After multiplying on the left by $d^{i}_{\vec{k},\vec{K}_m}$ and summing over all $\vec{K}_m$, the above equation reduces to

$$\sum_j (S^\dagger HS)_{ij} B_j(\vec{k}) = E_{\vec{k}} B_i(\vec{k}) , \tag{24}$$

where the matrix $H_{in}$ appearing in Eq. (24) is given by

$$H_{in} = \sum_{\vec{K}_m,\vec{K}_l} d^{i*}_{0,\vec{K}_m} H_{\vec{K}_m,\vec{K}_l} d^{n}_{0,\vec{K}_l}, \tag{25}$$

the rows and columns of $H_{in}$ being labeled by band indices.

It should be emphasized that the matrix $S_{nj}$ defined in Eq. (20) in terms of a sum over reciprocal-lattice vectors is numerically *identical* to the matrix $S_{nj}$ obtained by Zak[1] using the $kq$ representation. $S_{nj}$ in no way depends on the particular choice of $kq$ or $k\vec{K}_m$ representations.

The single-band part of the Hamiltonian $H_{in}$ may be separated out with the help of the definitions:

$$V_{in} = \sum_{\vec{K}_m,\vec{K}_l} d^{i*}_{0,\vec{K}_m} V(\vec{K}_m - \vec{K}_l) d^{n}_{0,\vec{K}_l} , \tag{26}$$

$$\vec{P}_{in} = \sum_{\vec{K}_m} d^{i*}_{0,\vec{K}_m} \hbar\vec{K}_m d^{n}_{0,\vec{K}_m} . \tag{27}$$

Then

$$H_{in} = \delta_{in}\left[\left(\frac{1}{2m}\right)\left(\hbar\vec{k} - \frac{ie}{2c} H\times\nabla_{\vec{k}}\right)^2 - ie\vec{E}\cdot\nabla_{\vec{k}}\right]$$

$$+ \sum_{\vec{K}_m,\vec{K}_l} d^{i*}_{0,\vec{K}_m}\left(\frac{\hbar^2 K_m^2}{2m}\delta_{\vec{K}_m\vec{K}_l} + V(\vec{K}_m - \vec{K}_l)\right) d^{n}_{0,\vec{K}_l}$$

$$+ \vec{P}_{in}\cdot\left(\hbar\vec{k} - \frac{ie}{2c}\vec{H}\times\nabla_{\vec{k}}\right)\Big/ m , \tag{28}$$

and using Eqs. (13) and (14)

$$H_{in} = \delta_{in}\left[\frac{1}{2m}\left(\hbar\vec{k} - \frac{ie}{2c} H\times\nabla_{\vec{k}}\right)^2 - ieE\cdot\nabla_{\vec{k}} + E^{i}_{0}\right]$$

$$+ \vec{P}_{in}\cdot\left(\hbar\vec{k} - \frac{ie}{2c} H\times\nabla_{\vec{k}}\right)\Big/ m. \tag{29}$$

A single-band effective Hamiltonian may be obtained by transforming away the interband terms in Eq. (29). In the absence of external fields, this can be accomplished by means of the matrix $S$ defined in Eq. (20), for in this case it is easily verified that

$$(S^\dagger HS)_{ij} = E^{i}_{\vec{k}}\delta_{ij} . \tag{30}$$

With nonzero fields, an appropriately symmetrized matrix $[S_{in}(\vec{k})]$ may be used, as discussed by Roth[6] and Zak.[1] Acceleration theorems may also be proved using the symmetrized $S$; the calculations in the $\vec{k}\vec{K}_m$ representation are, however, identical to those in the $kq$ representation, inasmuch as the matrix $S$ does not depend on which representation is chosen.

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# Application of Gutzwiller's Variational Method to the Metal-Insulator Transition

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It is shown that the approximate variational calculation of Gutzwiller predicts a metal-insulator transition as the intra-atomic Coulomb interaction is increased for the case of one electron per atom. The susceptibility and effective mass are calculated in the metallic phase and are found to be enhanced by a common factor which diverges at the critical value of the interaction.

