Exchange Induced Correlations

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Abstract. An explicit variational many body wave function, which contains correlations between Fermions of opposite spin, is discussed. Energetically it profits from the off-diagonal exchange part of a repulsive interaction. In a simple model the state can only exist, if the product of the exchange integral and the level density exceeds 3. The spectrum of the single particle excitations has a gap, which does not occur for certain double excitations. It is suggested that the theory applies to the 3d band of ferromagnetic transition elements, since it leads to a reduced observed band width and a majority spin polarisation of photo electrons.

1. The Variational Ansatz

Fermion states automatically contain a correlation: identical particles of equal spin are never at the same place. The basic example for this is the Hartree-Fock configuration

$$c_{a\sigma}^+ c_{b\sigma'}^+ \cdots |0\rangle \tag{1}$$

$|0\rangle$ is the vacuum state. $c_{a\sigma}^+$ creates a fermion with spin $\sigma = \pm 1$ in the orbital $\varphi_{a\sigma}(\mathbf{r})$.[1] Fermion operators anticommute:

$$c_{a\sigma}^+ c_{b\sigma'}^+ + c_{b\sigma'}^+ c_{a\sigma}^+ = 0, \quad c_{a\sigma}^+ c_{b\sigma'} + c_{b\sigma'} c_{a\sigma}^+ = \delta_{ab}\delta_{\sigma\sigma'}. \tag{2}$$

The spatial correlation is not immediately evident in the second quantized formulation (1), as it is in the equivalent Slater determinant. Wigner [1] has shown that it is feasible to write down states in the space representation which describe correlations also between particles of opposite spin. The surprisingly simple state introduced by Bardeen, Cooper and Schrieffer [2]

$$\prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}}\, c_{\mathbf{k}\uparrow}^+ c_{-\mathbf{k}\downarrow}^+)|0\rangle \tag{3}$$

$$0 \leqslant u_{\mathbf{k}}, v_{\mathbf{k}} \leqslant 1, \quad u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1 \tag{4}$$

reproduces correlations which occur in superconductors. This result was reached at a price: the state (3) does not belong to a fixed number of particles. In solid state applications, where the number of electrons is large, this defect is insignificant. The observables conserve the number of electrons and their matrix elements connect amplitudes which belong to the same number of particles. The fluctuation is of order $\sqrt{N_c}$, where N_c is the

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[1] In non-magnetic materials the orbitals do not depend on the spin: $\varphi_{a\sigma}(\mathbf{r}) = \varphi_a(\mathbf{r})$.

number of electrons in the coherence region in which $0 < v_k < 1$. In this narrow fluctuation range the properties of the amplitudes are practically constant.

Encouraged by the capabilities of (3) it is tempting to discuss the following Ansatz [3–5]:

$$|\psi\rangle = \prod_a (u_{a\uparrow} + v_{a\uparrow} c_{a\uparrow}^+)(u_{a\downarrow} + v_{a\downarrow} c_{a\downarrow}^+)|0\rangle \qquad (5)$$

$$0 \leqslant u_{a\sigma}, v_{a\sigma} \leqslant 1, \quad u_{a\sigma}^2 + v_{a\sigma}^2 = 1. \qquad (6)$$

We shall assume that the pairs of brackets follow in some random fashion in (5); often there is no natural sequence of orbitals anyway. Also we shall suppose that different orbitals have random phase relations. These requirements together with the reality of the amplitudes $u_{a\sigma}$, $v_{a\sigma}$ reduce most matrix elements to spurious terms.

In the state (5) not only the number of particles, but also the z-component of the total spin fluctuate. We shall discuss states with given mean value of S^z and since our Hamiltonian will commute with this variable, we regard the fluctuation as a defect of the Ansatz. The total x-component of spin S^x connects amplitudes of different z-component of spin; hence the non-vanishing value of $\langle\psi|S^x|\psi\rangle$ is unphysical, just as the expectation value of a pair creation operator is zero in an exact theory of superconductivity.

