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Electron correlations in narrow energy bands

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It is pointed out that one of the main effects of correlation phenomena in d- and f-bands is to give rise to behaviour characteristic of the atomic or Heitler–London model. To investigate this situation a simple, approximate model for the interaction of electrons in narrow energy bands is introduced. The results of applying the Hartree–Fock approximation to this model are examined. Using a Green function technique an approximate solution of the correlation problem for this model is obtained. This solution has the property of reducing to the exact atomic solution in the appropriate limit and to the ordinary uncorrelated band picture in the opposite limit. The condition for ferromagnetism of this solution is discussed. To clarify the physical meaning of the solution a two-electron example is examined.

1. Introduction

In recent years much attention has been given to the theory of correlation effects in the free electron gas (Bohm & Pines 1953; Gell-Mann & Brueckner 1957; Sawada, Brueckner, Fukuda & Brout 1957; Hubbard 1957, 1958; Pines & Nozières 1958). Apart from the intrinsic interest of this problem, the free electron gas serves as a model for the conduction bands of metals and alloys. Transition and rare-earth metals have in addition to their conduction bands partly filled d- or f-bands which give rise to the characteristic properties of these metals. Correlation phenomena are of great importance in determining the properties of these narrow energy bands, indeed more important than the corresponding effects in conduction bands. Unfortunately, however, the free-electron gas does not provide a good model for these bands. Rather, one requires a theory of correlations which takes into account adequately the atomistic nature of the solid. Indeed, in the case of the f-electrons of rare earth metals it is probable that for most purposes a purely atomic (sometimes referred to as a Heitler–London or localized) model will prove satisfactory. The same cannot be said, however, of the d-electrons of transition metals. It is with one approach to a theory of correlation effects in the d-bands of transition metals that this paper is concerned.

A theory of correlation effects in narrow energy bands is inevitably of a somewhat different nature from a theory of correlation effects in the free electron gas. The electron charge density in a d-band is concentrated near the nuclei of the solid and sparse between the atoms, making it possible to speak with some meaning of an electron being 'on' a particular atom. This circumstance gives rise to the possibility of an atomic description of the d-band despite its considerable bandwidth. It is, in fact, found experimentally that the d-electrons of transition metals exhibit behaviour characteristic of both the ordinary band model and the atomic model. For example, the occurrence of spin-wave phenomena in ferromagnetic metals and the strong temperature dependence of the susceptibilities of some transition metals represent properties which can be understood on the basis of an atomic

model, while the large d-electron contribution to the low temperature specific heat and the occurrence in ferromagnets of magnetic moments per atom which are far from integral numbers of Bohr magnetons are properties which are easily explained by band theory. As will be tried to make plausible below, it is correlation effects in narrow bands which lead to the atomic behaviour and it is only by taking correlation effects into account that one can understand how d-electrons exhibit both kinds of behaviour simultaneously. Thus a theory of correlations in d-bands will be mainly concerned with understanding this situation in greater detail and determining the balance between bandlike and atomic-like behaviour.

In its most naïve form the atomic theory would picture a transition metal as a collection of (say singly charged) ions immersed in the conduction electron gas and interacting with each other in much the same way as the corresponding ions in salts. If, as is generally supposed, the number of d-electrons per atom is non-integral this simple picture is untenable. However, it is possible to substitute for it a less restrictive model which nevertheless guarantees most of the characteristic properties of the atomic model. It is sufficient to assert that, despite the band motion of the d-electrons, the electrons on any atom are strongly correlated with each other but only weakly with electrons on other atoms; such intra-atomic correlations are inevitably of such a type as to make the metal behave to some extent according to the predictions of the atomic model.

It may be that this situation can be made clear by considering one or two examples. Consider first a partly filled d-band of non-interacting electrons. In such a system the spin of an atom (that is the total spin of all the electrons on that atom) is a quantity which fluctuates randomly in magnitude and direction, the characteristic time of fluctuation being of the order of the d-electron hopping time, i.e. the time ($\sim \hbar/\Delta$, $\Delta = d$-electron bandwidth) in which a d-electron hops from one atom to another in performing its band motion. In this situation it is reasonable to think of the spin being associated with each of the moving d-electrons.

Let us now inquire what effect one might expect the electron interaction will have in this situation. As a guide one may note that Hund's first rule for atoms indicates that the intra-atomic interactions are of such a nature as to aline the electron spins on an atom, so one may expect a similar effect in a metal. Suppose now that the electrons have their spins quantized in what will be called the up and down directions and that at some instant a given atom has its total spin in the up direction. Then the intra-atomic interactions are, according to Hund's rule, of such a nature that this atom tends to attract electrons with spin up and repel those with spin down. In this way the property of an atom on having total spin at some instant tends to be self-perpetuating. If these intra-atomic forces are strong enough to produce appreciable correlations, then it follows that the state of total spin up on an atom may persist for a period long compared with the d-electron hopping time. This persistence of the atomic spin state is not due to the same up-spin electrons being localized on the atom. The actual electrons on the atom are always changing as a result of their band motion, but the electron motions are correlated in such a way as to keep a preponderance of up-spin electrons on the atom. In these circumstances (i.e. if the correlations are strong enough) one can think of the spin

as being associated with the atom rather than with the electrons and the possibility of an atomic or Heisenberg model emerges.

This example illustrates the possibilities of the situation. Although one may still suppose the electrons to move rapidly from atom to atom as assumed in the band model, their motion may be correlated in such a manner as to give properties characteristic of the atomic theory. In this way one may understand how the electrons can exhibit both types of behaviour simultaneously. The degree of atomic behaviour exhibited depends upon the strength of the correlations.

A second example which has been studied by various authors (Slater 1937; Herring 1952; Thompson 1960; Edwards 1962; Kubo, Izuyama & Kim 1962) is the theory of spin-waves in the band model of ferromagnetic metals. These authors show that the spin-wave can be regarded as a collective motion which appears when the electron interactions are taken into account. More precisely, the spin-wave appears as a bound state of an electron of one spin with a hole of opposite spin, the relative motion of the electron and hole being such that they spend most of their time on the same atom. Now, an electron of one spin and a hole of opposite spin on the same atom look just like a reversed spin on that atom, the motion of the bound electron-hole pair resembling a motion of the reversed spin from atom to atom, which is just the Heisenberg model picture of a spin-wave. Thus again the atomic picture emerges as a consequence of correlation effects, this time the correlation between an electron and a hole.

Yet another important example concerns the fluctuation in the number of electrons on a given atom. It is, of course, one of the more obvious features of the atomic model that it assumes that there are the same number of electrons on each atom. But one can show that for uncorrelated electrons belonging to a band containing ν states per atom that the probability of finding n electrons on a given atom is given by the binomial distribution

$$\frac{\nu!}{n!\,(\nu-n)!}\left(\frac{s}{\nu}\right)^n\left(1-\frac{s}{\nu}\right)^{\nu-n},$$

where s is the mean number of electrons per atom. Thus n fluctuates about its mean value s, the root-mean-square fluctuation being $\sqrt{\{s(1-s/\nu)\}}$ and the frequency of fluctuation of the order of an electron hopping time. Now one general effect of electrostatic interactions is a tendency to even out the electron charge distribution, opposing the build-up of an excess of charge in one place and a deficiency in another. Thus the correlations produced by the interaction will be of such a nature as to reduce the fluctuation in the electron number on each atom. It is this type of correlation which is most important in the hypothetical case of a collection of atoms arranged on a lattice but widely separated from each other. Formally ordinary band theory is applicable to such a situation, but the correlation effects of the type discussed above are dominant and make the system behave like a set of isolated neutral atoms, which is clearly the correct description physically.

It is clear from the above discussion that an important requirement of a theory of correlations in narrow energy bands is that it have the property of reducing to the atomic solution in the appropriate limit, i.e. when applied to a hypothetical system

of atoms on a lattice but widely separated from each other and interacting only weakly. It is one of the purposes of this paper to describe a very simple, approximate theory having this property. Although one has always in mind the case of d-electrons, the theory to be described is concerned with the case of an s-band having two states per atom (up and down spin states). The advantage of this particular case is its comparative mathematical simplicity. One may expect that some important aspects of the real (d-electron) case will be missed in a study of the s-band case but may nevertheless hope to obtain some results of general application.

It might seem that in view of the fact that no adequate theory of correlations in free electron gases at metallic densities exists at the present time that it is over-ambitious to attempt a study of the formally more difficult case of band electrons. However, it turns out that in the case of narrow energy bands one can take account of the atomicity of the electron distribution to introduce a very simple approximate representation of the electron interactions. This approximate interaction is, in fact, mathematically much simpler to handle than the Coulomb interaction itself. This possibility has been well known for many years and has been applied to the spin-wave problem by the authors mentioned in that connexion above, but does not seem to have been exploited hitherto in connexion with the general correlation problem. In § 2 this approximate interaction and the adequacy of the approximation involved is discussed.

