamiltonian $\tilde{H}$, containing one-electron terms as well as certain important two-electron terms, but much simpler than the exact Hamiltonian. It is important to realize that if $\tilde{H}$ consisted of only a one-electron term, the thermal Hartree-Fock approximation would have been obtained from the variational principle, as the best one-electron Hamiltonian, which has been proved to have its failures for the narrow-band problem.

It has been recognized that one-electron approximations are definitely bad and that two-electron Coulomb interactions are very important for narrow-band electrons. Hubbard and Anderson, working not inconsistently with this view, presented theories in which one-electron-approximation terms (Hartree-Fock) are to be used in combination with

important two-electron terms, to make physical predictions. Although on the right track, their theories were shown to be unsatisfactory (sections II and III), essentially because they made a one-electron approximation first and then combined the resulting one-electron term with two-electron terms. Instead, we find the variationally best Hamiltonian $\tilde{H}$ with both types of terms: the best one-electron term is found simultaneously with the best two-electron terms. The investigations discussed in this paper in the context of the single-band model showed that our approach overcomes the difficulties cited in the previous theories.

In particular we studied two cases. In one, the trial Hamiltonian was taken to be of the form of the Hubbard Hamiltonian, and in the other, effective potential exchange terms were added to it. In the first case the low-T results matched the low-lying exchange splittings appropriate to both trial and exact Hamiltonians despite of the lack of potential exchange terms in $\tilde{H}$. Hence we accomplished Anderson's objective (not attained by him) of defining a non-magnetic one-electron Hamiltonian, whose transfer integral leads via the kinetic exchange to the exact low-lying splittings to leading order in the bandwidth. However this first approach fails to give a physically acceptable approximation to the properties of the exact Hamiltonian when the potential exchange dominates the

kinetic exchange. In the second case, explored so far in the simple case of two sites, the same matching of low-lying splittings is obtained, but for any ratio of potential exchange to kinetic exchange, which certainly is an important improvement over the first trial Hamiltonian. Further, the centers of gravity of the $(N_s \pm 1)$ - electron levels are matched to zero order in overlap[51]. (The first trial Hamiltonian erred in zero order for those levels).[52]

As far as the near future of the exploration of this new approach is concerned we have at least three immediate problems to consider. The first is the generalization of the results of the best Hubbard Hamiltonian augmented by the potential exchange, to an arbitrary number of sites. The second is connected with the problem of superexchange, where one has closed-shell ions and non-closed-shell ions (MnO, for example). Here we hope to find that the appropriate set of Wannier functions (the best in our procedure) will achieve the rapid convergence of the perturbation theory originally desired by Anderson. The third has to do with adding higher cation bands; our approach applied to a model containing such bands should enable one to take into account the quantitatively important "electron rearrangement" effect[35], as it modifies the one as well as the two-electron parameters.

Finally, we would like to point out that a rather remarkable suggestion concerning the broad-band or high-density limit results from our narrow-band considerations. As is known[10], the restricted HF approximation for the electron gas leads to the incorrect result that the density of states is zero at the Fermi energy, and the source of this error is the long range of the Coulomb interaction via the exchange integral. Thus it would seem that the addition in $\tilde{H}$, of a short range interaction (like the Hubbard intra atomic term) to the one-electron operator would not be able to overcome this fundamental difficulty. However, this view may be quite incorrect. We essentially saw (Sec. II) that the restricted HF approximation led to a hopping integral b_{ij} that behaved very badly in the narrow-band region, the source of the error again being the long range of the Coulomb interaction via the exchange contribution to the HF eigenvalues. But, as we saw, the addition in $\tilde{H}$ of the Hubbard intra atomic interaction was quite sufficient to overcome the difficulty found in the narrow band region. Thus the possibility that it might similarly overcome the difficulty in the region of large ratio of bandwidth to intra atomic interaction no longer appears to be an unlikely one. It is under investigation.

APPENDICES

APPENDIX A1

TWO-SITE SINGLE-BAND MODELS

The exact single-band Hamiltonian specialized for the two sites case is

$$H = h_{11}(N_1+N_2) + V(N_{1\uparrow}N_{1\downarrow} + N_{2\uparrow}N_{2\downarrow}) + v_{12}\,N_1N_2 +$$

$$+ \sum_{\sigma} [h_{12} + v'_{12}\,(N_{1\bar{\sigma}}+N_{2\bar{\sigma}})](c^{+}_{1\sigma}c_{2\sigma} + c^{+}_{2\sigma}c_{1\sigma}) +$$

$$+ X_{12} \sum_{\sigma} [\tfrac{1}{2}(c^{+}_{1\bar{\sigma}}c_{2\bar{\sigma}} + c^{+}_{2\bar{\sigma}}c_{1\bar{\sigma}})(c^{+}_{1\sigma}c_{2\sigma} + c^{+}_{2\sigma}c_{1\sigma}) - N_{1\sigma}N_{2\sigma}] \qquad \text{(A1.1)}$$

where

$$\begin{aligned} v_{12} &\equiv v_{1212} \\ v'_{12} &\equiv v_{1121} \\ X_{12} &\equiv v_{1221} \end{aligned} \qquad \text{(A1.2)}$$

This Hamiltonian can be straightforwardly diagonalized, the eigenfunctions and the eigenvalues being shown in Table 1. There we also display the H - μN eigenvalues for the special case of <N> = two electrons (in average) in the system. The chemical potential which fixes the number of electrons equal to two is determined by the equation:

$$\mathrm{tr}\; e^{-\beta(H-\mu N)}(N-2) = 0 \qquad \text{(A1.3)}$$

or

$$1 + e^{\frac{1}{2}\beta(V+2v_{12}-X_{12})} \left\{ [e^{\beta(t_{12}-v'_{12})} + e^{-\beta(t_{12}-v'_{12})}]\, e^{\beta\alpha} - \right.$$

$$\left. - [e^{\beta(t_{12}+v'_{12})} + e^{-\beta(t_{12}+v'_{12})}]\, e^{3\beta\alpha} \right\} - e^{4\beta\alpha} = 0 \qquad \text{(A1.4)}$$

where we have put

$$\mu = h_{11} + \frac{V}{2} + v_{12} - \frac{X_{12}}{2} + \alpha \qquad \text{(A1.5)}$$

and α is now to be determined. The solutions for some special interesting cases can be immediately found:

1) $kT >> |t_{12}| + |v'_{12}|$ $\qquad \alpha = 0$ $\qquad$ (A1.6)

2) $kT << ||t_{12}| - |v'_{12}||$

$$\begin{cases} |t_{12}| > |v'_{12}| & \alpha = -sv'_{12} \\ |t_{12}| < |v'_{12}| & \alpha = -s't_{12} \end{cases} \qquad \text{(A1.7)}$$

where s and s' are the signs of t_{12} and v'_{12}, respectively; in other words $t_{12} = s|t_{12}|$ and $v'_{12} = s'|v'_{12}|$.