2. Expectation Values

a) $|\psi\rangle$ is normalized:

$$\langle\psi|\psi\rangle = \prod_{a\sigma} (u_{a\sigma}^2 + v_{a\sigma}^2) = 1. \qquad (7)$$

b) $\langle\psi|c_{b\uparrow}^+|\psi\rangle = u_{b\uparrow} v_{b\uparrow} \prod_{d\sigma} (u_{d\sigma}^2 - v_{d\sigma}^2) \approx 0.$

The product extends over all orbitals which are situated to the left of the orbital b in (5). Excluding a few cases of b which are insignificant, the product contains a large number of factors smaller than one, so that it can be neglected. In the pure Hartree-Fock state, in which each $v_{d\sigma}$ equals zero or one, the factor $u_{b\uparrow} v_{b\uparrow}$ vanishes. Thus

$$\langle\psi|c_{b\sigma}^+|\psi\rangle = 0, \quad \langle\psi|c_{b\sigma}|\psi\rangle = 0. \qquad (8)$$

c) $\langle\psi|c_{b\sigma}^+ c_{d\sigma}|\psi\rangle = \delta_{bd} v_{b\sigma}^2. \qquad (9)$

Here terms with $b \neq d$ are spurious. $v_{b\sigma}^2$ is the mean occupation of the one particle state $b\sigma$.

d) $\langle\psi|c_{b\sigma}^+ c_{d-\sigma}|\psi\rangle = \delta_{bd} \lambda_b \qquad (10)$

$$\lambda_b = u_{b\uparrow} v_{b\uparrow} u_{b\downarrow} v_{b\downarrow}. \qquad (11)$$

λ_b is a measure of the extent to which the orbital b is used coherently in the state $|\psi\rangle$. The maximum value $\lambda_b = 0.25$ is reached for $v_{b\uparrow}^2 = v_{b\downarrow}^2 = 0.5$.

e) $\langle\psi|c_{b\uparrow}^+ c_{d\downarrow}^+|\psi\rangle = \langle\psi|c_{a\downarrow} c_{b\uparrow}|\psi\rangle = \delta_{bd} \lambda_b. \qquad (12)$

f)   The expectation value of any product of operators $c_{..}$ and $c_{..}^+$ with an odd number of factors is spurious. Only the expectation values of even products in which the orbitals occur pairwise count. There is also a product of four operators which belong to one orbital:

$$\langle \psi | c_{b\uparrow}^+ c_{b\uparrow} c_{b\downarrow}^+ c_{b\downarrow} | \psi \rangle = v_{b\uparrow}^2 \, v_{b\downarrow}^2. \tag{13}$$
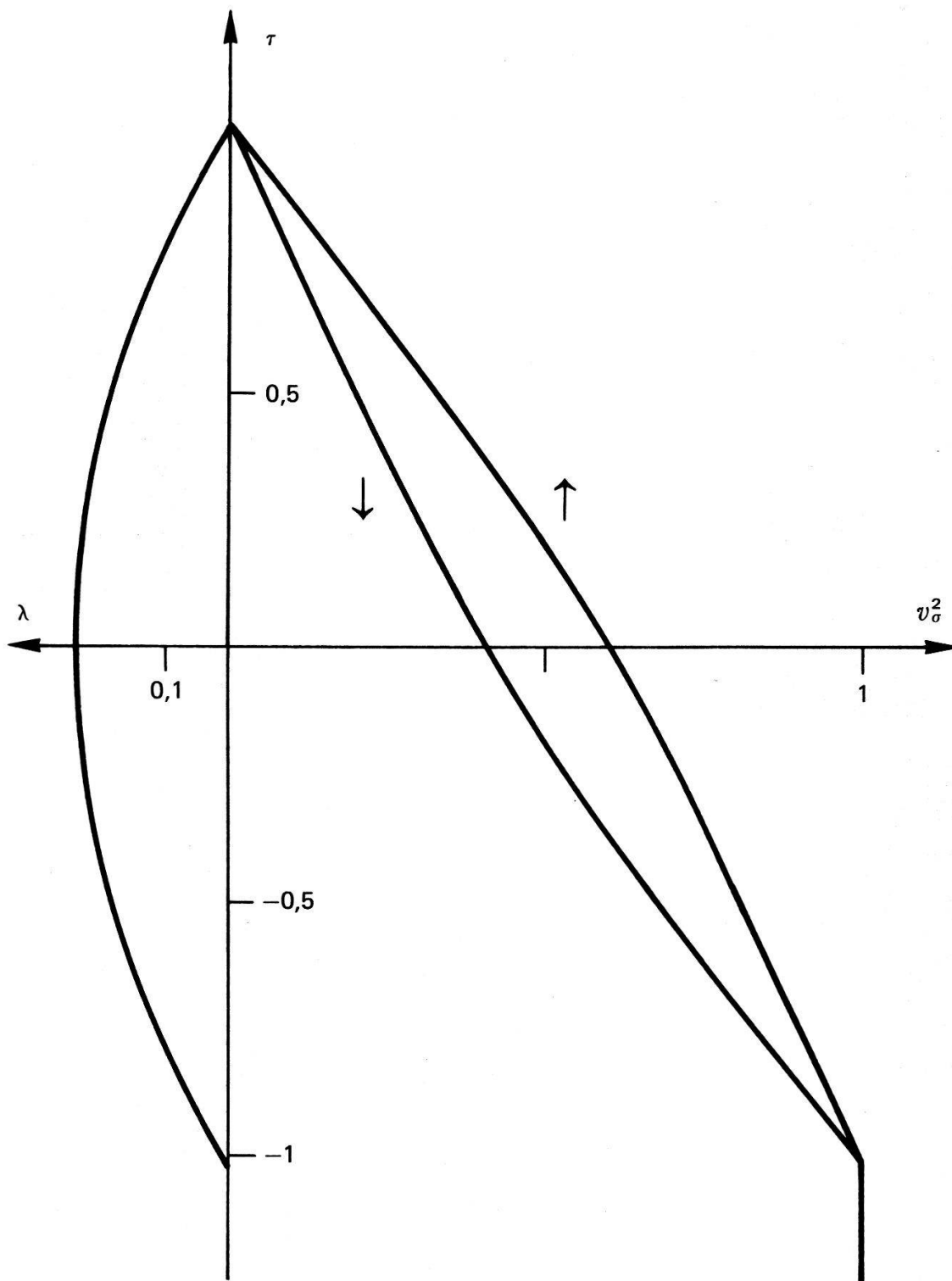