For the sake of comparison with the results of the theory of correlations developed later, in § 3 the application of the Hartree–Fock approximation to the simplified interaction is considered and in particular the condition for ferromagnetism predicted by Hartree–Fock theory is examined.

In §§ 5 and 6 the approximate correlation theory for an s-band mentioned above is developed. To this end a Green function technique of the type described by Zubarev (1960) is used; to establish the notation the basic definitions and equations of this technique are briefly reviewed in § 4. In § 5 it is shown how, using this technique, an exact solution can be obtained in the atomic (zero bandwidth) limit. In § 6 the same method is applied to the general (finite bandwidth) case to obtain the approximate solution. In § 7 the nature and some of the properties of this solution are discussed.

In § 8 we examine a 2-electron problem which has been studied previously in a related context (Slater, Statz & Koster 1953) and which throws some light upon the physical interpretation of the solution obtained in the preceding sections.

Finally in § 9 the condition for ferromagnetism predicted by the new calculation is discussed. It is found to be considerably more restrictive than the corresponding criterion derived from Hartree–Fock theory, and, in fact, can only be satisfied in rather special circumstances.

2. An approximate representation of electron interactions

In this section the approximate model of electron interactions in narrow energy bands used in later calculations is described. As pointed out in the introduction, for reasons of mathematical simplicity the case of an s-band will be considered. However, when discussing below the validity of the various approximations which

have gone into the derivation of the model we shall assume we are dealing with $3d$-transition metal electrons since this is the case of real interest.

Consider a hypothetical partly-filled narrow s-band containing n electrons per atom. The Bloch functions of the band will be denoted by $\psi_{\mathbf{k}}$ and the corresponding energy by $\epsilon_{\mathbf{k}}$ where $\mathbf{k}$ is the wave vector. These wave functions and energies are assumed to have been calculated in some appropriate Hartree–Fock potential representing the average interaction of the s-band electrons with the electrons of other bands and the n electrons per atom of the s-band itself. This Hartree–Fock potential will be assumed to be spin independent so one has the same energies and wave-functions for both spins.

Now let $c_{\mathbf{k}\sigma}$, $c_{\mathbf{k}\sigma}^{+}$ be the destruction and creation operators for electrons in the Bloch state $(\mathbf{k}, \sigma)$, where $\sigma = \pm 1$ is the spin label. Then the dynamics of the electrons of the band may be described approximately by the Hamiltonian

$$
\begin{aligned}
H = {} & \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \\
& + \tfrac{1}{2} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}' \mathbf{k}_2'} \sum_{\sigma_1 \sigma_2} (\mathbf{k}_1 \mathbf{k}_2 | \, 1/r \, | \mathbf{k}_1' \mathbf{k}_2') \, c_{\mathbf{k}_1 \sigma_1}^{\dagger} c_{\mathbf{k}_2 \sigma_2}^{\dagger} c_{\mathbf{k}_2' \sigma_2} c_{\mathbf{k}_1' \sigma_1} \\
& - \sum_{\mathbf{k}\mathbf{k}'} \sum_{\sigma} \{ 2(\mathbf{k}\mathbf{k}' | \, 1/r \, | \mathbf{k}\mathbf{k}') - (\mathbf{k}\mathbf{k}' | \, 1/r \, | \mathbf{k}'\mathbf{k}) \} \, \nu_{\mathbf{k}'} c_{\mathbf{k}\sigma}^{+} c_{\mathbf{k}\sigma}, \quad (1)
\end{aligned}
$$

where the $\mathbf{k}$ sums run over the first Brillouin zone (all sums over momenta in this paper are to be understood in this way) and where

$$
(\mathbf{k}_1 \mathbf{k}_2 \, | \, 1/r \, | \, \mathbf{k}_1' \mathbf{k}_2') = e^2 \int \frac{\psi_{\mathbf{k}_1}^{*}(\mathbf{x}) \, \psi_{\mathbf{k}_1'}(\mathbf{x}) \, \psi_{\mathbf{k}_2}^{*}(\mathbf{x}') \, \psi_{\mathbf{k}_2'}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \, d\mathbf{x} \, d\mathbf{x}'. \quad (2)
$$

The first term of H represents the ordinary band energies of the electrons, the second their interaction energy. The last term subtracts the potential energy of the electrons in that part of the Hartree–Fock field arising from the electrons of the s-band itself. This term has to be subtracted off to avoid counting the interactions of the electrons of the band twice, once explicitly in the Hamiltonian and also implicitly through the Hartree–Fock field determining the $\epsilon_{\mathbf{k}}$. The $\nu_{\mathbf{k}}$ are the assumed occupation numbers of the states of the band in the Hartree–Fock calculation; it has been assumed that up and down spin states are occupied equally.

It is convenient to transform the Hamiltonian of (1) by introducing the Wannier functions

$$
\phi(\mathbf{x}) = N^{-\frac{1}{2}} \sum_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{x}), \quad (3)
$$

where N is the number of atoms. One can then write

$$
\psi_{\mathbf{k}}(\mathbf{x}) = N^{-\frac{1}{2}} \sum_{i} e^{i\mathbf{k}.\mathbf{R}_i} \phi(\mathbf{x} - \mathbf{R}_i), \quad (4)
$$

where the sum runs over all the atomic positions $\mathbf{R}_i$. Introducing the creation and destruction operators $c_{i\sigma}^{\dagger}$ and $c_{i\sigma}$ for an electron of spin σ in the orbital state $\phi(\mathbf{x} - \mathbf{R}_i)$, one can also write

$$
c_{\mathbf{k}\sigma} = N^{-\frac{1}{2}} \sum_{i} e^{i\mathbf{k}.\mathbf{R}_i} c_{i\sigma}, \quad c_{\mathbf{k}\sigma}^{\dagger} = N^{-\frac{1}{2}} \sum_{i} e^{-i\mathbf{k}.\mathbf{R}_i} c_{i\sigma}^{\dagger}. \quad (5)
$$

These results can now be used to rewrite the Hamiltonian of (1) as

$$H = \sum_{i,j} \sum_{\sigma} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \tfrac{1}{2} \sum_{ijkl} \sum_{\sigma\sigma'} (ij \,|1/r|\, kl) \, c_{i\sigma}^{\dagger} c_{j\sigma'}^{\dagger} c_{l\sigma'} c_{k\sigma}$$

$$- \sum_{ijkl} \sum_{\sigma} \{2(ij \,|1/r|\, kl) - (ij \,|1/r|\, lk)\} \, \nu_{jl} c_{i\sigma}^{\dagger} o_{k\sigma}^{\dagger}, \tag{6}$$

where
$$T_{ij} = N^{-1} \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \, e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)}, \tag{7}$$

$$(ij| \, 1/r \, |kl) = e^2 \int \frac{\phi^*(\mathbf{x} - \mathbf{R}_i) \, \phi(\mathbf{x} - \mathbf{R}_k) \, \phi^*(\mathbf{x}' - \mathbf{R}_j) \, \phi(\mathbf{x}' - \mathbf{R}_l)}{|\mathbf{x} - \mathbf{x}'|} \, d\mathbf{x} \, d\mathbf{x}' \tag{8}$$

and
$$\nu_{jl} = N^{-1} \sum_{\mathbf{k}} \nu_{\mathbf{k}} \, e^{i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_l)}. \tag{9}$$

It is now possible to make the essential simplifying approximation. Since one is dealing with a narrow energy band the Wannier functions ϕ will closely resemble atomic s-functions. Furthermore, if the bandwidth is to be small these s-functions must form an atomic shell which has a radius small compared with the inter-atomic spacing. From (8) it may be seen that in this circumstance the integral $(ii| \, 1/r \, |ii) = I$ will be much greater in magnitude than any of the other integrals (8), suggesting that a possible approximation is to neglect all the integrals (8) apart from I. If this approximation, the validity of which is discussed in greater detail below, is made, then the Hamiltonian of (6) becomes

$$H = \sum_{i,j} \sum_{\sigma} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \tfrac{1}{2} I \sum_{i,\sigma} n_{i\sigma} n_{i,-\sigma} - I \sum_{i,\sigma} \nu_{ii} n_{i\sigma}, \tag{10}$$

where $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$. From (9), $\nu_{ii} = N^{-1} \sum_{\mathbf{k}} \nu_{\mathbf{k}} = \tfrac{1}{2}n$, so the last term of (10) reduces to $-\tfrac{1}{2} I n \sum_{i,\sigma} n_{i\sigma} = -\tfrac{1}{2} I N n^2 = \text{constant}$ and may be dropped. Equation (10) gives the approximate Hamiltonian used in the later sections of this paper.

