

Simple Narrow-Band Model of Ferromagnetism Due to Intra-Atomic Exchange*

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As a model of ferromagnetism due to intra-atomic exchange, we consider a narrow band with two orbital states, such as d_{22} states in a bcc lattice. We include hopping and intra-atomic Coulomb and exchange terms in the Hamiltonian. If we assume that the hopping process does not change the orbital state, it is found for one electron per atom and for sufficiently narrow bands that it is energetically favorable for two sublattices to form, each with predominantly one of the orbital states, and for the spins to line up ferromagnetically. We use the random-phase approximation to extend this result beyond the narrow-band limit. The stability of this ferromagnetic state is investigated by calculating its spin-wave spectrum, and the region of stability as well as the effective exchange parameter depend on the strength of the intra-atomic exchange integral. For one electron per atom, the mechanism is too weak for real ferromagnets, but it becomes stronger for less than one electron per atom.

ONE of the mechanisms which has been discussed a great deal¹ as being responsible for metallic ferromagnetism is intra-atomic exchange. We consider here a relatively simple model which exhibits ferromagnetism due to this mechanism. We make use of a simple treatment of correlation in narrow bands, a subject which has received a good deal of more sophisticated theoretical treatment recently.²⁻⁴

It has been argued by Van Vleck¹ that in the case of two weakly interacting atoms with one electron apiece, if the orbital state is degenerate the spins prefer to line up antiparallel owing to the possibility of lowering the energy of the pair by mixing in ionic states. However, if orbital degeneracy is present, ionic states with parallel spins are possible within the shell, and, in fact, are lower in energy than the antiparallel alignment, because of intra-atomic exchange in accordance with Hund's rule. Therefore, the presence of orbital degeneracy seems to be important in the occurrence of ferromagnetism.

The model we consider here assumes two orbital states, 1 and 2, which is not realistic, but is the simplest orbitally degenerate situation. We could imagine the states to be the d_{22} cubic field split d -states, or else some kind of isotopic spin states. We then suppose that there

are transfer or hopping integrals t_{11} , t_{22} , and t_{12} connecting states on two neighboring atoms. Let us consider the second-order contribution to the energy due to mixing in of ionic states for various configurations, as given in Table I, in which U and V are the Coulomb repulsion and exchange energies on an atom, assuming that only one U is involved.

Suppose the states are chosen such that $t_{11} = t_{22} > t_{12}$. Then we notice that the exchange interaction V is attempting to make state $1\uparrow, 2\uparrow$ the lowest energy, while the transfer energy t_{12} is trying to favor an anti-ferromagnetic arrangement. There is, consequently, a competition between the two effects. We shall assume that the ferromagnetic state wins and to ensure this, as well as to simplify the problem, we shall assume that $t_{12} = 0$, and $t_{11} = t_{22}$. This would actually be true if the states were isotopic spin states and it is also true for a particular representation of d_{22} function in a body-centered cubic lattice with nearest-neighbor interaction. For the model chosen we find that not only is the lowest state ferromagnetic, but that the two "orbital" states are to be reversed on the two atoms. This is for one electron per atom. We can also include nonintegral numbers of electrons by assuming an appropriate Fermi level, due to a broad s -band, but ignoring hybridization.

The second-quantized Hamiltonian for this model is

$$\mathcal{H} = \sum_i \left\{ U [n_{i\uparrow}n_{i\downarrow} + m_{i\uparrow}m_{i\downarrow} + \sum_{\sigma\sigma'} n_{i\sigma}m_{i\sigma'}] - V \sum_{\sigma\sigma'} c_{i\sigma}^\dagger c_{i\sigma'} d_{i\sigma}^\dagger d_{i\sigma'} \right\} + \sum_{ij} t_{ij} [c_{i\sigma}^\dagger c_{j\sigma} + d_{i\sigma}^\dagger d_{j\sigma}]. \quad (1)$$

Here c and $n = c^\dagger c$ refer to state 1, d and $m = d^\dagger d$ refer to state 2, and we have omitted matrix elements of the Coulomb interaction with, e.g., one 1 and three 2's, as we shall not need them. We assume $t_{ii} = 0$ for simplicity as this is a constant energy shift. We are thus including Coulomb and exchange energy only on the same atom.

Let us assume that the ground state is ferromagnetic, which we expect to be valid if there is about one electron per atom. Then we need only consider states of one spin, say spin up, so that we can work with the up spin

TABLE I. Interaction energy of two atoms due to admixture of ionic states.