The other model considered in this paper is the Hubbard Hamiltonian whose eigenstates can easily be drawn from the Table 1 just by replacing V, h_{11}, h_{12} respectively by U, b_{11}, b_{12} and setting $v_{12} = v'_{12} = X_{12} = 0$. The chemical potential that fixes the number of electrons equal to two is easily found to be

$$\mu = b_{11} + \frac{U}{2} \qquad \text{(A1.8)}$$

for all temperatures.

Another model Hamiltonian of interest, used in section V.C is

$$\tilde{H}_{HX} = b_{11}(N_1+N_2) + U(N_{1\uparrow}N_{1\downarrow} + N_{2\uparrow}N_{2\downarrow}) +$$

$$+ b_{12} \sum_{\sigma} (c^{+}_{1\sigma}c_{2\sigma}+c^{+}_{2\sigma}c_{1\sigma}) + U_{12} \sum_{\sigma} (c^{+}_{1\sigma}c_{2\sigma}c^{+}_{2\bar{\sigma}}c_{1\bar{\sigma}} - N_{1\sigma}N_{2\sigma}) \qquad \text{(A1.9)}$$

Its eigenstates can also be obtained from Table 1 by making the appropriate replacements, except for the singlets, which are listed separately in Table 2.

The chemical potential to fix the number of electrons equal to two is

$$\mu = b_{11} + \frac{U}{2} - \frac{U_{12}}{2} \qquad \text{(A1.10)}$$

The low-lying singlet-triplet splitting is listed below for the three two-site Hamiltonian models considered in the text; in each case we first show the splitting calculated exactly and next the approximation for small overlap:
For H, this splitting is $(E_{triplet} - E_{singlet})$

$$v_{12} - 2X_{12} - \frac{1}{2}\left[(V+v_{12}) - ((V-v_{12})^2 + 16\, t_{12}^2)^{\frac{1}{2}}\right] \cong \frac{4t_{12}^2}{V-v_{12}} - 2X_{12} \qquad \text{(A1.11)}$$

while for $\tilde{H}_H$

$$-\frac{1}{2}\,[U - (U^2 + 16\, b_{12}^2)^{\frac{1}{2}}] \cong \frac{4b_{12}^2}{U} \quad ; \tag{A1.12}$$

finally for $\tilde{H}_{HX}$, the splitting is

$$-U_{12} - \frac{1}{2}[(U+U_{12}) - ((U-U_{12})^2 + 16\, b_{12}^2)^{\frac{1}{2}}] \cong \frac{4b_{12}^2}{U} - 2\,U_{12}\,. \tag{A1.13}$$

Table 1. Listed are the eigenstates of the exact Hamiltonian H, (138), and E - μN for half-filled band condition; α is a function of temperature and other parameters in H (See Appendix A1.). Here,

$E^{\pm} = (1/2)\ [(V+v_{12}) \pm ((V-v_{12})^2 + 16t_{12}^2)^{\frac{1}{2}}]$,

$C = (v_{12} - E^{-})/2t_{12}$, $A = (1 + C^2)^{-\frac{1}{2}}$,

$t_{12} = h_{12} + v'_{12}$, $\xi = -\frac{1}{2} V - v_{12} + \frac{1}{2} X_{12}$,

$\eta = 3h_{11} + V + 2v_{12} - X_{12}$, $|a_1\rangle = (c^+_{1\uparrow}c^+_{2\downarrow} + c^+_{2\uparrow}c^+_{1\downarrow})|0\rangle$, $|a_2\rangle = (c^+_{1\uparrow}c^+_{1\downarrow} + c^+_{2\uparrow}c^+_{2\downarrow})|0\rangle$,

N	$\|\rangle$	$H\|\rangle = E\|\rangle$	$E - \mu N$
0	$\|0,0\rangle = \|0\rangle$	0	0
1	$\|1^-,\uparrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\uparrow}-c^+_{2\uparrow})\|0\rangle$ $\|1^-,\downarrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\downarrow}-c^+_{2\downarrow})\|0\rangle$	$h_{11}-t_{12}+v'_{12}$	$\xi-t_{12}+v'_{12}-\alpha$
	$\|1^+,\uparrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\uparrow}+c^+_{2\uparrow})\|0\rangle$ $\|1^+,\downarrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\downarrow}+c^+_{2\downarrow})\|0\rangle$	$h_{11}+t_{12}-v'_{12}$	$\xi+t_{12}-v'_{12}-\alpha$
2	$\|2^-,0\rangle = A[\|a_1\rangle - C\|a_2\rangle]$	$2h_{11}+X_{12}+E^-$	$-V-2v_{12}+2X_{12}+E^--2\alpha$
	$\|2^+,0\rangle = A[\|a_1\rangle + C\|a_2\rangle]$	$2h_{11}+X_{12}+E^+$	$-V-2v_{12}+2X_{12}+E^+-2\alpha$
	$\|2,0\rangle = 2^{-\frac{1}{2}}(c^+_{1\uparrow}c^+_{1\downarrow}-c^+_{2\uparrow}c^+_{2\downarrow})\|0\rangle$	$2h_{11}+V-X_{12}$	$-2v_{12}-2\alpha$
	$\|2,\uparrow\uparrow\rangle = c^+_{1\uparrow}c^+_{2\uparrow}\|0\rangle$		
	$\|2,\downarrow\downarrow\rangle = c^+_{1\downarrow}c^+_{2\downarrow}\|0\rangle$	$2h_{11}+v_{12}-X_{12}$	$-V-v_{12}-2\alpha$
	$\|2,\uparrow\downarrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\uparrow}c^+_{2\downarrow}-c^+_{2\uparrow}c^+_{1\downarrow})\|0\rangle$		
3	$\|3^-,\uparrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\uparrow}-c^+_{2\uparrow})c^+_{1\downarrow}c^+_{2\downarrow}\|0\rangle$ $\|3^-,\downarrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\downarrow}-c^+_{2\downarrow})c^+_{1\uparrow}c^+_{2\uparrow}\|0\rangle$	$\eta-t_{12}-v'_{12}$	$\xi-t_{12}-v'_{12}-3\alpha$
	$\|3^+,\uparrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\uparrow}+c^+_{2\uparrow})c^+_{1\downarrow}c^+_{2\downarrow}\|0\rangle$ $\|3^+,\downarrow\rangle = 2^{-\frac{1}{2}}(c^+_{1\downarrow}+c^+_{2\downarrow})c^+_{1\uparrow}c^+_{2\uparrow}\|0\rangle$	$\eta+t_{12}+v'_{12}$	$\xi+t_{12}+v'_{12}-3\alpha$
4	$\|4,0\rangle = c^+_{1\uparrow}c^+_{1\downarrow}c^+_{2\uparrow}c^+_{2\downarrow}\|0\rangle$	$4h_{11}+2V+4v_{12}-2X_{12}$	-4α

Table 1

Table 2. The singlet eigenstates of H_{HX}. Here $\tilde{E}'^{\pm} = (1/2)[(U + U_{12}) \pm ((U - U_{12})^2 + 16b_{12}^2)^{\frac{1}{2}}]$, $\tilde{C}' = (U_{12} - \tilde{E}'^{-})/2b_{12}$ and $\tilde{A}' = (1 + C'^2)^{-\frac{1}{2}}$.

