Correlations among Localized and Weakly Metallic Electrons*

TADASHI ARAI

Argonne National Laboratory, Argonne, Illinois

Excitation energies of an antiferromagnetic lattice of $2N$ one-electron atoms are calculated by using the double-time Green functions. The lattice will exhibit insulator-to-metal transitions under pressure but remain antiferromagnetic in the metallic phase.

For simplicity, we consider a bcc lattice of the $2N$ ion cores and assume that the $2N$ electrons are bound to ions but allowed to hop from one ion to another. At high densities, therefore, the motion of electrons may be described by the tight-binding Bloch wave functions, yielding a metallic conductivity. In the limit of low density, however, each ion core captures a single electron and the spins will line up antiferromagnetically. The lattice is then an insulator described by the Heitler–London picture with the two-sublattice structure.

The energy of the lattice may be calculated correctly by using nonorthogonal atomic functions ϕ_j as basis. Use of the cumulant-expansion method[1] yields the energy expression which, in its first approximation, is not very different from the calculation based on Wannier functions. In fact, the calculation may be converted to that of an effective Hamiltonian involving the core potentials $V(1; R_j)$, the Coulomb interaction $(jj^* \mid 1/r_{12} \mid jj^*)$ and the *screened* exchange interaction $(jj^* \mid H_{ex} \mid j^*j)$.

In the limit of low densities where each atom carries a single electron, the screened exchange interaction is the dominant effect, favoring antiferromagnetism. As soon as the electrons start to travel through the lattice, however, some of the ions have to accommodate two electrons at certain times and others have none. This introduces an electron–hole interaction as well as an intra-atomic interaction. Thus the effective interaction between two atoms depends on the number of electrons involved in the atoms. To include such contributions explicitly, we need to solve the equations of motion for Green functions of the type $\langle\langle N_{j'\alpha}{}^{\pm} N_{j'\beta}{}^{\pm} A_{j\alpha};\ A_{j''\alpha}{}^{\dagger}\rangle\rangle$, where $N_{j\sigma}{}^{+} \equiv N_{j\sigma} = A_{j\sigma}{}^{\dagger} A_{j\sigma}$ and $N_{j\sigma}{}^{-} = 1 - N_{j\sigma}$.

If we neglect Green functions of the type $\langle\langle \cdots A_{j_1\sigma}{}^{\dagger} A_{j_2\sigma} A_{j\alpha};\ A_{j''\alpha}{}^{\dagger}\rangle\rangle$, where $j_1 \neq j, j_2$, and use an appropriate decoupling approximation, the equations can be solved. In case of the fully antiferromagnetic state, where $N_{j_A\alpha} = N_{j_B\beta} = 1$ and $N_{j_A\beta} = N_{j_B\alpha} = 0$, the excitation energies are given by

$$\lambda(k) = \epsilon + \Delta\epsilon_k + \sum_{j^*}{}' V(j^* - j_A)_k + \sum_{j^*}{}' h(j^* - j_A)_k - \sum_{jA^*}{}' h^{ex}(j_A{}^* - j_A)_k, \tag{1}$$

where ϵ is the energy of the atom in free space, j_A an electron in sublattice A, and k is defined by either one of the sublattices, while

$$h(j^* - j)_k = \sum_{j'} (jj^* \mid 1/r_{12} \mid j'j^*) \exp[ik(R_j - R_{j'})], \tag{2}$$

and $\Delta\epsilon_k$, $V(j^* - j)_k$ and $h^{ex}(j^* - j)_k$ are similarly defined as Fourier transforms of integrals $[j \mid T + V(1, R_j) - \epsilon \mid j']$ $[j \mid V(1, R_{j^*}) \mid j']$ and $(jj^* \mid H_{ex} \mid j^*j')$.