Obviously many approximations, explicit and implicit, have gone into the derivation of the simplified Hamiltonian of (10). We will next try to assess the validity of these approximations when applied to the case of transition metal $3d$-electrons.

The most obvious approximation has been the neglect of all the interaction terms in (6) other than the $(ii| \, 1/r \, |ii)$ term. For the sake of comparison one may note that I has the order of magnitude 20 eV for $3d$-electrons in transition metals. The largest of the neglected terms are those of the type $(ij| \, 1/r \, |ij)$ where i and j are nearest neighbours. From (9) these integrals can be estimated to have the order of magnitude $(2/R) \, \text{Ry} \sim 6 \, \text{eV}$ ($R = $ interatomic spacing in Bohr units). Actually this figure should be reduced appreciably to allow for the screening of the interactions of electrons on different atoms by the conduction electron gas. This screening effect may be allowed for approximately by multiplying the above estimate by a factor $e^{-\kappa R}$ where κ is an appropriate screening constant. In the case of $3d$ transition metals $e^{-\kappa R} \sim \tfrac{1}{3} - \tfrac{1}{2}$, reducing the $(ij| \, 1/r \, |ij)$ term to the order of magnitude 2 to 3 eV. For the case in which i and j are now nearest neighbours

$$(ij| \, 1/r \, |ij) \sim \frac{2e^{-\kappa|\mathbf{R}_i - \mathbf{R}_j|}}{|\mathbf{R}_i - \mathbf{R}_j|} \, \text{Ry}$$

which falls off rapidly with increasing $|\mathbf{R}_i - \mathbf{R}_j|$ on account of the exponential factor. Thus the term

$$\tfrac{1}{2} \sum_{i,j} \sum_{\sigma,\sigma'} (ij| \, 1/r \, |ij) \, n_{i\sigma} n_{j\sigma}, \tag{11}$$

in (6) is quite appreciable, but can, perhaps be neglected compared to I as a first approximation.

The next biggest terms neglected are those of the types:

$$(ii| \, 1/r \, |ij) \sim q \, \mathrm{Ry} \sim \tfrac{1}{2}\mathrm{eV},$$
$$(ij| \, 1/r \, |ik) \sim \tfrac{1}{4}q \, \mathrm{Ry} \sim \tfrac{1}{10}\mathrm{eV},$$
$$(ii| \, 1/r \, |jj) \sim (ij| \, 1/r \, |ji) \sim q^2 \, \mathrm{Ry} \sim \tfrac{1}{40}\mathrm{eV},$$

where i, j and k are all nearest neighbours and $q \sim \tfrac{1}{20}$ is the overlap charge (in units of e) between two $3d$-electrons on nearest neighbour atoms. All the other interaction terms in (6) which have been neglected are smaller still than these which one sees are already small compared to those of (11).

A different type of approximation that has been made is to assume that only the interactions of importance are those between the $3d$-electrons (actually between the electrons of the s-band in the equations above), the interactions with electrons of other bands being represented only through the Hartree–Fock field. One question concerning this point is raised at once by the fact that in estimating the order of magnitude of the terms of (11) allowance was made for the screening effect of the conduction electron gas on the interactions. It might therefore be inquired whether there is not a similar screening effect reducing the magnitude of I. There is, in fact, such an effect. Because the speed at which d-electrons move from atom to atom is slow compared with the velocity of a typical conduction electron the latter can correlate efficiently with the d-electrons and screen their fields. Thus, if a given atom has an extra d-electron its negative charge will repel conduction electrons producing a correlation hole about that atom in the conduction electron gas. The presence of this correlation hole reduces the electrostatic potential at the atom (and therefore at each of its d-electrons) by about 5 V, which is equivalent to reducing I by 5 eV. This reduction is appreciable but does not change the order of magnitude of I.

It might also be thought that I will be reduced by the screening of the interactions of the d-electrons by the core electrons and by the d-electrons themselves. This is not expected to be a big effect, however, because the kinetic energies of the orbital motion of the d-electrons are large compared to I. In fact, one may estimate the reduction in I due to this effect by noticing that a similar effect will occur in free atoms. In the case of free atoms it has been found that these effects make the $F^2(3d, 3d)$ and $F^4(3d, 3d)$ parameters (using the notation of Condon & Shortley 1935) determined from experiment about 10 to 20 % smaller than those calculated from Hartree–Fock wave functions (see Watson 1960) so one may expect a reduction in I of a similar order of magnitude.

It would seem from the above discussion, although it may be more realistic to use in the Hamiltonian of (10) an 'effective' I ($\sim 10\,\mathrm{eV}$) rather than that given by the integral (8), the approximations involved in (10) are otherwise not so poor as to make it an unreasonable starting-point for a theory of correlations when suitably

generalized from the s-band to the d-band case. It may, perhaps, be hoped that the terms omitted in going from (6) to (10) may be treated as perturbations on solutions obtained from (10).

3. The Hartree–Fock approximation

For the sake of comparison with the results of the correlation theory developed in later sections it is convenient now to investigate the results obtained by applying the Hartree–Fock approximation to the Hamiltonian of (10). Actually, we shall not make an exhaustive study of all possible Hartree–Fock solutions, but will restrict attention to a particularly simple class of solutions which may represent non-magnetic or ferromagnetic states but not more complicated spin arrangements. A similar restriction applies also to the correlated solutions investigated in later sections.

As is well known, one may obtain the effective Hartree–Fock Hamiltonian by 'linearizing' the interaction terms in the true Hamiltonian. In the case of the Hamiltonian of (10) this amounts to simply replacing the term $n_{i\sigma} n_{i,-\sigma}$ by $n_{i\sigma} \langle n_{i,-\sigma} \rangle + n_{i,-\sigma} \langle n_{i\sigma} \rangle$ where $\langle n_{i\sigma} \rangle$ is the average of the expectation of $n_{i\sigma}$ over a canonical ensemble at some temperature Θ. Dropping the last term of (10) which has been shown to be a constant, the Hartree–Fock Hamiltonian is found to be

$$H_{hf} = \sum_{i,j} \sum_{\sigma} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + I \sum_{i,\sigma} n_{i\sigma} \langle n_{i,-\sigma} \rangle. \tag{12}$$

Attention will now be restricted to the class of solutions for which

$$\langle n_{i\sigma} \rangle = n_{\sigma} \quad \text{for all } i. \tag{13}$$

Then (12) becomes

$$H_{hf} = \sum_{i,j} \sum_{\sigma} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + I \sum_{i\sigma} n_{-\sigma} c_{i\sigma}^{\dagger} c_{i\sigma}, \tag{14}$$

or, transforming back to the operators $c_{\mathbf{k}\sigma}^{\dagger}$, $c_{\mathbf{k}\sigma}$

$$H_{hf} = \sum_{\mathbf{k}} \sum_{\sigma} \{\epsilon_{\mathbf{k}} + I n_{-\sigma}\} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma}, \tag{15}$$

which is simply the Hamiltonian for a collection of non-interacting electrons with a slightly modified band structure, the energy of the $(\mathbf{k}, \sigma)$ state now being $\epsilon_{\mathbf{k}} + I n_{-\sigma}$. It follows at once that if $P(E)$ is the density of states per atom corresponding to the band structure $\epsilon_{\mathbf{k}}$, then the densities of states $\rho_{\sigma}(E)$, where $\sigma = \pm 1$, for the electrons described by the Hamiltonian of (15) are

$$\rho_{\sigma}(E) = P(E - I n_{-\sigma}) = P(E - I n + I n_{\sigma}), \tag{16}$$

where the last step follows from

$$n_{\uparrow} + n_{\downarrow} = n. \tag{17}$$

If μ is the chemical potential of the electrons, then at the absolute zero of temperature one will have

$$n_{\sigma} = \int_{-\infty}^{\mu} \rho_{\sigma}(E) \, \mathrm{d}E = \int_{-\infty}^{\mu} P(E - I n + I n_{\sigma}) \, \mathrm{d}E. \tag{18}$$

The pair of equations (18) must now be solved together with (17) for $n_{\uparrow}$, $n_{\downarrow}$ and μ.