Singlet Eigenfunctions	$\tilde{H}_{HX}\|> = \tilde{E}'\|>$
$\tilde{A}'[(c^+_{1\uparrow}c^+_{2\downarrow} + c^+_{2\uparrow}c^+_{1\downarrow}) - \tilde{C}'(c^+_{1\uparrow}c^+_{1\downarrow} + c^+_{2\uparrow}c^+_{2\downarrow})]\|0>$	$2b_{11} + \tilde{E}'^-$
$\tilde{A}'[(c^+_{1\uparrow}c^+_{2\downarrow} + c^+_{2\uparrow}c^+_{1\downarrow}) + \tilde{C}'(c^+_{1\uparrow}c^+_{1\downarrow} + c^+_{2\uparrow}c^+_{2\downarrow})]\|0>$	$2b_{11} + \tilde{E}'^+$
$2^{-\frac{1}{2}}(c^+_{1\uparrow}c^+_{1\downarrow} - c^+_{2\uparrow}c^+_{2\downarrow})\|0>$	$2b_{11} + U$

Table 2

APPENDIX A2

NATURAL CONDITIONS FOR A UNIQUE CHOICE OF WANNIER FUNCTIONS IN THE CASE OF SINGLE BANDS.

The Bloch functions, in terms of the atomic functions $a(\underline{r}-\underline{R}_n)$ are as follows:

$$\Psi_{\underline{k}}(\underline{r}) = (N_s \Gamma_{\underline{k}})^{-\frac{1}{2}} \sum_n e^{i\underline{k}\cdot\underline{R}_n} a(\underline{r}-\underline{R}_n) \tag{A2.1}$$

where

$$\Gamma_{\underline{k}} \equiv \sum_m e^{i\underline{k}\cdot\underline{R}_m} \Delta(m)$$

$$\Delta(n) \equiv \int a(\underline{r})\, a(\underline{r}-\underline{R}_n)\, d^3r = \Delta(-n) \; . \tag{A2.2}$$

We have assumed $a(\underline{r}) = a^*(\underline{r}) = a(|\underline{r}|)$.

Let S be a unitary symmetry operation of the crystal such that $S\underline{R}_i = \underline{R}_i$, ; then one can show with (56-a) and (A2.1) that

$$Sw_{\underline{R}_i}(\underline{r}) = N_s^{-\frac{1}{2}} \sum_k e^{-i\underline{k}\cdot\underline{R}_i + i\gamma_{\underline{k}}} \Psi_{s\underline{k}}(\underline{r})$$

$$= N_s^{-\frac{1}{2}} \sum_{\underline{k}} e^{-i\underline{k}\cdot S\underline{R}_i + i\gamma_{s^{-1}\underline{k}}} \Psi_{\underline{k}}(\underline{r}) \tag{A2.3}$$

In particular let S be inversion through an origin at the lattice point: in which case $S\underline{R}_i = \underline{R}_i = 0$ and $\gamma_{s^{-1}\underline{k}} = \gamma_{-\underline{k}}$.

And further, demand that $w_{\underline{R}_i}(\underline{r})$ be invariant under S (as the atomic function):

$$Sw_{\underline{R}_i}(\underline{r}) = w_{\underline{R}_i}(\underline{r}) \ .$$

This requires

$$\gamma_{-\underline{k}} - \gamma_{\underline{k}} = 2\, n_{\underline{k}}\pi \tag{A2.4}$$

where $n_{\underline{k}}$ is an integer.

If we demand the Wannier functions to be also real, as are the atomic functions, we must have

$$\gamma_{-\underline{k}} + \gamma_{\underline{k}} = 2m_{\underline{k}}\pi \tag{A2.5}$$

where $m_{\underline{k}}$ is an integer.

From (A2.4) and (A2.5) it follows that

$$\gamma_{\underline{k}} = \ell_{\underline{k}}\pi \tag{A2.6}$$

with $\ell_{\underline{k}}$ being another integer. However, demanding that the Wannier functions go to the atomic functions as the overlap, (A2.2) for $n \neq 0$, goes to zero we finally get:

$$\gamma_{\underline{k}} = \text{constant} .$$

APPENDIX A3

SOLUTIONS OF EQUATIONS (60) and (61)

Because of (63) and (64), the thermal averages in equations (60) and (61) are very simple to evaluate. For instance, $\sum_j \langle N_i N_{j\uparrow} N_{j\downarrow} \rangle$ can be written as

$$\sum_j \mathrm{tr}\, \tilde{\rho}_o\, N_i N_{j\uparrow} N_{j\downarrow} = 2\, \mathrm{tr}\, \tilde{\rho}_o\, N_{i\uparrow} N_{i\downarrow} + \mathrm{tr}\, \tilde{\rho}_o\, N_i N_{j\uparrow} N_{j\downarrow} =$$

$$= 2\tilde{g} + (\mathrm{tr}\, \tilde{\rho}_i N_i) \sum_{j \neq i} \mathrm{tr}\, \tilde{\rho}_j N_{j\uparrow} N_{j\downarrow}$$

$$= 2\tilde{g} + \tilde{n}(N-1)\, \tilde{g} \qquad \text{(A3.1)}$$

where

$$\tilde{g} = \mathrm{tr}\, \tilde{\rho}_o\, N_{i\uparrow}\, N_{i\downarrow} = \mathrm{tr}\, \tilde{\rho}_i\, N_{i\uparrow}\, N_{i\downarrow} \qquad \text{(A3.2)}$$

and

$$\tilde{n} = \mathrm{tr}\, \tilde{\rho}_o\, N_i = \mathrm{tr}\, \tilde{\rho}_i\, N_i\ . \qquad \text{(A3.3)}$$

These quantities $\tilde{g}$ and $\tilde{n}$ can be easily calculated with the help of Table 3. It then follows that

$$\tilde{g} = e^{-\beta(2b_{11}-2\mu+U)}/\tilde{z} \qquad \text{(A3.4)}$$

and

$$\tilde{n} = 2(e^{-\beta(b_{11}-\mu)} + e^{-\beta(2b_{11}-2\mu+U)})/\tilde{z} \qquad \text{(A3.5)}$$

where

$$\tilde{z} = 1 + 2 + e^{-\beta(b_{11}-\mu)} + e^{-\beta(2b_{11}-2\mu+U)} \quad . \tag{A3.6}$$