Several years ago, Gutzwiller[1] performed an approximate variational calculation of the ground-state wave function for a model Hamiltonian with a single tight-binding band and with only intra-atomic Coulomb interactions between the electrons. This model Hamiltonian, introduced earlier by Hubbard,[2] Gutzwiller,[3] and Kanamori,[4] is generally known as the Hubbard model and has been studied by many authors. Using Gutzwiller's[1] notation, as we shall in this paper, the model Hamiltonian has the form

$$H = \sum_{\vec{k}} \epsilon_{\vec{k}} (a^\dagger_{\vec{k}\uparrow} a_{\vec{k}\uparrow} + a^\dagger_{\vec{k}\downarrow} a_{\vec{k}\downarrow}) + C\sum_{\vec{g}} a^\dagger_{\vec{g}\uparrow} a^\dagger_{\vec{g}\downarrow} a_{\vec{g}\downarrow} a_{\vec{g}\uparrow} , \tag{1}$$

where $a^\dagger_{\vec{k}}$ and $a^\dagger_{\vec{g}}$ are the creation operators for elec-

trons in the Bloch state $\{\vec{k}\}$ and the Wannier state $\{\vec{g}\}$, respectively, $C$ is the intra-atomic Coulomb repulsion, and $\epsilon_{\vec{k}}$ is the kinetic energy, with the zero of energy chosen so that $\sum_{\vec{k}} \epsilon_{\vec{k}} = 0$.

Gutzwiller[1] constructed a trial wave function by starting with the conventional Bloch state for noninteracting electrons and reducing the amplitude of all components in which $\nu$ atoms are doubly occupied by an amount $\eta^{\nu}$, where $0 < \eta < 1$. He calculated the needed matrix elements by neglecting the kinetic energy of the down-spin electrons, arguing that this procedure should be a good approximation to an optimally chosen generalization of his wave function. This led to an explicit and spin-symmetric expression for the energy as a function of $\eta$. This expression was then minimized with respect to $\eta$ and the ground-state energy obtained. Gutzwiller used his results to obtain a criterion for itinerant ferromagnetism. In this paper we wish to apply his calculation to the problem of the metal-insulator transition.

We consider only the case in which there is one electron per atom. (For any other number of electrons per atom Gutzwiller's variational state is always metallic.) With one electron per atom, Eqs. (B7) and (B8) of Gutzwiller's give $\eta$ and $q$ in terms of $\bar{\nu}(\equiv \langle n_{i\uparrow} n_{i\downarrow} \rangle_{\eta})$:

$$\eta = \bar{\nu}/(\tfrac{1}{2} - \bar{\nu}) , \tag{2}$$

$$q = 16\bar{\nu}\,(\tfrac{1}{2} - \bar{\nu}) . \tag{3}$$

Here $q$ is the discontinuity in the single-particle occupation number $\langle n_{\vec{k}} \rangle$ at the Fermi surface. Substituting these results into Eq. (36) for the energy and minimizing with respect to $\bar{\nu}$, we find for the lowest-energy state

$$\bar{\nu} = \tfrac{1}{4}\,(1 - C/C_0) , \tag{4}$$

$$q = 1 - (C/C_0)^2 , \tag{5}$$

and the expectation value of the energy in the (paramagnetic) ground state

$$\langle H \rangle_N = \bar{\epsilon}\,(1 - C/C_0)^2 . \tag{6}$$

Here

$$\bar{\epsilon} = 2 \sum_{k < k_F} \epsilon_{\vec{k}} < 0$$

is the average energy without correlation and $C_0 = -8\bar{\epsilon}$. Thus, at a critical value of the interaction strength $C = C_0$ the number of doubly occupied sites and the discontinuity in the single-particle occupation number at the Fermi surface go to zero. The value of the energy (6) also approaches zero, the expectation value of the energy of a paramagnetic localized insulating state. However, it is clear that some magnetically ordered insulating ground state will have a lower energy than the paramagnetic insulating state and a transition to an insulating magnetically ordered ground state will occur for a value of $C$ less than $C_0$.

Nevertheless, it is interesting to calculate the properties of this trial wave function in the metallic state. If we assume that the effective-mass renormalization $m^*/m$ is due to the frequency dependence of the self-energy only, as for example, in the electron-phonon and paramagnon problems,[5-7] then $m^*/m$ equals the reciprocal of the discontinuity at the Fermi surface in the single-particle occupation number,

$$m^*/m = q^{-1} = [1 - (C/C_0)^2]^{-1} . \tag{7}$$

The effective mass, therefore, diverges as $C$ approaches $C_0$. Gutzwiller also calculated the minimum energy for states with differing numbers of up- and down-spin electrons and the static susceptibility $\chi_s$ can be obtained by expanding his results to second order in the magnetization. Defining the magnetization $2\zeta = (\langle N_{\uparrow} \rangle - \langle N_{\downarrow} \rangle)/N$, we find

$$\bar{\epsilon}_{\zeta} = \bar{\epsilon} + \zeta^2/\rho(\epsilon_F) , \tag{8}$$

$$q_{\zeta} = 16\bar{\nu}\,(\tfrac{1}{2} - \bar{\nu})\,\{1 + \zeta^2[4 - \tfrac{1}{4}\,(\tfrac{1}{2} - \bar{\nu})^{-2}]\} , \tag{9}$$

where $\rho(\epsilon_F)$ is the noninteracting one electron density of states at the Fermi energy. Upon substituting (8) and (9) into the expression from the ground-state energy we find

$$\chi_s^{-1} = \frac{1 - (C/C_0)^2}{\rho(\epsilon_F)} \left[ 1 - \rho(\epsilon_F) C \left( \frac{1 + (C/2C_0)}{[1 + (C/C_0)]^2} \right) \right] . \tag{10}$$