One possible solution of (18) is that for which

$$n_\uparrow = n_\downarrow = \tfrac{1}{2}n, \tag{19}$$

which represents a non-magnetic state of the system: μ is determined by

$$\tfrac{1}{2}n = \int_{-\infty}^{\mu} P(E - \tfrac{1}{2}In)\,dE. \tag{20}$$

If I is sufficiently large it may also be possible to find ferromagnetic solutions for which $n_\uparrow \neq n_\downarrow$. In this case equation (18) must have two distinct solutions which are such that they can satisfy (17). The condition that ferromagnetism is just possible can now easily be seen to be the condition that (19) and (20) give a double solution of (18). But this condition can at once be found from (18) to be

$$1 = IP(\mu - \tfrac{1}{2}In). \tag{21}$$

Thus, if for any E the condition $IP(E) > 1$ is satisfied, then for some n and μ determined by (20) and (21) Hartree–Fock theory predicts that the system will become ferromagnetic. It will be found that when correlation effects are taken into account one obtains a somewhat more restrictive condition for ferromagnetism.

4. A Green function technique

In the next two sections an approximate solution of the correlation problem for the Hamiltonian of (10) is derived. The method of calculation is based upon the Green function technique described by Zubarev (1960). In order to establish the notation, the principal definitions and basic equations of this technique are briefly reviewed in this section.

Let X be any operator. Then define

$$\langle X \rangle = Z^{-1} \operatorname{tr}\{X\, e^{-\beta(H-\mu N)}\}, \quad Z = \operatorname{tr}\{e^{-\beta(H-\mu N)}\}, \tag{22}$$

where H is the Hamiltonian and N the total number operator, $\beta = 1/\kappa\Theta$, $\kappa =$ Boltzmann's constant, $\Theta =$ absolute temperature and $\mu =$ chemical potential of the electrons.

Now let $A(t) = e^{iHt}A(0)\,e^{-iHt}$ (in units in which $\hbar = 1$) and $B(t')$ be two operators. Then retarded ($+$) and advanced ($-$) Green functions may be defined by

$$\langle\langle A(t); B(t') \rangle\rangle^{(\pm)} = \mp\, i\theta\{\pm(t-t')\}\,\langle[A(t), B(t')]_\eta\rangle, \tag{23}$$

where $[A, B]_\eta = AB - \eta BA$, $\eta = \pm 1$ (whichever is the more convenient), and $\theta(x)$ is the step function $\theta(x) = 1$ if $x > 0$, $= 0$ otherwise. These Green functions can be shown to satisfy the equation of motion

$$i\frac{d}{dt}\langle\langle A(t); B(t')\rangle\rangle^{(\pm)} = \delta(t-t')\,\langle[A(t), B(t)]_\eta\rangle + \langle\langle[A(t), H]; B(t')\rangle\rangle^{(\pm)}. \tag{24}$$

Since $\langle\langle A(t); B(t')\rangle\rangle^{(\pm)}$ are functions of $t-t'$ only, one can define for real E the Fourier transforms

$$\langle\langle A; B\rangle\rangle_E^{(\pm)} = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle A(t); B(0)\rangle\rangle^{(\pm)}\,e^{iEt}\,dt. \tag{25}$$

In the case of the retarded $(+)$ function the integral (25) converges also for complex E provided $\mathscr{I}E > 0$, so $\langle\langle A; B \rangle\rangle_E^{(+)}$ can be defined and is a regular function of E in the upper half of the complex E-plane. Similarly, $\langle\langle A; B \rangle\rangle_E^{(-)}$ is a regular function in the lower half of the complex E-plane. One may now define

$$\langle\langle A; B \rangle\rangle_E = \langle\langle A; B \rangle\rangle_E^{(+)} \quad \text{if} \quad \mathscr{I}E > 0,$$
$$\langle\langle A; B \rangle\rangle_E^{(-)} \quad \text{if} \quad \mathscr{I}E < 0, \tag{26}$$

which will be a function regular throughout the whole complex E-plane except on the real axis. From (24) it can be shown that $\langle\langle A; B \rangle\rangle_E$ satisfies

$$E \langle\langle A; B \rangle\rangle_E = 1/2\pi \langle [A, B]_\eta \rangle + \langle\langle [A, H]; B \rangle\rangle_E. \tag{27}$$

It can be shown (Zubarev 1960) that

$$\langle B(t') A(t) \rangle = i \lim_{\epsilon \to 0+} \int_{-\infty}^{\infty} [\langle\langle A; B \rangle\rangle_{E+i\epsilon} - \langle\langle A; B \rangle\rangle_{E-i\epsilon}] \frac{e^{-iE(t-t')}}{e^{\beta(E-\mu)} - \eta} \, dE. \tag{28}$$

Equations (27) and (28) together with the method of approximation described by Zubarev (1960) form the essential basis of calculations with these Green functions.

5. The exact solution in the atomic limit

In this section the application of the technique described in the preceding section to the Hamiltonian (10) in the limiting case of zero bandwidth is discussed. This limit corresponds to the situation in which the wave functions on different atoms have only a negligible overlap, in which case one knows that the atomic theory gives the exact solution. It will be shown that in this case the Green function technique also leads to an exact solution. Of course, for the Hamiltonian (10) the results of these calculations are rather trivial, but they do serve to reveal the essential trick required to make more elaborate theories go over into the exact atomic solution in the appropriate limit.

All effort will be concentrated on obtaining an expression for the Green's function.

$$G_{jk}^{\sigma}(E) = \langle\langle c_{j\sigma}; c_{k\sigma}^{\dagger} \rangle\rangle_E \quad (\eta = -1), \tag{29}$$

since, as is well known, a knowledge of this Green function enables one to calculate pseudo-particle energies, the Fermi energy, free energy, etc. For example, substituting (29) into (28), putting $j = k$, $t - t' = 0$ and summing on j, one obtains for the mean number n_σ of electrons per atom of spin σ the expression

$$n_\sigma = N^{-1} \sum_j \langle c_{j\sigma}^{\dagger} c_{j\sigma} \rangle$$
$$= \frac{i}{N} \lim_{\epsilon \to 0+} \sum_j \int [G_{jj}^{\sigma}(E + i\epsilon) - G_{jj}^{\sigma}(E - i\epsilon)] \frac{dE}{e^{\beta(E-\mu)} + 1}, \tag{30}$$

from which one may infer that

$$\rho_\sigma(E) = \frac{i}{N} \lim_{\epsilon \to 0+} \sum_j [G_{jj}^{\sigma}(E + i\epsilon) - G_{jj}^{\sigma}(E - i\epsilon)] \tag{31}$$

gives the density of (pseudo-particle) states per atom of spin σ.

Define

$$T_0 = N^{-1} \sum_{\mathbf{k}} \epsilon_{\mathbf{k}}; \tag{32}$$

T_0 is the mean band energy. In the limit of zero bandwidth $\epsilon_{\mathbf{k}} = T_0$ for all $\mathbf{k}$, whence it follows that $T_{ij} = T_0 \delta_{ij}$ and the Hamiltonian (10) becomes

$$H = T_0 \sum_{i,\sigma} n_{i\sigma} + \tfrac{1}{2} I \sum_{i,\sigma} n_{i\sigma} n_{i,-\sigma}, \tag{33}$$

from which it follows that

$$[c_{i\sigma}, H] = T_0 c_{i\sigma} + I c_{i\sigma} n_{i,-\sigma}, \tag{34}$$

so equation (27) gives

$$E G_{ij}^{\sigma}(E) = \frac{1}{2\pi} \delta_{ij} + T_0 G_{ij}^{\sigma}(E) + I \Gamma_{ij}^{\sigma}(E), \tag{35}$$

where

$$\Gamma_{ij}^{\sigma}(E) = \langle\langle n_{i\,-\sigma} c_{i\sigma}; c_{j\sigma}^{\dagger} \rangle\rangle_E \quad (\eta = -1). \tag{36}$$

Now, $[n_{i,-\sigma} c_{i\sigma}, c_{j\sigma}^{\dagger}]_+ = \delta_{ij} n_{i,-\sigma}$; also from (33) $[n_{i\sigma}, H] = 0$, so (27) gives for $\Gamma_{ij}^{\sigma}(E)$ the equation

$$E \Gamma_{ij}^{\sigma}(E) = \frac{1}{2\pi} \delta_{ij} \langle n_{i,-\sigma} \rangle + T_0 \Gamma_{ij}^{\sigma} + I \langle\langle n_{i,-\sigma}^2 c_{i\sigma}; c_{j\sigma}^{\dagger} \rangle\rangle_E. \tag{37}$$

At this point one may notice that since $n_{i\sigma}^2 = n_{i\sigma}$, the last term of (37) is just $I \Gamma_{ij}^{\sigma}$, so (37) can be solved at once to give

$$\Gamma_{ij}^{\sigma}(E) = \frac{1}{2\pi} \delta_{ij} \frac{\langle n_{i,-\sigma} \rangle}{E - T_0 - I}. \tag{38}$$

The usual infinite sequence of equations of the type (27) involving higher and higher order Green functions has been avoided here by the simple observation that the last term of (37) can be expressed in terms of Γ_{ij}^{σ}. It is this possibility that enables one to obtain an exact solution in the present case and solutions reducing to the correct solution in the zero bandwidth limit in the general case discussed in the next section.