In the same way we did for (A3.1), we can show that eq. (60) and (61) can finally be written in terms of $\tilde{g}$ and $\tilde{n}$ as

$$(U-V)(\tilde{n}-2)\tilde{g} + [h_{11}-b_{11} + \tilde{n}\sum_{j\neq 1} v_{1j1j}][2\tilde{g} + \tilde{n}(1-\tilde{n})] = 0 \tag{A3.7}$$

and

$$(U-V)(1-\tilde{g}) + [h_{11}-b_{11} + \tilde{n}\sum_{j\neq 1} v_{1j1j}](\tilde{n}-2) = 0 \quad . \tag{A3.8}$$

From these two equations we find

$$(U-V)f(\tilde{n},\tilde{g}) = 0 \tag{A3.9}$$

and

$$[h_{11}-b_{11} + \tilde{n}\sum_{j\neq 1} v_{1j1j}]f(\tilde{n},\tilde{g}) = 0 \tag{A3.10}$$

where

$$f(\tilde{n},\tilde{g}) = \tilde{n}(1-\tilde{n}) + \tilde{g}(3\tilde{n}-2) - 2\tilde{g}^2 \quad . \tag{A3.11}$$

If $f(n,g) = 0$, U and b_{11} will be undetermined although there will be a relation between them. Let us study (A3.11). Assume $f(\tilde{n},\tilde{g})$ is zero and solve for $\tilde{n}$ in terms of $\tilde{g}$. The solutions are $\tilde{n} = 1+\tilde{g}$ and $\tilde{n} = 2\tilde{g}$. From (A3.4) and A3.5) $\tilde{n}$ can never be equal to $1 + \tilde{g}$;

and also $\tilde{n}$ can only be equal to $2\tilde{g}$ if $\tilde{n} = \tilde{g} = 0$, which of course is of no interest here. Hence $f(\tilde{n},\tilde{g}) \neq 0$ and (65) and (66) follow immediately.

Table 3. Eigenstates of $\tilde{H}_l$ and $\tilde{H}_l - \mu N_l$. The last column is for $\mu = b_{ll} + \frac{U}{2}$ (half-filled band).

N	$\tilde{H}_1\|> = \tilde{E}_1\|>$		$(\tilde{H}_1-\mu N_1)\|> = (\tilde{E}_1-\mu N_1)\|>$	
	$\|>$	E_1	$E_1 - \mu N_1$	$E_1 - (b_{11}+\frac{U}{2})N_1$
0	$\|0>$	0	0	0
1	$\|\uparrow>$	b_{11}	$b_{11} - \mu$	$- U/2$
1	$\|\downarrow>$	b_{11}	$b_{11} - \mu$	$- U/2$
2	$\|\uparrow\downarrow>$	$2b_{11} + U$	$2b_{11} - 2\mu + U$	0

Table 3

Straightforwardly we can show that

$$[\tilde{H}_o,\ c^+_{k\sigma}(s)] = U\ N_{k\sigma}\ c^+_{k\sigma}(s) - \mu\ c^+_{k\sigma}(s) \tag{A4.8}$$

$$[\tilde{H}_o,\ c_{\ell\sigma}(s)] = -U\ N_{k\sigma}\ c_{\ell\sigma}(s) + \mu\ c_{\ell\sigma}(s)\ . \tag{A4.9}$$

Then we can rewrite (A4.5) in the following form

$$\frac{\partial}{\partial s}\ A_{k\ell\sigma}(s) = \beta U(N_{k\bar{\sigma}} - N_{\ell\bar{\sigma}})\ A_{k\ell\sigma}(s) \tag{A4.10}$$

which after being formally integrated from zero to s gives

$$A_{k\ell\sigma}(s) = e^{s\beta U(N_{k\bar{\sigma}} - N_{\ell\bar{\sigma}})}\ c^+_{k\sigma}\ c_{\ell\sigma} \tag{A4.11}$$

which proves (A4.1).

APPENDIX A5

SOLUTION OF EQUATION (101)

Taking into account (77), (78) and (79), and neglecting terms which are higher than first order in the overlap, we can write (101) in the following way:

$$\sum_{\sigma} \int_{o}^{1} dx[(h_{ji}-b_{ji})\langle g_{ij\bar{\sigma}}(x)\ c^{+}_{i\sigma}\ c_{j\sigma}\ c^{+}_{j\sigma}\ c_{i\sigma}\rangle_{o} +$$

$$+ v_{jjij}\langle g_{ij\bar{\sigma}}(x)\ c^{+}_{i\sigma}\ c_{j\sigma}\ (N_{i\bar{\sigma}}+N_{j\bar{\sigma}})\ c^{+}_{j\sigma}\ c_{i\sigma}\rangle_{o}$$

$$+ \sum_{k\neq i,j} v_{jkik}\langle g_{ij\bar{\sigma}}(x)\ c^{+}_{i\sigma}\ c_{j\sigma}\ N_{k}\ c^{+}_{j\sigma}\ c_{i\sigma}\rangle_{o}]$$

$$+\beta\sum_{\sigma} b_{ji} \int_{o}^{1} dx \left\{\int_{o}^{x} ds \quad [\langle g_{ij\bar{\sigma}}(s)\ c^{+}_{j\sigma}\ c_{i\sigma}\ c^{+}_{i\sigma}\ c_{j\sigma}\ d\rangle_{o} -\right.$$

$$-\langle g_{ij\bar{\sigma}}(x) g_{ji\bar{\sigma}}(s)\ c^{+}_{i\sigma}\ c_{j\sigma}\ c^{+}_{j\sigma}\ c_{i\sigma}\ d\rangle_{o}]$$

$$-\int_{o}^{1} ds\ \langle g_{ij\bar{\sigma}}(x) g_{ji\bar{\sigma}}(s)\ c^{+}_{j\sigma}\ c_{i\sigma}\ c^{+}_{i\sigma}\ c_{j\sigma}\ d\rangle_{o}$$

$$\left.+\langle g_{ji\bar{\sigma}}(x)\ c^{+}_{j\sigma}\ c_{i\sigma}\ c^{+}_{i\sigma}\ c_{j\sigma}\rangle\langle d\rangle_{o}\right\} = 0 \qquad \text{(A5.1)}$$

where

$$d \equiv \sum_{k} (h_{kk} - b_{kk})\ N_{k} + \frac{1}{2}\sum_{k,\ell}{}' v_{k\ell k\ell}\ N_{k}N_{\ell} \qquad \text{(A5.2)}$$

We have used the fact that $g_{ji\bar{\sigma}}(x)\ g_{ij\bar{\sigma}}(x) = 1$ by the definition (93), and also that $U = V$.