Configuration	Second-order Energy
$1\uparrow, 2\uparrow$	$-(t_{11}^2 + t_{22}^2)/(U - V)$
$1\uparrow, 2\downarrow$	$-(t_{11}^2 + t_{22}^2 + 2t_{12}^2)/U$
$1\uparrow, 1\uparrow$	$-2t_{12}^2/(U - V)$
$1\uparrow, 1\downarrow$	$-2(t_{11}^2 + t_{12}^2)/U$

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¹ J. H. Van Vleck, *Rev. Mod. Phys.* **25**, 220 (1953).

² J. Hubbard, *Proc. Roy. Soc. (London)* **A276**, 238 (1963); **A227**, 237 (1964).

³ J. Hubbard, *Proc. Roy. Soc. (London)* **A281**, 401 (1964).

⁴ J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **30**, 275 (1963); M. C. Gutzwiller, *Phys. Rev.* **134**, A923 (1964).

Hamiltonian

$$\mathcal{H}_\uparrow = \sum_i (U - V)n_{i\uparrow}m_{i\uparrow} + \sum_{ij} t_{ij}(c_{i\uparrow}c_{j\uparrow} + d_{i\uparrow}d_{j\uparrow}). \quad (2)$$

This Hamiltonian has exactly the same form as that for particles with spin and no orbital degeneracy under similar assumptions. This Hamiltonian has been discussed by Hubbard^{2,3} and others, as a simple model for studying narrow bands and insulator-to-metal transitions. As we noted above, the tendency is to have neighboring atoms in different states, or, effectively, spin states. The treatment we shall give of this problem is that of Cloizeaux,⁵ who assumed that the system breaks up into two sublattices arranged antiferromagnetically (for the spin case). The lattice must admit this type of arrangement, of course. For our model we assume an arrangement of two sublattices, *A* and *B*, with predominantly state 1 on sublattice *A*, and 2 on sublattice *B*, and we solve the problem self-consistently. This scheme allows the electrons' motion to be correlated in such a way as to gain kinetic energy from both bands while avoiding each other spatially. Another approach to this problem is that of Hubbard,² whose correlated state is probably rather like a disordered antiferromagnet. Our primary reason for adopting the simple Cloizeaux scheme is that it will be easier to study the low-lying excitations.

We therefore replace *n* and *m* by their expectation values in the necessary places to arrive at an effective self-consistent Hamiltonian

$$\begin{aligned} \mathcal{H}_{\text{SC}\uparrow} = & (U - V) \sum_{i,A} [\langle m_{A\uparrow} \rangle c_{i\uparrow}^\dagger c_{i\uparrow} + \langle n_{A\uparrow} \rangle d_{i\uparrow}^\dagger d_{i\uparrow}] \\ & + (U - V) \sum_{i,B} [\langle m_{B\uparrow} \rangle c_{i\uparrow}^\dagger c_{i\uparrow} + \langle n_{B\uparrow} \rangle d_{i\uparrow}^\dagger d_{i\uparrow}] \\ & + \sum_{iA, jB} t_{ij} [c_{i\uparrow}^\dagger c_{j\uparrow} + c_{i\uparrow}^\dagger c_{j\uparrow} + d_{i\uparrow}^\dagger d_{j\uparrow} + d_{i\uparrow}^\dagger d_{j\uparrow}]. \quad (3) \end{aligned}$$

We are assuming only nearest-neighbor interactions. Since the sublattices should be equivalent, we shall assume

$$\begin{aligned} \langle n_{A\uparrow} \rangle = \langle n_{B\uparrow} \rangle &= (n + \delta)/2, \\ \langle m_{A\uparrow} \rangle = \langle m_{B\uparrow} \rangle &= (n - \delta)/2, \end{aligned} \quad (4)$$

where *n* is the number of electrons per atom. We then Fourier transform over a Brillouin zone half as large as the original, and make a transformation to obtain normal modes. We write

$$\begin{aligned} c_{i\uparrow} &= \left(\frac{2}{N}\right)^{1/2} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{R}_i} (u_{\mathbf{k}} c_{\mathbf{k}\uparrow-} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow+}), \\ c_{i\uparrow}^\dagger &= \left(\frac{2}{N}\right)^{1/2} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{R}_i} (-v_{\mathbf{k}} c_{\mathbf{k}\uparrow-} + u_{\mathbf{k}} c_{\mathbf{k}\uparrow+}), \end{aligned} \quad (5)$$

⁵ J. Cloizeaux, J. Phys. Radium **20**, 606 (1959). See also D. Adler, Phys. Rev. (to be published).