It follows from the definition (22) and the symmetry of the problem that $\langle n_{i\sigma} \rangle$ is independent of i and σ, so one has at once $\langle n_{i\sigma} \rangle = \tfrac{1}{2} n$. Using this result and substituting (38) into (35) one obtains

$$G_{ij}^{\sigma}(E) = \frac{1}{2\pi} \delta_{ij} \left\{ \frac{1 - \tfrac{1}{2} n}{E - T_0} + \frac{\tfrac{1}{2} n}{E - T_0 - I} \right\}, \tag{39}$$

which gives at once from (31)

$$\rho_{\sigma}(E) = (1 - \tfrac{1}{2} n) \delta(E - T_0) + \tfrac{1}{2} n \delta(E - T_0 - I). \tag{40}$$

Thus the calculation shows that the system behaves as though it has two energy levels T_0 and $T_0 + I$ containing $1 - \tfrac{1}{2} n$ and $\tfrac{1}{2} n$ states per atom respectively. Thus as electrons are added to the band, initially the Fermi-energy will be fixed at $\mu = T_0$ whilst the lower level fills up. The lower level will become full when $\tfrac{1}{2} n = 1 - \tfrac{1}{2} n$, i.e. $n = 1$, and the chemical potential μ then jumps to $\mu = T_0 + I$ whilst the remaining electrons are added. This is just the correct result. As electrons are added they will (at $\Theta = 0$) distribute themselves on different atoms giving $\mu = T_0$ until when $n = 1$ this is no longer possible and any further electrons added have to go on atoms which have already one electron so μ jumps to $T_0 + I$. A similar discussion can be given for other properties such as specific heat, behaviour in a magnetic field, at $\Theta = 0$ and at finite temperatures; in all cases the Green function solution yields the correct result for a collection of isolated atoms.

6. AN APPROXIMATE SOLUTION OF THE CORRELATION PROBLEM

In this section the correlation problem for the Hamiltonian (10) will be studied in the finite bandwidth case by the same technique used in the last section. In the present calculation, however, certain additional terms appear which have to be treated approximately to obtain a solution.

Returning to the Hamiltonian (10), one finds

$$[c_{i\sigma}, H] = \sum_j T_{ij} c_{j\sigma} + I n_{i,-\sigma} c_{i\sigma}, \tag{41}$$

$$[n_{i\sigma}, H] = \sum_j T_{ij} (c_{i\sigma}^\dagger c_{j\sigma} - c_{j\sigma}^\dagger c_{i\sigma}), \tag{42}$$

so the equation for G_{ij}^σ defined by (29) becomes

$$E G_{ij}^\sigma(E) = \frac{1}{2\pi} \delta_{ij} + \sum_k T_{ik} G_{kj}^\sigma + I \Gamma_{ij}^\sigma, \tag{43}$$

where Γ_{ij}^σ is again defined by (36), but now satisfies the equation

$$E \Gamma_{ij}^\sigma(E) = \frac{1}{2\pi} \delta_{ij} \langle n_{i,-\sigma} \rangle + T_0 \Gamma_{ij}^\sigma + I \Gamma_{ij}^\sigma$$

$$+ \sum_{k \neq i} T_{ik} \langle\langle n_{i,-\sigma} C_{k\sigma}; c_{j\sigma}^\dagger \rangle\rangle_E$$

$$+ \sum_{k \neq i} T_{ik} \{ \langle\langle c_{i,-\sigma}^\dagger c_{k,-\sigma} c_{i\sigma}; c_{j\sigma}^\dagger \rangle\rangle_E - \langle\langle c_{k,-\sigma}^\dagger c_{i,-\sigma} c_{i\sigma}; c_{j\sigma}^\dagger \rangle\rangle_E \}. \tag{44}$$

The term $I \Gamma_{ij}^\sigma$ has been obtained by using $n_{i,-\sigma}^2 = n_{i,-\sigma}$, while the term $T_0 \Gamma_{i,j}^\sigma$ has been obtained by separating out the $i = k$ part of the fourth term. The first three terms are identical with those of (37) while the latter pair of terms vanish in the zero band-width limit. Thus, whatever approximations are made in the last pair of terms of (44), one will obtain a theory that goes over into the exact solution in the zero bandwidth limit.

In order to break off the sequence of Green function equations an approximate expression will be substituted for the last pair of terms in (44). These approximations are obtained by the methods indicated by Zubarev, and are given by

$$\langle\langle n_{i,-\sigma} c_{k\sigma}; c_{j\sigma}^\dagger \rangle\rangle_E \simeq \langle n_{i,-\sigma} \rangle G_{kj}^\sigma(E); \tag{45}$$

$$\langle\langle c_{i,-\sigma}^\dagger c_{k,-\sigma} c_{i\sigma}; c_{j\sigma}^\dagger \rangle\rangle_E \simeq \langle c_{i,-\sigma}^\dagger c_{k-\sigma} \rangle G_{ij}^\sigma(E); \tag{46}$$

$$\langle\langle c_{k-\sigma}^\dagger c_{i,-\sigma} c_{i\sigma}; c_{j\sigma}^\dagger \rangle\rangle_E \simeq \langle c_{k-\sigma}^\dagger C_{i,-\sigma} \rangle G_{ij}^\sigma(E). \tag{47}$$

By making these approximations one obtains what is practically the crudest theory possible consistent with the condition that it reduces to the correct zero bandwidth limit. One shortcoming of the theory which arises from these approximations is pointed out in § 8.

Other important physical effects neglected as a consequence of these approximations are associated with collective motions of the spin-wave type (see authors cited in the Introduction) and zero-sound type (Landau 1957).

With the approximations (46), (47), the last term of (44) vanishes as a consequence of translational symmetry, since

$$\sum_{k \neq i} T_{ik} \langle c_{i,-\sigma}^{\dagger} c_{k,-\sigma} \rangle = N^{-1} \sum_{i,k}' T_{ik} \langle c_{i,-\sigma} c_{k,-\sigma} \rangle$$

$$= N^{-1} \sum_{i,k}' T_{ik} \langle c_{k,-\sigma}^{\dagger} c_{i,-\sigma} \rangle = \sum_{k \neq i} T_{ik} \langle c_{k,-\sigma}^{\dagger} c_{i,-\sigma} \rangle,$$

where $T_{ik} = T_{ki}$ which follows from $\epsilon_{\mathbf{k}} = \epsilon_{-\mathbf{k}}$ has been used, and $\sum_{i,k}'$ means the double sum with the term $i = k$ omitted.

In (45) we will now put
$$\langle n_{i\sigma} \rangle = n_{\sigma}, \tag{48}$$

which follows from translational symmetry. Strictly speaking it follows from the symmetry of the problem that n_{σ} is independent of σ and therefore equal to $\frac{1}{2}n$. However, it would seem intuitively evident that when solutions of the equations with $n_{\uparrow} \neq n_{\downarrow}$ exist, these solutions are connected with the possible ferromagnetism of the system (provided they have lower energy than the non-magnetic solution). One can, perhaps, rationalize this situation by imagining that a minute magnetic field is applied to the system; this field destroys the symmetry between up and down spin, but is so small that it can be neglected in the calculations. To discuss this situation in detail would go far beyond the scope and intent of the present paper. It may be remarked that a similar situation exists in the zero bandwidth case discussed in the preceding section, but that nothing new would be found there by considering solutions for which $n_{\uparrow} \neq n_{\downarrow}$. One might also inquire whether meaning can be assigned to solutions (forbidden by symmetry) for which $\langle n_{i\sigma} \rangle$ is not independent of i or even for which quantities like $\langle c_{i\sigma}^{\dagger} c_{j,-\sigma} \rangle$ do not vanish. The answer would seem to be that these solutions correspond to the possibilities of antiferromagnetism, spiral spin arrangements, etc., but only solutions falling under (46) will be investigated here.