To evaluate the thermal averages in (A5.1) we recall the fact that $\tilde{\rho}_o = \prod_k \tilde{\rho}_k$, where

$$\tilde{\rho}_k = e^{-\beta[\tilde{H}_k - \mu N_k]} / \tilde{z} \qquad \text{(A5.3)}$$

$$\tilde{z} \equiv \tilde{z}_k = \text{tr } e^{-\beta[\tilde{H}_k - \mu N_k]} \qquad \text{(A5.4)}$$

and

$$\tilde{H}_k = b_{kk} N_k + U N_{k\uparrow} N_{k\downarrow} \; ; \qquad \text{(A5.5)}$$

and because (99), (100), and (63), for half-filled band we have

$$\tilde{H}_k - \mu N_k = V/2 \; [-N_k + 2 N_{k\uparrow} N_{k\downarrow}] \quad . \qquad \text{(A5.6)}$$

The traces in (A5.1) should be taken over the eigenstates of $\tilde{H}_k - \mu N_k$, which are shown in Table 3. But before doing that, it is convenient to write:

$$d = v_{ijij}[N_i N_j - (N_i + N_j)] + \sum_{k \neq i,j} v_{kiki}[(N_i + N_j)(N_k - 1) - 2 N_k]$$

$$+ \sum_{k,\ell \neq i,j}{}' v_{k\ell k\ell} \; [(1/2) \; N_k N_\ell - N_k] \quad . \qquad \text{(A5.7)}$$

We have considered $\sum_{k \neq i,j} v_{kiki} = \sum_{k \neq i,j} v_{kjkj}$. Above, $\sum_{k,\ell \neq i,j}$ means sum with $k \neq i,j$ and $\ell \neq i,j$ and the prime means $k \neq \ell$.

Then eq. (A5.1) becomes

$$\sum_{\sigma} \int_{o}^{1} dx(h_{ji} - b_{ji} + \sum_{k\neq i,j} v_{jkik})\langle g_{ij\bar{\sigma}}(x)\ c^{+}_{i\sigma}\ c_{j\sigma}\ c^{+}_{j\sigma}\ c_{i\sigma}\rangle_{o} +$$

$$+ v_{jjij}\langle g_{ij\bar{\sigma}}(x)\ c^{+}_{i\sigma}\ c_{j\sigma}\ (N_{i\bar{\sigma}} + N_{j\bar{\sigma}})\ c^{+}_{j\sigma}\ c_{i\sigma}\rangle_{o}] +$$

$$+ \beta \sum_{\sigma} b_{ji} \int_{o}^{1} dx \Big\{ v_{ijij} [\int_{o}^{x} ds\, (\langle g_{ij\bar{\sigma}}(s)\ c^{+}_{j\sigma}\ c_{i\sigma}\ c^{+}_{i\sigma}\ c_{j\sigma}$$

$$(N_iN_j - N_i - N_j)\rangle_{o}$$

$$-\langle g_{ij\bar{\sigma}}(x)\ g_{ji\bar{\sigma}}(s)\ c^{+}_{i\sigma}\ c_{j\sigma}\ c^{+}_{j\sigma}\ c_{i\sigma}\ (N_iN_j - N_i - N_j)\rangle_{o})$$

$$-\int_{o}^{1} ds\langle g_{ij\bar{\sigma}}(x) g_{ji\bar{\sigma}}(s) c^{+}_{j\sigma}c_{i\sigma}c^{+}_{i\sigma}c_{j\sigma}(N_iN_j - N_i - N_j)\rangle_{o}$$

$$-\langle g_{ji\bar{\sigma}}(x) c^{+}_{j\sigma}c_{i\sigma}c^{+}_{i\sigma}c_{j\sigma}\rangle_{o}]$$

$$-[2 \sum_{k\neq i,j} v_{kiki} + 1/2 \sum_{\ell,k\neq i,j} v_{k\ell k\ell}] [\int_{o}^{x} ds(\langle g_{ij\bar{\sigma}}(s) c^{+}_{j\sigma}c_{i\sigma}c^{+}_{i\sigma}c_{j\sigma}\rangle_{o} -$$

$$-\langle g_{ij\bar{\sigma}}(x)\ g_{ji\bar{\sigma}}(s)\ c^{+}_{i\sigma}c_{j\sigma}c^{+}_{j\sigma}c_{i\sigma}\rangle_{o})$$

$$-\int_{o}^{1} ds\langle g_{ij\bar{\sigma}}(x)\ g_{ji\bar{\sigma}}(s)\ c^{+}_{j\sigma}c_{i\sigma}c^{+}_{i\sigma}c_{j\sigma}\rangle_{o}$$

$$+ \langle g_{ji\bar{\sigma}}(x)\ c^{+}_{j\sigma}c_{i\sigma}c^{+}_{i\sigma}c_{j\sigma}\rangle_{o}]\Big\} = 0 \qquad \text{(A5.8)}$$

The next step is then to evaluate the thermal averages and then do the integrals. As an example we do the first one:

$$\sum_{\sigma} \int_{o}^{1} dx \, \langle g_{ij\bar{\sigma}}(x) \; c_{i\sigma}^{+} \; c_{j\sigma} \; c_{j\sigma}^{+} \; c_{i\sigma} \rangle_{o}$$

$$= \sum_{\sigma} \int_{o}^{1} dx \, \langle e^{x\beta V N_{i\bar{\sigma}}} \; N_{i\sigma} \rangle_{o} \, \langle e^{-x\beta V N_{j\bar{\sigma}}} \; c_{j\sigma} \; c_{j\sigma}^{+} \rangle_{o}$$

$$= (2/z^{2}) \int_{o}^{1} dx \, (e^{\frac{1}{2}\beta V} + e^{x\beta V}) \, (1 + e^{(\frac{1}{2}-x)\beta V})$$

$$= (4/z^{2}) \, (e^{\frac{1}{2}\beta V} + \frac{e^{\beta V}-1}{\beta V}) \quad . \tag{A5.9}$$

Similarly we calculate the others and finally find the result given in (102).

APPENDIX A6

PROOF THAT $\tilde{H}_{eff}$ IN (114) CORRESPONDS TO A HEISENBERG HAMILTONIAN

The operator $\tilde{H}_{eff}$ in (114) can be written as

$$\tilde{H}_{eff} = -\sum_{ij}{}' \sum_{\sigma\sigma'} \frac{b_{ij}}{U} P[c^{+}_{i\sigma}c_{j\sigma}c^{+}_{j\sigma'}c_{i\sigma'}]P =$$

$$= -\sum_{ij}{}' \sum_{\sigma} \frac{b_{ij}^2}{U} P[N_{i\sigma} - N_{i\sigma}N_{j\sigma} - c^{+}_{i\sigma}c_{i\bar{\sigma}}c^{+}_{j\bar{\sigma}}c_{j\sigma}]P \qquad \text{(A6.1)}$$

The P operator can be dropped if we remember that $\tilde{H}_{eff}$ is to operate on the ground level only; in other words on states containing only one electron on each site.