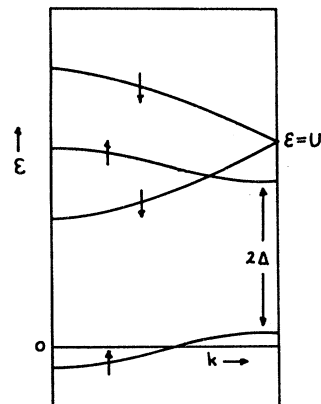


FIG. 1. Sketch of eigenvalues of self-consistent Hamiltonian for up (↑) and down (↓) spins.

where

$$\begin{aligned} U_{\mathbf{k}} &= (1 - v_{\mathbf{k}}^2)^{1/2} = \frac{1}{\sqrt{2}} \left(1 + \frac{\Delta}{(\Delta^2 + t_{\mathbf{k}}^2)^{1/2}} \right)^{1/2}, \\ t_{\mathbf{k}} &= t_1 \sum_{\rho} e^{i\mathbf{k} \cdot \rho} \end{aligned} \quad (6)$$

with $\Delta = (U - V)\delta/2$ and $t_1 = t_{0\rho}$, assumed independent of ρ , which goes over nearest neighbors. The analogous transformation for the *d*'s has *u* and *v* reversed. The diagonalized \mathcal{H}_{sc} has eigenvalues

$$\epsilon_{\mathbf{k}\uparrow\pm} = n \left(\frac{U - V}{2} \right) \pm (\Delta^2 + t_{\mathbf{k}}^2)^{1/2}. \quad (7)$$

The energies are the same for the two bands, which are now split, with an energy gap 2Δ , as indicated in Fig. 1. Δ can be determined self-consistently by calculating $\langle n_{A\uparrow} \rangle$ from Eq. (5). The condition is, for $n \leq 1$,

$$1 = -\frac{2}{N} \sum_{\mathbf{k}} n_{\mathbf{k}-} \frac{(U - V)/2}{(\Delta^2 + t_{\mathbf{k}}^2)^{1/2}}, \quad (8)$$

where $n_{\mathbf{k}-}$ is the occupation number for the lower branch of either band. For *n* between 1 and 2, we expect the one spin scheme to break down, as can be seen in Fig. 1.

The gap can be estimated for $n \leq 1$ by noting from the mean value theorem that there is a value \bar{t} of $t_{\mathbf{k}}$ in the band for which $\bar{t}^2 + \Delta^2 = [n(U - V)/2]^2$ so that $\Delta = [(n(U - V)/2)^2 - \bar{t}^2]^{1/2}$. In particular, we find that Δ vanishes when $\bar{t} = n(U - V)/2$. For $n = 1$, the vanishing of the gap can be thought of as an insulator to metal transition.⁶ However, as Cloizeaux points out,⁵ the integral in Eq. (7) has a logarithmic singularity when $t_{\mathbf{k}} \rightarrow 0$, so that the gap never vanishes for zero temperature. This is analogous to the case of superconductivity and, in fact, Eq. (7) is quite similar to the BCS gap equation. However, in our case the above result is clearly an artifact, as it depends on the fact that $t_{\mathbf{k}}$ vanishes over the entire surface of the new

⁶ N. Mott, Nuovo Cimento Suppl. **7**, 318 (1957).

Brillouin zone, so that the density of states of the split band is infinite near the gap. The inclusion of second-nearest-neighbor transfer integrals would alter this situation completely.

Incidentally, a somewhat similar result occurs in Hubbard's first treatment² of this problem. He finds a band splitting which persists for a large bandwidth. Hubbard points out, however, that the number of states in the lower band is not exactly one per atom in general. It is one per atom for the nearest-neighbor case we deal with here, so that in Hubbard's first solution, conduction would begin as soon as second-neighbor interactions became important. His second treatment of the problem³ includes some additional effects, such as broadening, and results in a transition to a metallic state for $BW \sim U - V$, where BW is the band width. We therefore view with caution results in this range of bandwidth.

We now wish to investigate the stability of the state and the elementary excitations. The down spin states for a self-consistent treatment are readily seen to be

$$\epsilon_{\mathbf{k}\uparrow\pm} = nU \pm t_{\mathbf{k}}, \quad (9)$$

so that the down spin bands are not split. An excited down spin electron has a strong interaction with an up spin hole, however, so that the elementary excitations are exciton-like states, i.e., spin waves, as has been shown by Izuyama⁷ and Antanoff.⁸ There are several possible modes in our problem and we shall consider those in which the spins are reversed but not the states (i.e., 1 or 2). The spin wave spectrum is then obtained in the random-phase approximation by an equation of motion method,⁹ in which we assume a creation operator which is a linear combination of the four operators $c_{\mathbf{k}+\mathbf{q}\uparrow\pm}^\dagger c_{\mathbf{q}\mathbf{k}\uparrow-}$, $d_{\mathbf{k}+\mathbf{q}\uparrow\pm}^\dagger d_{\mathbf{q}\mathbf{k}\uparrow-}$, where \mathbf{k} goes over the zone, if we assume $n \leq 1$ so that only the $-$ states are occupied. We shall quote the result only for long wavelength, assuming cubic symmetry:

$$\epsilon_{\mathbf{q}} = \frac{2}{Nn} \frac{q^2}{6} \sum_{\mathbf{k}} (\nabla_{\mathbf{k}} t_{\mathbf{k}})^2 \left\{ \frac{(-\partial n_{\mathbf{k}-} / \partial \epsilon_{\mathbf{k}-\uparrow}) t_{\mathbf{k}}^2}{\Delta^2 + t_{\mathbf{k}}^2} + \frac{n_{\mathbf{k}-}}{(\Delta^2 + t_{\mathbf{k}}^2)^{1/2}} \right. \\ \left. \times \left[\frac{[(U+V)n/2]^2 - \Delta^2 - 4t_{\mathbf{k}}^2}{[n(U+V)/2]^2 + \Delta^2 + n(U+V)(\Delta^2 + t_{\mathbf{k}}^2)^{1/2}} - \frac{t_{\mathbf{k}}^2}{\Delta^2 + t_{\mathbf{k}}^2} \right] \right\}. \quad (10)$$

If we examine this in the case $n=1$, the first term goes out and $n_{\mathbf{k}-}=1$. If $t_{\mathbf{k}} \ll U, U-V$, we can set $t_{\mathbf{k}}=0$

⁷ T. Izuyama, *Progr. Theoret. Phys. (Kyoto)* **23**, 969 (1960).

⁸ M. Antanoff, thesis, Cornell University, 1962 (unpublished).

⁹ K. Sawada, K. A. Brueckner, N. Fukuda, and R. Brout, *Phys. Rev.* **108**, 507 (1957).

and $\Delta = (U-V)/2$ in the curly bracket, and the extreme narrow-band result is

$$\epsilon_{\mathbf{q}} = [t_1^2 V / U(U-V)]^{1/3} q^2 \rho^2 z, \quad (11)$$

where t_1 is given by Eq. (6) and z is the number of nearest neighbors. For finite bandwidth the square bracket decreases as a function of $t_{\mathbf{k}}$. If we evaluate the square bracket at $t_{\mathbf{k}} = \bar{t}$, we have, assuming $V \ll U, t_{\mathbf{k}} \ll U$, an extra factor $1 - 7\bar{t}^2 / UV$ over the extreme narrow-band limit. We can approximate $\epsilon_{\mathbf{q}}$ by Eq. (11) times this factor for finite bandwidth, in which case we expect the ferromagnetic state to become unstable for $\bar{t}^2 \sim UV/7$.

We can define an effective exchange integral by comparing Eq. (10) with the result from the Heisenberg model¹⁰ with spin $\frac{1}{2}$

$$J = 6\epsilon_{\mathbf{q}} / z\rho^2 q^2 \cong \frac{2t_1^2 V}{U(U-V)} (1 - 7\bar{t}^2 / UV) \quad (12)$$

for $n=1$. For the narrow-band limit this is just what we expect from the energy difference between the ferromagnetic and antiferromagnetic states in Table I. We can make an estimate of J by putting in typical values for the constants. Thus, assuming $n=1$, $U=10$ eV, $V=1$ eV, $BW=5$ eV $= 2zt_1 \cong 2z^{1/2}\bar{t}$, and $z=8$, we obtain $Jz \sim 0.008$ eV $= 100^\circ\text{K}$, which is actually too small for transition metal ferromagnets by a factor of 10. Note that the numbers quoted keep us well away from the insulator-metal transition.

For $n < 1$, the spin wave energy, Eq. (10), becomes larger in the narrow-band limit. We expect to investigate this region further as well as the region for n between 1 and 2. For $n \sim 2$, we expect an antiferromagnetic state to be favored, and for $n \sim 0$ we expect the system to be paramagnetic.

This simple model shows that Van Vleck's argument can work in a particular case to produce ferromagnetism due to intra-atomic exchange. For one electron per atom the mechanism appears to be too weak for real ferromagnets, but it becomes stronger for less than one electron per atom. The model assumes a spatial ordering of orbitals which may or may not be relevant to a real situation. It is interesting that for the appropriate choice of d_{z^2} functions $[(3z^2 - r^2) \pm i\sqrt{3}(x^2 - y^2)]$, for which t_{12} vanishes for body-centered directions, the density is the same for the states 1 and 2, so that the spatial ordering affects only the phase of the wave functions. It is possible to construct other phase-ordering parameters for d -functions, and this may turn out to be a useful way to treat the correlation problem in orbitally degenerate narrow bands.

¹⁰ C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 49.