Figure 1
Occupation probability v_σ^2 and coherence parameter λ as functions of a dimensionless Hartree energy. $[\tau - \sigma\kappa = \tau_\sigma$ (46), v_σ^2 from (48), $\kappa = 0.2]$.

3. Density Correlations

The density operator for particles with spin σ is:

$$\rho_\sigma(\mathbf{x}) = \sum_{a,b} \varphi_{a\sigma}^*(\mathbf{x}) \varphi_{b\sigma}(\mathbf{x}) c_{a\sigma}^+ c_{b\sigma}. \tag{14}$$

Thus

$$\langle\psi|\rho_\sigma(\mathbf{x})|\psi\rangle \equiv \langle\rho_\sigma(\mathbf{x})\rangle = \sum_a |\varphi_{a\sigma}(\mathbf{x})|^2 v_{a\sigma}^2. \tag{15}$$

In the case of plane waves $\varphi_{\mathbf{k}\sigma}(\mathbf{x}) = V^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{x})$, normalized for a volume V, the particle density remains homogeneous in the state $|\psi\rangle$.
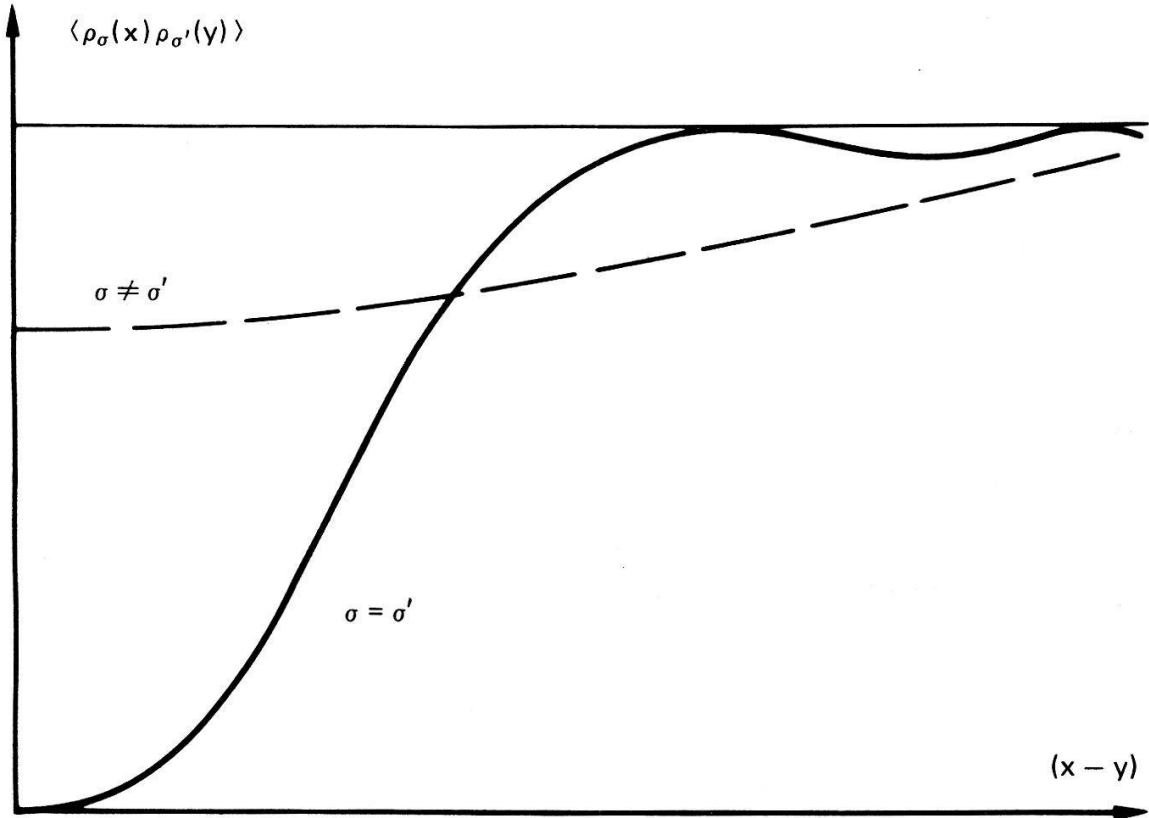