Substituting the approximations (45) to (47) into (44) one obtains

$$E\Gamma_{ij}^{\sigma} = n_{-\sigma} \frac{\delta_{ij}}{2\pi} + (T_0 + I)\, \Gamma_{ij}^{\sigma} + n_{-\sigma} \sum_{k \neq i} T_{ik} G_{kj}^{\sigma}, \tag{49}$$

whence
$$\Gamma_{ij}^{\sigma}(E) = \frac{n_{-\sigma}}{E - T_0 - I} \left\{ \frac{\delta_{ij}}{2\pi} + \sum_{k \neq i} T_{ik} G_{kj}^{\sigma} \right\}, \tag{50}$$

which when substituted into (43) gives

$$E G_{ij}^{\sigma}(E) = T_0 G_{ij}^{\sigma} + \left\{ 1 + \frac{I n_{-\sigma}}{E - T_0 - I} \right\} \left\{ \frac{\delta_{ij}}{2\pi} + \sum_{k \neq i} T_{ik} G_{kj}^{\sigma} \right\}. \tag{51}$$

This equation may be solved by Fourier transformation. Writing

$$G_{ij}^{\sigma}(E) = N^{-1} \sum_{\mathbf{q}} G^{\sigma}(\mathbf{q}, E) \exp\left[i\mathbf{q} . (\mathbf{R}_i - \mathbf{R}_j) \right] \tag{52}$$

and using (7), one obtains from (51)

$$E G^{\sigma}(\mathbf{q}, E) = T_0 G^{\sigma}(\mathbf{q}, E) + \left\{ 1 + \frac{I n_{-\sigma}}{E - T_0 - I} \right\} \left\{ \frac{1}{2\pi N} + (\epsilon_{\mathbf{q}} - T_0) G^{\sigma}(\mathbf{q}, E) \right\}, \tag{53}$$

whence
$$G^\sigma(\mathbf{q}, E) = \frac{1}{2\pi N} \frac{E - T_0 - I(1 - n_{-\sigma})}{(E - \epsilon_\mathbf{q})(E - T_0 - I) + n_{-\sigma}I(T_0 - \epsilon_\mathbf{q})}, \tag{54}$$

which gives the approximate solution to the correlation problem which has been sought. The properties of this solution are discussed in the next section.

7. Properties of the approximate solution

The general nature of the solution given by (54) will next be investigated. The expression (54) for $G^\sigma(E)$ is a rational function of E and may be resolved into partial fractions according to

$$G^\sigma(\mathbf{q}, E) = \frac{1}{2\pi N} \frac{1}{E^{(1)}_{\mathbf{q}\sigma} - E^{(2)}_{\mathbf{q}\sigma}} \left\{ \frac{E^{(1)}_{\mathbf{q}\sigma} - T_0 - I(1 - n_{-\sigma})}{E - E^{(1)}_{\mathbf{q}\sigma}} - \frac{E^{(2)}_{\mathbf{q}\sigma} - T_0 - I(1 - n_{-\sigma})}{E - E^{(2)}_{\mathbf{q}\sigma}} \right\}, \tag{55}$$

where $E^{(1)}_{\mathbf{q}\sigma} < E^{(2)}_{\mathbf{q}\sigma}$ are the two roots of

$$(E - \epsilon_\mathbf{q})(E - T_0 - I) + n_{-\sigma}I(T_0 - \epsilon_\mathbf{q}) = 0. \tag{56}$$

It can be shown that $E^{(1)}_{\mathbf{q}\sigma} < T_0 + I(1 - n_{-\sigma}) < E^{(2)}_{\mathbf{q}\sigma}$, so (56) has the form

$$G^\sigma(\mathbf{q}, E) = \frac{1}{2\pi N} \left\{ \frac{A^{(1)}_{\mathbf{q}\sigma}}{E - E^{(1)}_{\mathbf{q}\sigma}} + \frac{A^{(2)}_{\mathbf{q}\sigma}}{E - E^{(2)}_{\mathbf{q}\sigma}} \right\}, \tag{57}$$

with $A^{(1)}_{\mathbf{q}\sigma}, A^{(2)}_{\mathbf{q}\sigma} > 0$. If one had $A^{(1)}_{\mathbf{q}\sigma} = A^{(2)}_{\mathbf{q}\sigma} = 1$, then the expression (57) would be the Green function appropriate to a band structure having two bands with the dispersion laws $E = E^{(1)}_{\mathbf{q}\sigma}$ and $E = E^{(2)}_{\mathbf{q}\sigma}$. The effect of the factors $A^{(i)}_{\mathbf{q}\sigma}$ cannot be given any very simple interpretation beyond saying that they reduce the density of states in each band in such a way that the total number of states per atom in both bands together is just 1 and not 2 as it would be if $A^{(1)}_{\mathbf{q}\sigma} = A^{(2)}_{\mathbf{q}\sigma} = 1$. One may see this directly by noticing that from (31) and (52) one has

$$\rho_\sigma(E) = i \lim_{\epsilon \to 0+} \sum_\mathbf{q} \{ G^\sigma(\mathbf{q}, E + i\epsilon) - G^\sigma(\mathbf{q}, E - i\epsilon) \}, \tag{58}$$

which gives on substitution of the expression (57) for $G^\sigma(\mathbf{q}, E)$

$$\rho_\sigma(E) = N^{-1} \sum_\mathbf{q} \{ A^{(1)}_{\mathbf{q}\sigma} \delta[E - E^{(1)}_{\mathbf{q}\sigma}] + A^{(2)}_{\mathbf{q}\sigma} \delta[E - E^{(2)}_{\mathbf{q}\sigma}] \}, \tag{59}$$

and finally noting that
$$A^{(1)}_{\mathbf{q}\sigma} + A^{(2)}_{\mathbf{q}\sigma} = 1. \tag{60}$$

The general form of the band structure $E^{(1)}_{\mathbf{q}\sigma}, E^{(2)}_{\mathbf{q}\sigma}$ given by (56) is sketched in figure 1. In the limit $I \to 0$, the lower $E^{(1)}_{\mathbf{q}\sigma}$ curve goes over into APX and at the same time $A^{(1)}_{\mathbf{q}\sigma} \to 1$ along AP and $A^{(1)}_{\mathbf{q}\sigma} \to 0$ along PX. Similarly, the upper curve goes over into BPY, $A^{(2)}_{\mathbf{q}\sigma} \to 1$ along PY. Thus as the interaction is switched off the two portions AP and PY combine to make up the unperturbed band structure, the other parts disappearing. That $G^\sigma(E)$ goes over into the unperturbed Green function $(2\pi N)^{-1}(E - \epsilon_\mathbf{q})^{-1}$ as $I \to 0$ can also be seen directly from (54).

In the limit of zero bandwidth, $\epsilon_\mathbf{q} \to T_0$, the $E^{(1)}_{\mathbf{q}\sigma}, E^{(2)}_{\mathbf{q}\sigma}$ curves become flat and go into $E^{(1)}_{\mathbf{q}\sigma} = T_0$, $E^{(2)}_{\mathbf{q}\sigma} = T_0 + I$, giving the two levels containing $(1 - n_{-\sigma})$ and $n_{-\sigma}$ states respectively discussed in § 5, the expression (59) going over into that of (40) after $\mathbf{q}$-summation.

Next, a more explicit expression than (59) for $\rho_\sigma(E)$ will be derived. From (55) and (58) one can obtain after a little manipulation the formula

$$\rho_\sigma(E) = |E - T_0 - I(1 - n_{-\sigma})|\, N^{-1} \sum_q \delta[(E - \epsilon_q)(E - T_0 - I) + In_{-\sigma}(T_0 - \epsilon_q)]$$

$$= \int_{-\infty}^{\infty} dt\, |E - T_0 - I(1 - n_{-\sigma})|\, \delta[(E - t)(E - T_0 - I) + In_{-\sigma}(T_0 - t)] N^{-1} \sum_q \delta[t - \epsilon_q]$$

$$= \int_{-\infty}^{\infty} dt\, P(t)\, \delta\left[\frac{E(E - T_0 - I) + In_{-\sigma}T_0}{E - T_0 - I(1 - n_{-\sigma})} - t\right]$$
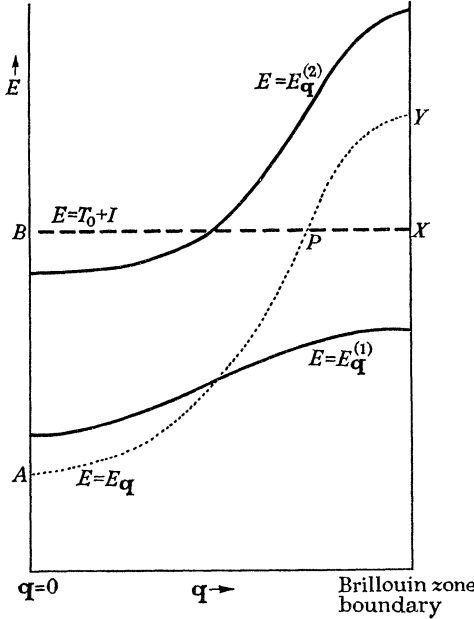
$$= P\{g(E, n_{-\sigma})\}, \tag{61}$$

FIGURE 1. A sketch of a typical pseudo-particle band structure $E_{q\sigma}^{(1)}$, $E_{q\sigma}^{(2)}$. APY gives the unperturbed band structure while BPX is the line $E = T_0 + I$.

where

$$g(E, n_{-\sigma}) = E - In_{-\sigma} - \frac{I^2 n_{-\sigma}(1 - n_{-\sigma})}{E - T_0 - I(1 - n_{-\sigma})} \tag{62}$$

and

$$P(E) = N^{-1} \sum_q \delta(E - \epsilon_q) \tag{63}$$

is the density of states corresponding to the band structure ϵ_k.