The relations between the above creation and destruction operators with the spin operators are[6,29]:

$$c^{+}_{i\uparrow}c_{i\downarrow} = S_{i+} = S_{ix} + iS_{iy}$$

$$c^{+}_{i\downarrow}c_{i\uparrow} = S_{i-} = S_{ix} - iS_{iy}$$

$$\frac{1}{2}(N_{i\uparrow} - N_{i\downarrow}) = S_{iz} \quad .$$

Since in our case $N_{i\uparrow} + N_{i\downarrow} = 1$ then

$$N_{i\uparrow} = \frac{1}{2} + S_{iz}$$

$$N_{i\downarrow} = \frac{1}{2} - S_{iz} \quad .$$

With (A6.2) and (A6.3) in (A6.1) we can write

$$\tilde{H}_{eff} = - \sum_{ij} \frac{b_{ij}^2}{U} [1 - (\tfrac{1}{2}+S_{iz})(\tfrac{1}{2}+S_{jz}) - (\tfrac{1}{2}-S_{iz})(\tfrac{1}{2}-S_{jz})$$

$$- S_{i+}S_{j-} - S_{i-}S_{j+}] =$$

$$= - \sum_{ij}{}' \frac{b_{ij}^2}{U} [\tfrac{1}{2} - 2\underline{S}_i \cdot \underline{S}_j] \quad .$$

The eigenvalues E_n, (115), of $\tilde{H}_H$ calculated through second order degenerate perturbation theory, differ from the eigenvalues of the Heisenberg Hamiltonian with $J_{ij} = -2b_{ij}^2/U$, by the constant

$$N_s b_{11} + \sum_{ij}{}' b_{ij}^2/2U \quad .$$

APPENDIX A7

CALCULATION OF EQUATION (121)

Taking the expression for the exact Hamiltonian given in (3) we have for the first term in (121)

$$\langle\tilde{m}_o|H|\tilde{n}_o\rangle = \frac{1}{2}\sum_{k\ell}{}' v_{k\ell k\ell}\langle\tilde{m}_o|N_k N_\ell|\tilde{n}_o\rangle + \tag{A7.1}$$

$$+ \frac{1}{2}\sum_{\sigma}\sum_{k\ell}{}' v_{k\ell\ell k}[\langle\tilde{m}_o|c^+_{k\sigma}c_{\ell\sigma}c^+_{\ell\bar{\sigma}}c_{k\bar{\sigma}}|\tilde{n}_o\rangle - \langle\tilde{m}_o|N_{k\sigma}N_{\ell\sigma}|\tilde{n}_o\rangle] \ .$$

The other terms in H give no contribution to this matrix element; their sequence of creation and destruction operator are unable to, starting from $|\tilde{n}_o\rangle$ with only singly-occupied sites, give back another function $|\tilde{m}_o\rangle$ with also only singly-occupied sites. The first term in (A7.1) is clearly $\frac{1}{2}\sum_{k\ell}{}' v_{k\ell k\ell}\delta_{nm}$ because $N_k N_\ell|\tilde{n}_o\rangle = |\tilde{n}_o\rangle$; the second term, after adding and subtracting $\langle\tilde{m}_o|c^+_{k\sigma}c_{\ell\sigma}c^+_{\ell\sigma}c_{k\sigma}|\tilde{n}_o\rangle$ inside the curly bracket, can be written as

$$\frac{1}{2}\sum_{k\ell}{}' v_{k\ell\ell k}[\sum_{\sigma\sigma'}\langle\tilde{m}_o|c^+_{k\sigma}c_{\ell\sigma}c^+_{\ell\sigma'}c_{k\sigma'}|\tilde{n}_o\rangle - \delta_{nm}] \ . \tag{A7.2}$$

The potential exchange integral $v_{k\ell\ell k}$ is a quantity of the order of the square of the overlap between k and ℓ . It's clear that overlap between non-nearest neighour sites is smaller than nearest neighbour overlap; then neglecting

terms which are higher than second order in the nearest neighbour overlap we can then write (A7.2) as

$$X_{12} \sum_{<k\ell>} \sum_{\sigma\sigma'} \langle \tilde{m}_o | c^+_{k\sigma} c_{\ell\sigma} c^+_{\ell\sigma'} c_{k\sigma'} | \tilde{n}_o \rangle - \frac{1}{2} X_{12}\, \delta_{nm} \quad . \qquad (A7.3)$$

Because $\sum'_{k\ell} c^+_{k\sigma} c_{\ell\sigma} c^+_{\ell\sigma'} c_{k\sigma'}$ is proportional to

$H_{eff} = \frac{\tilde{P}\tilde{T}\, Q^{(1)} \tilde{T} P}{U}$ of which $|\tilde{n}_o\rangle$ is an eigenfunction we then get

$$\langle \tilde{m}_o | H | \tilde{n}_o \rangle = \delta_{nm} \quad [\frac{1}{2} \sum'_{k\ell} v_{k\ell k\ell} - \frac{1}{2} X_{12} + \frac{1}{2} X_{12}\, A_n] \quad . \qquad (A7.4)$$

The second matrix element in (121) can be written as

$$2b_{12} \Big[\sum_{<ij>} \sum_{\sigma\sigma'} h_{ij} \langle \tilde{m}_o | c^+_{i\sigma} c_{j\sigma} c^+_{j\sigma'} c_{i\sigma'} | \tilde{n}_o \rangle +$$

$$+ \sum_{<ij>} \sum_{\sigma\sigma'} v_{iiji} \langle \tilde{m}_o | (N_{i\bar{\sigma}} + N_{j\bar{\sigma}}) c^+_{i\sigma} c_{j\sigma} c^+_{j\sigma'} c_{i\sigma'} | \tilde{n}_o \rangle + \qquad (A7.5)$$

$$+ \sum_{<ij>} \sum_{k \neq i,j} v_{ikjk} \sum_{\sigma\sigma'} \langle \tilde{m}_o | N_k\, c^+_{i\sigma} c_{j\sigma} c^+_{j\sigma'} c_{i\sigma'} | \tilde{n}_o \rangle \Big] \quad .$$

It is clear that $c^+_{i\sigma} c_{j\sigma} c^+_{j\sigma'} c_{i\sigma'} |\tilde{n}_o\rangle$ is an eigenfunction of $N_{i\bar{\sigma}}$, $N_{j\bar{\sigma}}$ and N_k, with eigenvalues 0,1 and 1, respectively ($k \neq i,j$). Then it follows that

$$\langle \tilde{m}_o | H\, Q^{(1)} \tilde{T} | \tilde{n}_o \rangle = b_{12} t_{12}\, A_n\, \delta_{nm} \quad . \qquad (A7.6)$$

The third term in (121), after neglecting higher order terms, becomes

$$\langle\tilde{m}_o|\tilde{T}\, Q^{(1)} H\, Q^{(1)}\tilde{T}|\tilde{n}_o\rangle = b_{12}^2 V \sum_{\langle i,j\rangle} \sum_{k} \sum_{\sigma\sigma'} \langle\tilde{m}_o|c_{i\sigma}^+ c_{j\sigma} N_{k\uparrow} N_{k\downarrow} c_{j\sigma'}^+ c_{i\sigma'}|\tilde{n}_o\rangle$$

$$+ b_{12}^2 \sum_{k\ell}{}' v_{k\ell k\ell} \sum_{\langle ij\rangle} \sum_{\sigma\sigma'} \langle\tilde{m}_o|c_{i\sigma}^+ c_{j\sigma} N_k N_\ell c_{j\sigma'}^+ c_{i\sigma'}|\tilde{n}_o\rangle =$$

$$= b_{12}^2 V A_n \delta_{nm} + 2b_{12}^2 \sum_{\langle ij\rangle} \sum_{\sigma\sigma'} \Big[\frac{1}{2} \sum_{k,\ell\neq ij}{}' v_{k\ell k\ell} + 2 \sum_{k\neq i,j} v_{kjkj}\Big]$$

$$\times \langle\tilde{m}_o|c_{i\sigma}^+ c_{j\sigma} c_{j\sigma'}^+ c_{i\sigma'}|\tilde{n}_o\rangle$$

$$= b_{12}^2 \Big[V - v_{12} + \frac{1}{2} \sum_{k,\ell}{}' v_{k\ell k\ell}\Big] A_n \delta_{nm} \quad . \qquad \text{(A7.7)}$$

Finally, we obtain the result shown in (122).