Figure 2
Correlations between particles of equal and opposite spin (schematic).

The density-density correlation for particles with equal or opposite spin is:

$$\langle\psi|\rho_\sigma(\mathbf{x})\rho_{\sigma'}(\mathbf{y})|\psi\rangle = \sum_{a,b,c,d} \varphi_{a\sigma}^*(\mathbf{x}) \varphi_{b\sigma}(\mathbf{x}) \varphi_{c\sigma'}^*(\mathbf{y}) \varphi_{d\sigma'}(\mathbf{y}) \langle\psi|c_{a\sigma}^+ c_{b\sigma} c_{c\sigma'}^+ c_{d\sigma'}|\psi\rangle \tag{16}$$

For $\sigma = \sigma'$ non spurious terms arise from $a = b$, $c = d$ and $a = d$, $b = c$. With the help of the completeness relation $\sum_b \varphi_{b\sigma}^*(\mathbf{x})\varphi_{b\sigma}(\mathbf{y}) = \delta(\mathbf{x} - \mathbf{y})$ these combine to:

$$\langle\psi|\rho_\sigma(\mathbf{x})\rho_\sigma(\mathbf{y})|\psi\rangle = \langle\rho_\sigma(\mathbf{x})\rangle\langle\rho_\sigma(\mathbf{y})\rangle + \delta(\mathbf{x}-\mathbf{y})\langle\rho_\sigma(\mathbf{x})\rangle - |v_\sigma^2(\mathbf{x},\mathbf{y})|^2 \tag{17}$$

where

$$v_\sigma^2(\mathbf{x},\mathbf{y}) = \sum_b \varphi_{b\sigma}^*(\mathbf{x}) \varphi_{b\sigma}(\mathbf{y}) v_{b\sigma}^2. \tag{18}$$

For $\mathbf{x} = \mathbf{y}$ the last term cancels the first; it represents the 'Fermi hole'. With plane waves for $\varphi_{b\sigma}(\mathbf{x})$ the function $v_\sigma^2(\mathbf{x}, \mathbf{y}) = v_\sigma^2(\mathbf{x} - \mathbf{y})$ is the Fourier transformed of $v_{k\sigma}^2$. It typically extends over a distance, which is reciprocal to the highest occupied wavenumber.