Note that the bandwidth has appeared due to the nonvanishing overlap integrals between atomic functions used as basis. If electron j_A is moved to atom j_B, however, we find the following energy spectra for the electron j_B and the hole j_A:

$$\lambda_{j_A \to j_B}(k) = \lambda(k) + h(0)_k - h(j_A - j_B)_k. \tag{3}$$

The intra-atomic interaction $h(0)_k$ is of course the dominant term on the right of (3). This expression shows that the energy required to move an electron from an atomic site j_A to j_B is $h(0)_0 - h(j_A - j_B)_0$ in the low-density limit where the bandwidth $\Delta\lambda$ is negligible. If j_B is a nearest neighbor of j_A, the Coulomb interaction may become appreciable and hence the electron and the hole will form a bound exciton traveling through the lattice. As the distance $R_{jA} - R_{jB}$ increases, the interaction $h(j_A - j_B)_k$ decreases exponentially and the exciton will dissociate into a freely moving electron and hole, yielding a metallic conductivity. The minimum energy required for the conductivity is given by

$$\Delta E = h(0)_{min} - \delta\lambda, \tag{4}$$

where $h(0)_{min}$ is the minimum value of $h(0)_k$, while $\delta\lambda$ is the bandwidth of the spectra $\lambda(k)$ which is relatively small and does not involve $h(0)_k$. At low densities, therefore, the energy gap ΔE is positive demonstrating the insulating characteristics of the lattice.

When the lattice constant decreases and the density increase, the up-spin wave functions will penetrate appreciably into the cells of the down-spin lattice and vice versa. Such an interpenetrating structure may be formed if we assume that atomic functions created by the operators $A_{j\sigma}{}^{\dagger}$ are not simple atomic functions, but the following linear combinations of them:

$$\bar{\phi}_j \sim \phi_j - a \sum_{j' \neq j}{}' (j \mid j')\phi_{j'}. \tag{5}$$

* Based on work performed under the auspices of the U. S. Atomic Energy Commission. A detailed report of this work will be published elsewhere.

[1] T. Arai, Phys. Rev. **165**, 706 (1968).

Since $a(j \mid j')$ decreases exponentially as the distance $R_j - R_{j'}$ increases, $\bar{\phi}_j$ is still localized at the atomic site j and the expression (4) is still valied except that $\delta\lambda$ includes $h(0)_k$ because the functions $\bar{\phi}_j$ provide for chances that two electrons occupy a single atom at certain times. Due to the dominant term $h(0)_k$, the energy gap ΔE will be reduced rapidly with the increase of a, yielding a metallic conductivity without loss of the spin-polarization characteristic of the antiferromagnetism.

In conclusion, the present method will predict a fully antiferromagnetic insulating state in the low-density limit, but, as the lattice constant is gradually reduced, it will lead to an excitonic antiferromagnetic state, a metallic antiferromagnetic state and finally a normal metal.

Discussion of Arai's Paper

W. KOHN (University of California, San Diego): I just want to mention that it seems to me that although the model and method of calculation is very different, the succession of phases is probably related to these nested excitonic phases that we talked about.

T. ARAI: In fact, the order (a fully antiferromagnetic insulator→an excitonic antiferromagnet→a metallic antiferromagnet→a normal metal) is slightly different from the order normally presumed, but the usual order may be observed at finite temperatures as follows. At low temperature, I find an antiferromagnetic insulator, and due to the smallness of the exchange interaction, the Néel point will be low. However, the energy gap depends on the intra-atomic interaction and can be larger than the exchange interaction energy so that the temperature where the metallic state appears can be higher than the Néel point. Consequently, the insulating antiferromagnet will become paramagnetic first and then metallic when the temperature is raised. So far, I have considered a system of one-electron atoms, but if there are degeneracies involved in the atoms, then it is not impossible to find a parallel spin arrangement, just like the ground state of an oxygen molecule is a triplet rather than a singlet. This way I can find ferromagnetism in the present method. Although the method is very close to a localized model, the Fermi surface still cuts through the excitation spectra so that the advantages of both a localized model and band theory are combined in the present method.

H. BROOKS (Harvard University): How does this relate to the so-called Lidiard model that was published some years ago?

T. ARAI: I don't really remember.

H. BROOKS: It looks very similar but I'm not quite sure.