Thus $\rho_\sigma(E)$ is obtained from $P(E)$ by the simple transformation (61), (62). This transformation is illustrated graphically in figure 2 which shows a typical $g(E)$ curve and the projection of $P(E)$ into $\rho_\sigma(E)$. In the limit $I \to 0$ the curve $g(E)$ goes over into the straight line AOB. The splitting of the band into two parts is seen to be due to the infinity of $g(E)$ at $E = T_0 + I(1 - n_{-\sigma})$.

In order to obtain some feel for the properties of the solution, it is, perhaps, useful to consider the simple example given by the 'square' density of states formula

$$P(E) = 1/\Delta \quad \text{if} \quad T_0 - \tfrac{1}{2}\Delta < E < T_0 + \tfrac{1}{2}\Delta$$

$$= 0 \qquad \text{otherwise}, \tag{64}$$

for which one easily finds

$$\rho_\sigma(E) = 1/\Delta \quad \text{if} \quad E^\sigma_{-1,-1} < E < E^\sigma_{-1,1}$$

or

$$\text{if} \quad E^\sigma_{1,-1} < E < E_{1,1},$$

$$= 0 \quad \text{otherwise}, \tag{65}$$

where $(\alpha, \beta = \pm 1)$

$$E^\sigma_{\alpha\beta} = T_0 + \tfrac{1}{2}I + \tfrac{1}{4}\beta\Delta + \alpha\sqrt{\{(\tfrac{1}{2}I - \tfrac{1}{4}\beta\Delta)^2 + \tfrac{1}{2}\beta\Delta I n_{-\sigma}\}}. \tag{66}$$

One may note that since $(E_{-1,1} - E_{-1,-1}) + (E_{1,1} - E_{1,-1}) = \Delta$, the $\rho_\sigma(E)$ band contains just one state per atom as it must.
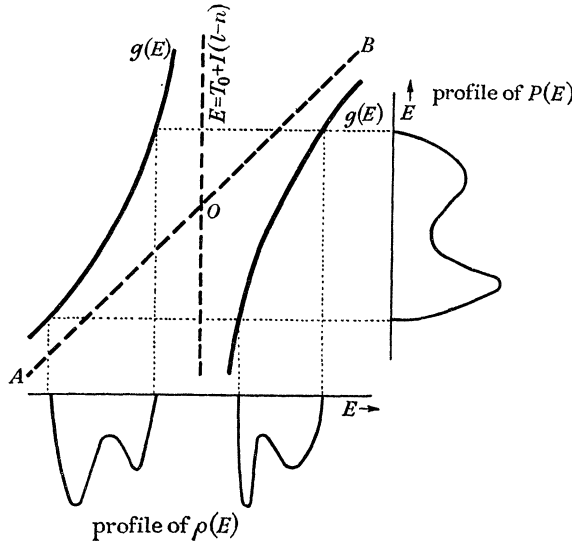

FIGURE 2. A sketch of a typical $g(E, n)$ curve. The projection of the unperturbed density of states function $P(E)$ into the pseudo-particle density of states $\rho_\sigma(E)$ is indicated.

Turning attention now to non-magnetic solutions for which $n_\uparrow = n_\downarrow = \tfrac{1}{2}n$ (ferromagnetic solutions will be considered in § 9), the Fermi energy μ will be determined by the equation

$$\tfrac{1}{2}n = \int_{-\infty}^{\mu} P\{g(E, \tfrac{1}{2}n)\} \, \mathrm{d}E. \tag{67}$$

Thus μ increases as electrons are added until the lower band is just full. It will then jump discontinuously as further electrons are added and then continue to increase smoothly until the whole band is full. If $E_{\max.}$, $E_{\min.}$ are the highest and lowest energies of the band structure one can see at once from figure 2 that this jump occurs from a value $\mu_<$ to a value $\mu_>$ at a density n_c determined by the equations

$$E_{\max.} = g(\mu_<, \tfrac{1}{2}n_c), \tag{68}$$

$$E_{\min.} = g(\mu_>, \tfrac{1}{2}n_c), \tag{69}$$

$$\tfrac{1}{2}n_c = \int_{-\infty}^{\mu_<} P\{g(E, \tfrac{1}{2}n_c)\} \, \mathrm{d}E,$$

where in (68) the smaller and in (69) the larger root must be taken.

In general $n_c \neq 1$, but in the case of the density of states curve (64), the symmetry between electrons and holes or, to be more precise, the fact that in this case $P(E)$ has the property $P(2T_0 - E) = P(E)$, requires that $n_c = 1$, giving a discontinuity in μ of

$$\mu_> - \mu_< = \sqrt{(I^2 + \tfrac{1}{4}\Delta^2)} - \tfrac{1}{2}\Delta, \tag{70}$$

which goes to 0 as $I \to 0$ and tends to I as $\Delta \to 0$.

8. A TWO-ELECTRON EXAMPLE

In order to obtain a better physical understanding of the solution obtained in the preceding sections, and in particular how the band splits into two parts, it is instructive to consider the problem of two electrons moving and interacting in the manner described by the Hamiltonian (10). Essentially the same problem has been considered by Slater *et al.* (1953) who were mainly interested in the effect of correlations on the condition for ferromagnetism.

Denote by $\psi(i, j)$ the spatial wave function of an eigenstate of the two electron system, $|\psi(i, j)|^2$ measuring the probability of finding one electron on atom i and the other on atom j. Of the $4N^2$ possible states of the system $3N^2$ are spin triplets for which $\psi(i, j) = -\psi(j, i)$, and the other N^2 are singlet states for which $\psi(i, j) = \psi(j, i)$. If $\psi(i, j)$ is an eigenstate with energy E of the Hamiltonian (10), then

$$E\psi(i, j) = \sum_k T_{ik}\psi(k, j) + \sum_k T_{jk}\psi(i, k) + I\delta_{ij}\psi(i, i). \tag{71}$$

Since for the triplet states $\psi(i, i) = 0$, the last term of (71) vanishes for these states, so the triplet states are quite undisturbed by the interaction. This is simply because the Hamiltonian (10) only contains interactions between electrons of opposite spin. Thus attention can be restricted to the singlet states.

In the singlet case we now write

$$\psi(i, j) = N^{-1} \sum_{\mathbf{K}} \sum_{\mathbf{k}} \phi(\mathbf{k}, \mathbf{K}) \exp\{i\mathbf{K}.(\mathbf{R}_i + \mathbf{R}_j) + \tfrac{1}{2}i\mathbf{k}.(\mathbf{R}_i - \mathbf{R}_j)\}. \tag{72}$$

Substituting this into (71) and using (7) one obtains

$$E\phi(\mathbf{k}, \mathbf{K}) = \{\epsilon_{\mathbf{K}+\frac{1}{2}\mathbf{k}} + \epsilon_{\mathbf{K}-\frac{1}{2}\mathbf{k}}\} \phi(\mathbf{k}, \mathbf{K}) + IN^{-1} \sum_{\mathbf{k}'} \phi(\mathbf{k}', \mathbf{K}). \tag{73}$$

Thus solutions with different 'total momentum' $\mathbf{K}$ are not coupled to each other, a consequence of translational symmetry. From (73) one has at once

$$\phi(\mathbf{k}, \mathbf{K}) = \frac{IN^{-1} \sum_{\mathbf{k}'} \phi(\mathbf{k}', \mathbf{K})}{E - \epsilon_{\mathbf{K}+\frac{1}{2}\mathbf{k}} - \epsilon_{\mathbf{K}-\frac{1}{2}\mathbf{k}}} \tag{74}$$

whence

$$1 = \frac{I}{N} \sum_{\mathbf{k}} \frac{1}{E - \epsilon_{\mathbf{K}+\frac{1}{2}\mathbf{k}} - \epsilon_{\mathbf{K}-\frac{1}{2}\mathbf{k}}} \tag{75}$$

gives the energy levels for a given $\mathbf{K}$.