For $\sigma \neq \sigma'$ the contributions to (16) come from the terms $a = b$, $c = d$ and $a = d \neq b = c$:

$$\langle \psi | \rho_\sigma(\mathbf{x}) \rho_{-\sigma}(\mathbf{y}) | \psi \rangle = \langle \rho_\sigma(\mathbf{x}) \rangle \langle \rho_{-\sigma}(\mathbf{y}) \rangle - |\lambda(\mathbf{x}, \mathbf{y})|^2 + \sum_a |\varphi_{a\sigma}(\mathbf{x})|^2 |\varphi_{a-\sigma}(\mathbf{y})|^2 \lambda_a^2 \quad (19)$$

with

$$\lambda(\mathbf{x}, \mathbf{y}) = \sum_a \varphi_{a\sigma}^*(\mathbf{x}) \varphi_{a-\sigma}(\mathbf{y}) \lambda_a. \quad (20)$$

The last term in (19) corrects for $a = d = b = c$ which is included in the second; it can be neglected when the orbitals are extended waves. The terms $a = c$, $b = d$ lead to sums

$$\sum_a \varphi_{a\sigma}^*(\mathbf{x}) \varphi_{a-\sigma}^*(\mathbf{y}) \lambda_a \quad (21)$$

which are spurious, since the phases of different orbitals are assumed to be random. The state $|\psi\rangle$ thus describes a negative correlation $-|\lambda(\mathbf{x}, \mathbf{y})|^2$ between particles of opposite spin, which is determined by the occupation probabilities $v_{a\sigma}^2$. In the non-magnetic case, $v_{a\uparrow} = v_{a\downarrow} = v_a$, we have $\lambda_a = v_a^2 u_a^2 < v_a^2$. The correlation hole therefore cannot be as deep as the Fermi hole for $\mathbf{x} = \mathbf{y}$.

4. The Energy

We consider a system of electrons with a Hamiltonian of the form

$$H = \sum_{a,b,\sigma} T_{ab} c_{a\sigma}^+ c_{b\sigma} + \frac{1}{2} \sum_{a,b,c,d,\sigma,\sigma'} W_{abcd} c_{a\sigma}^+ c_{b\sigma'}^+ c_{c\sigma'} c_{d\sigma} \quad (22)$$

where, in order to avoid cumbersome notation, the matrix elements refer to a spin independent system of orbitals $\varphi_{a\sigma}(\mathbf{x}) = \varphi_a(\mathbf{x})$. The expectation value $\langle \psi | H | \psi \rangle$ involves only the diagonal 'kinetic energy'

$$T_{aa} = T_a, \quad (23)$$

the 'Coulomb coupling between two orbitals'

$$W_{abba} = U_{ab} \quad (24)$$

and the corresponding exchange energy

$$W_{abab} = J_{ab} \quad \text{if } a \neq b, \quad J_{aa} = 0. \quad (25)$$

The expectation value of (22) is therefore the same as that of a reduced Hamiltonian H_{red}.

$$H_{\text{red}} = \sum_{a,\sigma} T_a c_{a\sigma}^+ c_{a\sigma} + \frac{1}{2} \sum_{a,b,\sigma,\sigma'} U_{ab} c_{a\sigma}^+ c_{b\sigma'}^+ c_{b\sigma'} c_{a\sigma} - \frac{1}{2} \sum_{a,b,\sigma,\sigma'} J_{ab} c_{a\sigma}^+ c_{a\sigma'} c_{b\sigma'}^+ c_{b\sigma}. \quad (26)$$

It is illuminating to introduce the variables [6]:

$$n_a = c_{a\uparrow}^+ c_{a\uparrow} + c_{a\downarrow}^+ c_{a\downarrow} \quad (27)$$

$$2S_a^z = c_{a\uparrow}^+ c_{a\uparrow} - c_{a\downarrow}^+ c_{a\downarrow} \quad (28)$$

$$S_a^\sigma = c_{a\sigma}^+ c_{a-\sigma} = S^x + i\sigma S^y \quad (29)$$

which according to (2) satisfy the following commutation relations, cyclic in x, y, z:

$$[S_a^x, S_b^y] = i\delta_{ab} S^z, \quad [n_a, S_b^x] = 0 \tag{30}$$

(26) becomes:

$$H_{\text{red}} = \sum_a T_a n_a + \tfrac{1}{2} \sum_{a,b} U_{ab} n_a (n_b - \delta_{ab}) - \sum_{a,b} J_{ab} (\mathbf{S_a} \cdot \mathbf{S_b} + \tfrac{1}{4} n_a n_b). \tag{31}$$

To the expectation value of a Hartree-Fock configuration the terms

$$-2J_{ab} (S_a^x S_b^x + S_a^y S_b^y) \tag{32}$$

do not contribute. The improvement of the state $|\psi\rangle$ over the Hartree-Fock scheme lies in the fact that it can make use of these terms. The correlations (19) are therefore induced by the non-diagonal part of the exchange energy.