Therefore, as $C$ approaches $C_0$ both the susceptibility and the effective mass diverge in proportion to $[1 - (C/C_0)^2]^{-1}$. This result is quite different from the type of result obtained from paramagnon theory[6,7] near a ferromagnetic instability. In that theory the mass is proportional to the logarithm of the susceptibility, and although both $\chi_0$ and $m^*$ diverge, the ratio of the two goes to infinity. In the present case this ratio goes to a finite value. We note that if range effects are ignored in paramagnon theory, corresponding to a uniform enhancement of the static wave-vector-dependent susceptibility, then $\chi_0$ and $m^*$ would scale as we find.

Examining Eqs. (7) and (10), it is clear that the susceptibility enhancement is not coming from the usual Stoner enhancement factor $[1 - \rho(\epsilon_F) C]^{-1}$, but rather from the effective mass. The Stoner factor has been replaced by the expression in the brackets in (10). This expression becomes small only if $\rho(\epsilon_F)$ is considerably larger than the average density of states in the band. Therefore, the possibility of itinerant ferromagnetism prior to the metal-insulator transition is greatly reduced. We have not been able to calculate $\chi(\vec{Q})$, the static wave-vector-dependent susceptibility. However, if we accept that $\chi(\vec{Q})$ is roughly independent of $Q$, as one naively expects for a localized instability, then it

is interesting to speculate that the correlation effects could possibly also suppress itinerant antiferromagnetism and lead to a first-order transition between a paramagnetic metallic state and an antiferromagnetic insulating state.

The results obtained from Gutzwiller's method are to be contrasted with those found by Hubbard[2] using a Green's-function decoupling approximation. While Hubbard's approximation is reasonable for the insulating phase, it certainly is incorrect for the metallic phase since it does not properly describe the Fermi surface as emphasized by Herring[8] and by Edwards and Hewson.[9] Further, in the Hubbard approximation the density of states at the Fermi surface approaches zero as $C \to C_0$. The Gutzwiller calculation, on the other hand, builds in the Fermi surface from the start and gives an appealing description of a metallic state in which the discontinuity in the single-particle occupation number at the Fermi surface becomes small as the system becomes closer to the metal-insulator transition.

In conclusion, it is interesting to compare the above results with the experimental properties of the metallic state of $V_2O_3$.[10-12] This type of comparison may be meaningless since $V_2O_3$ is surely a complicated many-band situation for which the simple model studied by Gutzwiller is not applicable. Nevertheless, the Gutzwiller results are not strongly dependent on the density of states, and it is interesting that the specific heat and the susceptibility appear to be enhanced by roughly the same amount. In $V_2O_3$ the susceptibility and specific-heat density of states of the metallic phase both appear to be quite large. An extrapolation of the susceptibility to 0 °K gives a value for $\chi_s$, expressed as a density of states, of 35 states/eV molecule. A rough estimate of the specific-heat density of states $N(\epsilon_F)$, can be obtained as follows. If we assume that the difference between the metallic and insulating specific heats is of the form $\Delta C_v = \gamma T + \beta T^3$, then the parameters $\gamma$ and $\beta$ can be estimated by setting (a) $\int_0^{T_N} \Delta C_v dT/T = \Delta S$, the change in entropy at the metal-to-antiferromagnetic-insulating phase transition in pure $V_2O_3$ at 1 atm, and (b) $\Delta C_v(T_N = 170\,^\circ\mathrm{K}) = 0$, in agreement with Anderson's[13] experimental results. This gives $N(\epsilon_F) = 20$ states/eV molecule, which is quite large. However, the ratio $\chi_s/N(\epsilon_F)$ is only 1.75, so that the two quantities appear to be roughly equally enhanced.

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# Magnetic Circular Polarization of $F$-Center Emission in KCl †

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In a recent Letter,[1] the first observation of a magnetic-field-induced circular polarization (MCP) of the emission of $F$ centers was reported for potassium fluoride. Two things were remarkable about the effect: It was quite small, and it appeared to be independent of temperature. The small size implied a strong reduction of the orbital $g$ value for the emitting state, while the temperature independence implied that any spin-orbit contribution to the effect was negligible. In a subsequent paper,[2] it was shown that the $F$-electron spin polarization had been completely quenched by the intense optical pumping