The nature of the solutions of equations of the type (75) are well known. The equation has N roots. The right-hand side has infinities at the N energies given by

$$E = \epsilon_{\mathbf{K}+\frac{1}{2}\mathbf{k}} + \epsilon_{\mathbf{K}-\frac{1}{2}\mathbf{k}} \tag{76}$$

for the N values of $\mathbf{k}$, so there are $(N-1)$ roots trapped between these infinities. These $N-1$ roots lie in the unperturbed energy band given by (76). There is one other root. For large enough I this root is quite separate from the band (76), forming a 'bound' state. When I is large compared to the width of the band (76), this root is given by T_0+I as may easily be seen from (75). For small I this 'bound' state does not separate from the band (76).

Thus for large I there are $N(N-1)$ singlet 'scattering' states lying in the unperturbed band and N 'bound' states (one for each of the N values $\mathbf{K}$) with high energy. In the limit $I \to \infty$ the latter states disappear altogether. This is a result of an 'excluded' volume effect of the type familiar from van der Waals's equation. When $I \to \infty$ no two electrons can be on the same site. Thus if one electron is already present (in any one of its N possible states) and another electron is added, then there are only $N-1$ states available to this second electron, whence it follows that there are only $N(N-1)$ possible states available to the two electron system rather than the N^2 possible states for a pair of non-interacting electrons. When I is large but finite the remaining N states reappear with high energy. One may now surmise that when m electrons are already present then only $N-m$ states are available (in the limit $I \to \infty$) to any further electron added to the system, the remaining m states reappearing with high energy when I is finite but large. In this way one can understand how the two bands of figure 1 arise. The lower band is essentially the unperturbed band with some states excluded, these states reappearing in the upper band.

This example reveals a weakness of the approximate solution of § 6. The discussion given above only applies when I is sufficiently large for the 'bound' states to separate, but the solution of § 6 gives a splitting into two bands for all non-zero I. Obviously the approximation is over-estimating the importance of correlation effects for small I, presumably as a consequence of the drastic approximations of equations (45) to (47).

9. The condition for ferromagnetism

In § 3 the condition for ferromagnetism predicted by Hartree–Fock theory was considered. Here the way in which this condition is affected when correlation effects are taken into account (in the approximation of § 6) will be examined.

One expects the condition for ferromagnetism to be more restrictive in a theory which takes into account correlation effects than in Hartree–Fock theory. The reason is simply that ferromagnetism occurs when the (free) energy of the ferromagnetically alined state is less than that of the non-magnetic state. Now, when correlation effects are taken into account it is mainly the correlations between electrons with anti-parallel spin which are being introduced since electrons with parallel spin are already kept apart by the Fermi–Dirac statistics even in the Hartree–Fock approximation. Thus the introduction of correlation effects will lower the energy of non-magnetic states more than that of the ferromagnetic states, and so make the condition for ferromagnetism more stringent. This is indeed found to be the case.

Using the formula (61) for the density of states and the condition (17), n_σ is determined at the absolute zero of temperature by the condition

$$n_\sigma = \int_{-\infty}^{\mu} P\{g(E, n - n_\sigma)\} \, \mathrm{d}E, \tag{77}$$

which is the analogue of (18); μ is determined by the condition (17). One can now take over the discussion of the condition for ferromagnetism in Hartree–Fock theory given in §3 almost word for word. One finds that the condition that ferromagnetism just be possible is that $n_\uparrow = n_\downarrow = \frac{1}{2}n$ is a double solution of (77). This condition is just (67) together with

$$-\tfrac{1}{2} = \int_{-\infty}^{\mu} \frac{\partial}{\partial n} [P\{g(E, \tfrac{1}{2}n)\}] \, \mathrm{d}E. \tag{78}$$

It is difficult to picture the condition (78) without reference to some specific density of states function $P(E)$. Consider then the density of states function given by (64). In this case Hartree–Fock theory gives according to (21) the condition for ferromagnetism

$$I > \Delta \tag{79}$$

independently of n. To investigate the form taken by the condition (78) in this case one may note that the density of states formula (65) can also be written

$$\rho_\sigma(E) = (1/\Delta)\{\theta(E - E_{-1,-1}^\sigma) - \theta(E - E_{-1,1}^\sigma) + \theta(E - E_{1,-1}^\sigma) - \theta(E - E_{1,1}^\sigma)\}, \tag{80}$$

which when substituted into (78) gives

$$-1 = \frac{1}{\Delta} \int_{-\infty}^{\mu} \sum_{\alpha = \pm 1} \sum_{\beta = \pm 1} \beta \frac{\mathrm{d}E_{\alpha\beta}^\sigma}{\mathrm{d}n} \delta(E - E_{\alpha\beta}^\sigma) \, \mathrm{d}E. \tag{81}$$

If μ is in the lower band, $E_{-1,-1}^\sigma < \mu < E_{-1,1}^\sigma$ (one need only consider this case because of the symmetry between electrons and holes) then this condition becomes

$$1 < \frac{1}{\Delta} \frac{\partial E_{-1,-1}^\sigma}{\partial n}, \tag{82}$$

or, using the formula (66) with $n_{-\sigma} = \frac{1}{2}n$

$$1 < \frac{\tfrac{1}{4}I}{\sqrt{\{(\tfrac{1}{2}I + \tfrac{1}{4}\Delta)^2 - \tfrac{1}{4}n\Delta I\}}}. \tag{83}$$

Since μ is in the lower band one must have $n < 1$. But for $n < 1$ the condition (83) cannot be satisfied for any I and Δ. Thus the approximate correlation theory of §6 predicts that ferromagnetism is not possible for the density of states function of (64) even though Hartree–Fock theory gives the condition (79).

It might now be inquired whether the impossibility of ferromagnetism in a general consequence which can be deduced from the approximate solution of §6. That the answer to this question is no, can be demonstrated at once by giving an example of a density of states function $P(E)$ for which ferromagnetism is possible.

Consider the density of states function

$$P(E) = 1/\delta \quad \text{if} \quad T_0 - \tfrac{1}{2}\Delta < E < T_0 - \tfrac{1}{2}\Delta + \tfrac{1}{2}\delta$$

or

$$\qquad\qquad\quad \text{if} \quad T_0 + \tfrac{1}{2}\Delta - \tfrac{1}{2}\delta < E < T_0 + \tfrac{1}{2}\Delta$$

$$= 0 \quad \text{otherwise}, \tag{84}$$

which represents two square bands of width $\frac{1}{2}\delta$ symmetrically disposed about T_0. This density of states might be thought of as an approximation to a more general

density of states function which has two high peaks at each end of the band and a low density of states in between. By a discussion similar to that given above for the density of states function (64) one may show that for small μ the condition for ferromagnetism is

$$\delta < \frac{\frac{1}{4}\Delta I}{\sqrt{\{(\frac{1}{2}I + \frac{1}{4}\Delta)^2 - \frac{1}{4}n\Delta I\}}}, \tag{85}$$

which can always be satisfied by making δ small enough.

From this example some impression can be gained of what conditions are favourable to ferromagnetism. It is clear that (85) can only be satisfied if δ is somewhat smaller than Δ from which one may infer that it is necessary that the Fermi energy be in a part of the band in which the density of states is rather greater than the mean density of states throughout the band. Further, one may note that since the right-hand side of (85) is a monotonic increasing function of Δ, for fixed δ the condition (85) is more easily satisfied for large Δ. This suggests that the most favourable condition for ferromagnetism is when the Fermi energy lies in a high density of states peak which is well away from the centre of gravity of the band, and that a high density of states peak in the middle of the band would be ineffective in producing ferromagnetism.

Finally, one may note that since for the band structure (85) $\rho(\mu) = 1/\delta$, the condition (85) can formally be written

$$1 < I_{\mathrm{ex.}}\rho(\mu) \tag{86}$$

analogous to (21) provided one defines an 'effective intra-atomic exchange energy' $I_{\mathrm{ex.}}$ by

$$I_{\mathrm{ex.}} = I \frac{\frac{1}{4}\Delta}{\sqrt{\{(\frac{1}{2}I + \frac{1}{4}\Delta)^2 - \frac{1}{4}n\Delta I\}}} \tag{87}$$

$I_{\mathrm{ex.}}$ is always less than I, the reduction being due to the weakening of exchange interactions by correlation effects. From (87) one sees that even when I becomes very large $I_{\mathrm{ex.}}$ never becomes much greater than the bandwidth Δ.

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