With the help of (26), (9), (10) and (11) the mean energy becomes

$$E = \langle \psi | H | \psi \rangle = \sum_{a,\sigma} T_a v_{a\sigma}^2 + \tfrac{1}{2} \sum_{a\sigma \neq b\sigma'} (U_{ab} - \delta_{\sigma\sigma'} J_{ab}) v_{a\sigma}^2 v_{b\sigma'}^2 - \sum_{a,b} J_{ab} \lambda_a \lambda_b. \tag{33}$$

This can be written as

$$E = \sum_{a,\sigma} (T_a + \tfrac{1}{2} C_{a\sigma} - \tfrac{1}{2} K_{a\sigma}) v_{a\sigma}^2 - \sum_a L_a \lambda_a \tag{34}$$

The Coulomb energy

$$C_{a\sigma} = \sum_{b\sigma'(\neq a\sigma)} U_{ab} v_{b\sigma'}^2 \tag{35}$$

depends weakly on a and only spuriously on σ for extended waves, while the Fock potential

$$K_{a\sigma} = \sum_b J_{ab} v_{b\sigma}^2 \tag{36}$$

is spin dependent in ferromagnets. The sum

$$L_a = \sum_b J_{ab} \lambda_b \tag{37}$$

is a measure of the off-diagonal spin coherence. The combination

$$T_a + \tfrac{1}{2} C_{a\sigma} - \tfrac{1}{2} K_{a\sigma} \tag{38}$$

is the Hartree-Fock contribution to the energy from an occupied level.

5. The Variational Problem

The energy E is a functional of the system of orbitals $\varphi_{a\sigma}(\mathbf{x})$ and of the occupation probabilities $v_{a\sigma}^2$. Both can be varied to minimize the energy.

We first consider the variations $\delta\varphi_{a\sigma}(\mathbf{x})$ [3]. Since the varied system of orbitals is again to be orthonormal:

$$(\varphi_i, \varphi_j) - \delta_{ij} = 0. \tag{39}$$

Lagrange multipliers γ_{ij} are introduced for these side-conditions.

The functional derivative

$$\delta \left\{ E - \sum_{i,j} \gamma_{ij} \left(\varphi_i, \varphi_j \right) \right\} / \delta \varphi_{f\sigma}(\mathbf{x}) = 0 \tag{40}$$

with respect to the orbital f belonging to the spin σ becomes in the space representation with the operators

$$T_{\mathbf{x}} = -(\hbar^2/2m)\, \varDelta + \phi(\mathbf{x}) \quad \text{and} \quad W(\mathbf{x}, \mathbf{y}) = e^2/|\mathbf{x} - \mathbf{y}|:$$

$$T_{\mathbf{x}} \varphi_f(\mathbf{x}) v_{f\sigma}^2 + \sum_{b\sigma'(\neq f\sigma)} \int d^3 y\, \varphi_b^*(\mathbf{y})\, W(\mathbf{x}, \mathbf{y})\, \varphi_b(\mathbf{y})\, \varphi_f(\mathbf{x})\, v_{b\sigma}^2 v_{f\sigma}^2$$

$$- \sum_{b(\neq f)} \int d^3 y\, \varphi_b^*(\mathbf{y})\, W(\mathbf{x}, \mathbf{y})\, \varphi_f(\mathbf{y})\, \varphi_b(\mathbf{x})\, (v_{b\sigma}^2 v_{f\sigma}^2 + 2\lambda_b \lambda_f) = h\, \varphi_f(\mathbf{x}) = \sum_j \gamma_{fj}\, \varphi_j(\mathbf{x}) \tag{41}$$

This non-linear set of equations is a generalization of the Hartree-Fock equations. At best it can be treated in some self-consistent manner. If the left hand side of (41) can be considered as the action of an operator h on $\varphi_f(\mathbf{x})$, an orthogonal system of eigenstates of h solves the problem with $\gamma_{fj} = \delta_{fj}\gamma_f$. When $T_{\mathbf{x}}$ and $W(\mathbf{x},\mathbf{y})$ are translation-invariant, plane waves are a solution of (41). Similarly if $T_{\mathbf{x}}$ and $W(\mathbf{x},\mathbf{y})$ are invariant with the discrete translations of a Bravais lattice, Bloch waves are self-consistent.