APPENDIX A8

CALCULATION OF TERMS IN EQUATION (127)

With (127) and (128) we can write

$$\langle\tilde{n}|\frac{\partial\tilde{H}}{\partial\lambda}|\tilde{\gamma}\rangle\langle\tilde{\gamma}|H|\tilde{n}\rangle$$

$$= \tilde{C}_n^2\tilde{C}_\gamma^2 \quad \langle\tilde{n}_o|(1-\frac{1}{U}\tilde{T}\,Q^{(1)})\,\frac{\partial\tilde{H}}{\partial\lambda}(1-S\tilde{T}Q^{(1)})|\tilde{\gamma}_o\rangle\langle\tilde{\gamma}_o|(1-\frac{1}{U}\,Q^{(1)}\tilde{T})|\tilde{n}_o\rangle \ . \quad \text{(A8.1)}$$

And for $\lambda=U$ this becomes

$$\{-\frac{1}{U}\langle\tilde{n}_o|\tilde{T}Q^{(1)}N_{i\uparrow}N_{i\downarrow}|\tilde{\gamma}_o\rangle[\langle\tilde{\gamma}_o|H|\tilde{n}_o\rangle - \frac{1}{U}\langle\tilde{\gamma}_o|H\,Q^{(1)}\tilde{T}|\tilde{n}_o\rangle + \frac{1}{U}\langle\tilde{\gamma}_o|\tilde{T}PH|\tilde{n}_o\rangle]\} +$$

$$+ \text{higher order terms.} \quad \text{(A8.2)}$$

Evaluation of (A8.2) is similar to the ones we did before, as we see if we rewrite it in the form

$$-\frac{1}{U}\langle\tilde{n}_o|\tilde{T}\,Q^{(1)}N_{i\uparrow}N_{i\downarrow}Q^{(1)}H|\tilde{n}_o\rangle + \frac{1}{U^2}\langle\tilde{n}_o|\tilde{T}\,Q^{(1)}\,N_{i\uparrow}N_{i\downarrow}Q^{(1)}\,H\,Q^{(1)}\,\tilde{T}|\tilde{n}_o\rangle$$

$$-\frac{1}{U^2}\langle\tilde{n}_o|\tilde{T}\,Q^{(1)}N_{i\uparrow}N_{i\downarrow}Q^{(1)}\,\tilde{T}\,P\,\tilde{H}|\tilde{n}_o\rangle \ . \quad \text{(A8.3)}$$

Then it becomes

$$[-\frac{b_{12}t_{12}}{U} + \frac{b_{12}^2}{U^2}(V-v_{12})]\,A_n \ , \quad \text{(A8.4)}$$

and the whole second set of terms in (124) is, for $\lambda = U$:

$$kT \frac{b_{12}}{U} \left[\frac{b_{12}}{U} (V-v_{12}) - t_{12}\right] A_n \tag{A8.5}$$

For $\lambda = b$ (A8.1) turns out to be

$$\sum_{<ij>} \langle \tilde{n}_o | c^+_{i\sigma} c_{j\sigma} | \tilde{\gamma}_o \rangle \left[\langle \tilde{\gamma}_o | H | \tilde{n}_o \rangle - \frac{1}{U} \langle \tilde{\gamma}_o | \tilde{T} \; P \; H | \tilde{n}_o \rangle - \right.$$

$$\left. - \frac{1}{U} \langle \tilde{\gamma}_o | H \; Q^{(1)} \tilde{T} | \tilde{n}_o \rangle \right] = -\left[\frac{b_{12}}{U}(V-v_{12}) - t_{12}\right] A_n \;, \tag{A8.6}$$

and the whole second set of terms in (64) is, for $\lambda = b$,

$$-\frac{kT}{U} \left[\frac{b_{12}}{U} (V-v_{12}) - t_{12}\right] \quad . \tag{A8.7}$$

LIST OF REFERENCES

REFERENCES

1 - J. C. Slater, Phys. Rev. 81, 385 (1951); 82, 538 (1951).

2 - P. Hohenberg and W. Kohn, Phys. Rev. 136 B, 864 (1964); W. Kohn and L. J. Sham, Phys. Rev. 140 A, 1133 (1965).

3 - L. Hedin and S. Lundqvist, Solid State Phys. 23, (1969).

4 - F. Seitz, Modern Theory of Solids (McGraw-Hill Book Co., New York, 1940) p. 329.

5 - J. Hubbard, Proc. Roy. Soc. A 276, 238 (1963).

6 - P. W. Anderson, Solid State Phys. 14 (1963).

7 - By this term we mean the standard thermal Hartree-Fock approximation. For the special case of zero-temperature, see e.g., ref. 8; and for the general case see ref. 9.

8 - J. C. Slater, Quantum Theory of Molecules and Solids (McGraw-Hill Book Co., New York, 1963) Vol 1.

9 - For a recent review see A. Huber in Mathematical Methods in Solid State and Superfluid Theory, Scottish Universities Summer School (1967) (Ed's R. C. Clark and G. H. Derrick), Plenum Press, N.Y. (1968).

10 - J. Bardeen, Phys. Rev. 50, 1098 (1936).

11 - C. Herring, Magnetism, Vol IV (ed. by G. T. Rado and H. Suhl, Academic Press, New York and London (1966)) p. 310-311.

12 - T. A. Kaplan, Bull. Am. Phys. Soc. 13, 386 (1968).

13 - T. A. Kaplan and P. N. Argyres, Phys. Rev. B1, 2457 (1970).

14 - R. Bari and T. A. Kaplan, Phys. Rev. B6, 4623 (1972).

15 - The conclusion that the HFA is unsatisfactory for such systems has been reached by Slater, Mann, Wilson, Wood, Phys. Rev. 184, 692 (1969), sec. IX, on grounds which apparently differ from those of ref. 12 but really are very similar. Namely, it was noted by Slater (reference 8 secs 5-2, 6-2) that atomic excited states which conserve the number of electrons are not given at all correctly by the HFA. Whereas Kaplan's point (ref. 12) that the zero-point entropy is incorrect in the HFA in the atomic limit, is essentially the statement that the low-lying spin-flip excitations in a small magnetic field (which conserve electron-number) are given very badly by the HFA(even for a hydrogen lattice in the atomic limit).