We now turn to the variations $\delta v_{a\sigma}$, $\delta u_{a\sigma} = -\delta v_{a\sigma} v_{a\sigma}/u_{a\sigma}$. To maintain the number of particles $\langle \psi | N | \psi \rangle = \sum_{a,\sigma} v_{a\sigma}^2$ constant, we introduce a chemical potential μ. On the other hand the magnetization will be left free to choose its optimum value.

$$\delta \left(E - \mu \sum_{b\sigma'} v_{b\sigma'}^2 \right) / \delta v_{a\sigma} = 0 \tag{42}$$

results in

$$(T_a - \mu) v_{a\sigma} u_{a\sigma} + \sum_{b\sigma'(\neq a\sigma)} (U_{ab} - \delta_{\sigma\sigma'} J_{ab}) v_{b\sigma'}^2\, v_{a\sigma} u_{a\sigma}$$

$$- \sum_b J_{ab} \lambda_b (u_{a\sigma}^2 - v_{a\sigma}^2) v_{a-\sigma} u_{a-\sigma} = 0 \tag{43}$$

or with (35), (36) and (37)

$$(T_a - \mu + C_{a\sigma} - K_{a\sigma}) v_{a\sigma} u_{a\sigma} - L_a (u_{a\sigma}^2 - v_{a\sigma}^2) v_{a-\sigma}^2 u_{a-\sigma}^2 = 0. \tag{44}$$

It is convenient to use the Hartree-Fock one particle energy

$$T_a - \mu + C_{a\sigma} - K_{a\sigma} = \epsilon_{a\sigma}^{\text{H.F.}} \tag{45}$$

in the dimensionless form

$$\tau_{a\sigma} = \epsilon_{a\sigma}^{\text{H.F.}}/L_a. \tag{46}$$

6. Solutions

The two equations (44) with $\sigma = \pm 1$ always allow the Hartree-Fock solutions

$$v_{a\sigma}^2 = 0 \quad \text{or} \quad 1. \tag{47}$$

A further solution is

$$v_{a\sigma}^2 = \tfrac{1}{2}\left(1 - \tau_{a\sigma}\sqrt{\frac{1+\tau_{a-\sigma}^2}{1+\tau_{a\sigma}^2}}\right) \tag{48}$$

which is acceptable if $0 \leqslant v_{a\sigma}^2 \leqslant 1$. In the non-magnetic case (48) gives:

$$v_a^2 = \tfrac{1}{2}(1 - \tau_a), \qquad \lambda_a = \tfrac{1}{4}(1 - \tau_a^2). \tag{49}$$

Let us consider the simple model in which the exchange integral and the density of states are constants:

$$J_{ab} = J, \qquad \nu(\epsilon_{a\sigma}^{\text{H.F.}}) = \nu. \tag{50}$$

The self-consistency requirement (37) becomes for (49):

$$L = J\int_{\epsilon_1}^{\epsilon_2} d\epsilon^{\text{H.F.}}\,\nu(\epsilon^{\text{H.F.}})\lambda(\epsilon^{\text{H.F.}}) = J\nu L\int_{\tau_1}^{\tau_2} d\tau\tfrac{1}{4}(1-\tau^2) = LJ\nu\tfrac{1}{4}(\tau - \tfrac{1}{3}\tau^3)\Big|_{\tau_1}^{\tau_2}. \tag{51}$$

Since the coherence can at best exist in the range $\tau_2 = 1$, $\tau_1 = -1$, (51) requires

$$J\nu \geqslant 3. \tag{52}$$

Magnetic solutions of (48) lead to smaller values of λ_a and exist only if $J\nu > 3$.

The general self-consistency problem demands that the quantities $C_{a\sigma}$, $K_{a\sigma}$ and L_a which occur in (48) are given by the sums (35), (36) and (37), and that the total number of particles is

$$\langle\psi|N|\psi\rangle = \sum_{a\sigma} v_{a\sigma}^2. \tag{53}$$

The chemical potential μ and the limits of the range, for which the coherent solution is chosen, are the adaptable parameters. It is noteworthy that with (52) the description itself sets a limit on its possible applicability.

A serious problem is the stability with respect to other states. In the model (50) and with the condition (52) the Hartree-Fock theory predicts complete ferromagnetic polarization. An elementary calculation shows that this has a lower energy (34) than the non-magnetic solution (49). For plane waves a constant exchange integral corresponds to a point interaction; a more realistic long-range repulsion might make better use of the correlation (19). The spin coherence should not be expected to be a common phenomenon; its occurrence depends on especially favourable conditions.