16 - See J. C. Slater, T. M. Wilson, J. H. Wood, Phys. Rev. 179, 28 (1969).

17 - J. C. Slater, Phys. Rev. 165, 658 (1968).

18 - Despite wide study of this method in atoms (see, e.g. ref. 16 and 17).

19 - They are actually overcomplete as can be seen from the simple exactly soluble two-site two-electron Hubbard model.

20 - This contrasts with the broad-band or high-density situation where the interactions presumably can be treated perturbatively in a calculation of the single-particle propagator. In this case the $f_s(x)$ which grow out of the non-interacting set $f_s^o(x)$ will have large norms (~1) whereas the others will have small norms.

It is these "large" $f_s(x)$ that are apparently taken (ref. 3) to correspond to the results of a band calculation.

21 - L. Matheiss, Phys. Rev. B2, 3918 (1970).

22 - See J. C. Slater et al, of ref. 15.

23 - For more recent work along these lines see D. J. Newman, J. Phys. C 6, 2203 (1973).

24 - Nilton P. Silva and T. A. Kaplan, Bull. Am. Phys. Soc. 18, 450 (1973); Nilton P. Silva and T. A. Kaplan, AIP Conf. Proc., No. 18, Magnetism and Magnetic Materials (1973), p. 656.

25 - J. Kanamori, Prog. Theo. Phys. 30, 275 (1963);
M. Gutzwiller, Phys. Rev. Letters, 10, 159 (1963);
Y. Nagaoka, Phys. Rev. 147, 392 (1966);
D. I. Khomskiy, Phys. Metal Metallor. 29, 31 (1970);
E. H. Lieb, and F. Y. Wu, Phys. Rev. Letters, 20, 1445 (1968);
A. A.Ovchinnikov, Sov. Phys. JETP 30, 1160 (1970);
D. Cabib, and T. A. Kaplan, Phys. Rev. B7, 2199 (1973);
R. A. Bari, and T. A. Kaplan, Phys. Rev. B6, 4623 (1972);
and many others; to find other refs. see H. Shiba, and P. A. Pincus, Phys. Rev. B5, 1966 (1972).

26 - This model has been used quite commonly, e.g. by Slater (ref. 27) for H_2 and by Mattheiss, Phys. Rev. 123, 1219 (1961).

27 - Reference 8, Chapters 3 and 4.

28 - E. C. Kemble (1937), "The Principles of Quantum Mechanics", Sec 48C, McGraw-Hill, New York. (Reprinted by Dover, New York, 1958).

29 - T. A. Kaplan, unpublished lecture notes for a course in Magnetism given at Michigan State University in 1971 and 1972.

30 - The exponential behavior of $w_i(\underline{r})$ was found under the assumption of zero phases γ_k of the Bloch functions (see App. A2).

31 - Also see W. Kohn, Phys. Rev. 115, 809 (1959) for a similar result in the case of one-dimensional bands of arbitrary width.

32 - Since Hubbard's explicit intent was to consider a model appropriate to transition metals, where presumably it is essential to have a broad band (4s) cross the narrow band (3d), our proof that Hubbard's derivation leads to grossly incorrect results is perhaps unfair because we consider an isolated s-band (more appropriate to an insulator). However Hubbard did apply his model to insulators (Proc. Roy. Soc. A 281, 401 (1964)). In any case, it is important to realize that this type of Hartree-Fock approach fails.

33 - See discussion in Kaplan and Argyres, page 2457 of ref. 13.

34 - In particular, Kaplan (ref. 12) noted that in the thermal HFA the entropy $\to 0$ as $T \to 0$ for zero bandwidth as compared to the exact result $Nk \ln (2S+1)$, where S is the ionic spin; this is essentially the reason for the fact that as $T \to 0$ the spin-susceptibility $\chi \to 0$ in HF whereas the exact result is $\chi \to \infty$ (the Curie law). These show that the

non-zero-T HFA gives results that are vastly different from the picture in the Heisenberg model, where in the atomic limit $J_{ij} \to 0$, so that there are N non-interacting spins. See T. A. Kaplan, AIP Conf. Proc. No. 5, Magnetism and Magnetic Materials (1971) p. 1305.

35 - N. Fuchikami, J. Phys. Soc. Japan 28, 871 (1970).

36 - It is interesting to note that t_{12} is the average of the two b_{12}^{σ} $(\uparrow,\uparrow)$.

37 - Fuchikami (ref. 35) gave unique values for b_{12}^{σ} $(\uparrow,\uparrow)$; she presumably considered $b_{12}^{\uparrow}$ $(\uparrow,\uparrow)$.

38 - Furthermore, this σ dependence has been shown explicitly (T. A. Kaplan, unpublished).

39 - Nai Li Huang Liu and R. Orbach, AIP Conf. Proc. No. 10, Magnetism and Magnetic Materials (1972) p. 1238.

40 - K. I. Gondaira and Y. Tanabe, J. Phys. Soc. Japan 21, 1527 (1966).

41 - Hubbard, Rimmer and Hopgood, Proc. Phys. Soc. 88, 13 (1966).

42 - Petros N. Argyres, T. A. Kaplan, Nilton P. Silva, Phys. Rev. A9, 1716 (1974).

43 - Hund's rule was implicitly assumed in ref. 21.

44 - S. V. Tyablikov, Methods in the Quantum Theory of Magnetism, (Plenum Press, New York, 1967) p. 196.

45 - Actually $v_{ijji} \simeq \ell n\, \alpha\, R_{ij}\, e^{-2\alpha R_{ij}}$ for $a_i(r) \simeq e^{-\alpha|\underline{r}-\underline{R}_i|}$ in which case $\Delta_{ij} \simeq e^{-\alpha R_{ij}}$; thus $v_{ijji} = 0(\Delta_{ij}^{\nu})$ where ν is less than but arbitrarily close to 2 and it is in this sense that the term second order is used. See ref. 13.

46 - R. S. Tu and T. A. Kaplan, Physica Status Solidi (b) 63, 659 (1974).

47 - R. A. Bari, Phys. Rev. B3, 2662 (1971).

48 - See also D. J. Klein, W. A. Seitz, Phys. Rev. B8, 2236 (1973).

49 - It can be seen that the second order corrections to the wave-functions omitted in Eq. (109) contribute to Eq. (118) only in higher order than the terms we keep.

50 - That this might occur in situations of physical interest has been noted in ref. 39.

51 - Under certain conditions ($|v'_{12}|<|t_{12}|$), the location of the bottom of the ($N_s \pm 1$)-electron levels relative to the ground state energy is matched perfectly to second order in overlap.

52 - It is interesting to note that the free energy variational (minimal) principle leads to information concerning excited states, (and therefore dynamics), even as $T \to 0$.

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