7. Excited States

In general, orthogonality to an approximate ground state is a poor criterion for the definition of an excited state. Since, however, each orbital is treated individually in the definition (5) of $|\psi\rangle$, a state which is orthogonal within the Hilbert space of one orbital may represent a simple excitation. An orthogonal and normalized state is obtained by the following substitution of any bracket in (5):

$$(u_{a\sigma} + v_{a\sigma}c_{a\sigma}^+) \rightarrow (v_{a\sigma} - u_{a\sigma}c_{a\sigma}^+). \tag{54}$$

There is an abundance of degenerate states, since the energy (33) is invariant with respect to the transformation

$$v_{b\uparrow}, v_{b\downarrow} \rightarrow -v_{b\uparrow}, -v_{b\downarrow} \tag{55}$$

applied to any orbital. It is convenient to define one particle excited states in such a way, that they have simple matrix elements. We therefore define:

$|a\sigma, \psi\rangle$ is obtained from $|\psi\rangle$ through the transformation (54) applied to $a\sigma$ and (55) applied to all orbitals situated to the left of a.

Then

$$\langle a\sigma, \psi | b\sigma', \psi \rangle = \delta_{ab}\delta_{\sigma\sigma'}, \quad \langle a\sigma, \psi | \psi \rangle = 0 \tag{56}$$

The energy of excitation

$$\epsilon_{a\sigma} = \langle a\sigma, \psi | H - \mu N | a\sigma, \psi \rangle - \langle \psi | H - \mu N | \psi \rangle \tag{57}$$

becomes with (33) and (45)

$$\epsilon_{a\sigma} = \epsilon_{a\sigma}^{\text{H.F.}} (u_{a\sigma}^2 - v_{a\sigma}^2) + 2L_a\lambda_a. \tag{58}$$

In the first term both factors have the same sign and they vanish at the Fermi level. The second term is positive because of the minus sign in (54). It represents a gap in the coherence region.

A double excitation in the orbital a is obtained by successively exciting $a\uparrow$ and $a\downarrow$. Thus:

$|a, \psi\rangle$ is given by (5), however, with the brackets of the orbital a replaced by

$$(v_{a\uparrow} - u_{a\uparrow} c_{a\uparrow}^+)(v_{a\downarrow} - u_{a\downarrow} c_{a\downarrow}^+).$$

The corresponding excitation energy

$$\epsilon_a = \sum_\sigma \epsilon_{a\sigma}^{\text{H.F.}} (u_{a\sigma}^2 - v_{a\sigma}^2) \tag{59}$$

shows that with the two minus signs the correlation is in phase again. With the non-magnetic solution (49) the excitation energies become:

$$\epsilon_{a\sigma}/L = \begin{cases} \frac{1}{2}(1 + \tau^2) \\ |\tau| \end{cases}, \qquad \epsilon_a/L = \begin{cases} 2\tau^2 & \lambda \neq 0 \\ 2|\tau| & \lambda = 0 \end{cases}. \tag{60}$$

The double excitation reverses the sign of the spin-magnetization which the orbital contributes. For this reason the spectrum of ϵ_a starts at a finite energy in ferromagnetic materials; the two terms of (59) vanish at different orbitals.

Some useful matrix elements are:

$$\langle a\uparrow, \psi | c_{a\uparrow}^+ | \psi \rangle = -u_{a\uparrow}^2 \tag{61}$$

$$\langle a\downarrow, \psi | c_{a\downarrow}^+ | \psi \rangle = -u_{a\downarrow}^2 (u_{a\uparrow}^2 - v_{a\uparrow}^2) \tag{62}$$

$$\langle a\uparrow, \psi | c_{a\uparrow} | \psi \rangle = v_{a\uparrow}^2 \tag{63}$$

$$\langle a, \psi | c_{a\uparrow}^+ c_{a\downarrow} | \psi \rangle = u_{a\uparrow}^2 v_{a\downarrow}^2 \tag{64}$$

$$\langle a\uparrow, b\uparrow, \psi | c_{a\uparrow}^+ c_{b\uparrow} | \psi \rangle = -v_{b\uparrow}^2 u_{a\uparrow}^2. \tag{65}$$
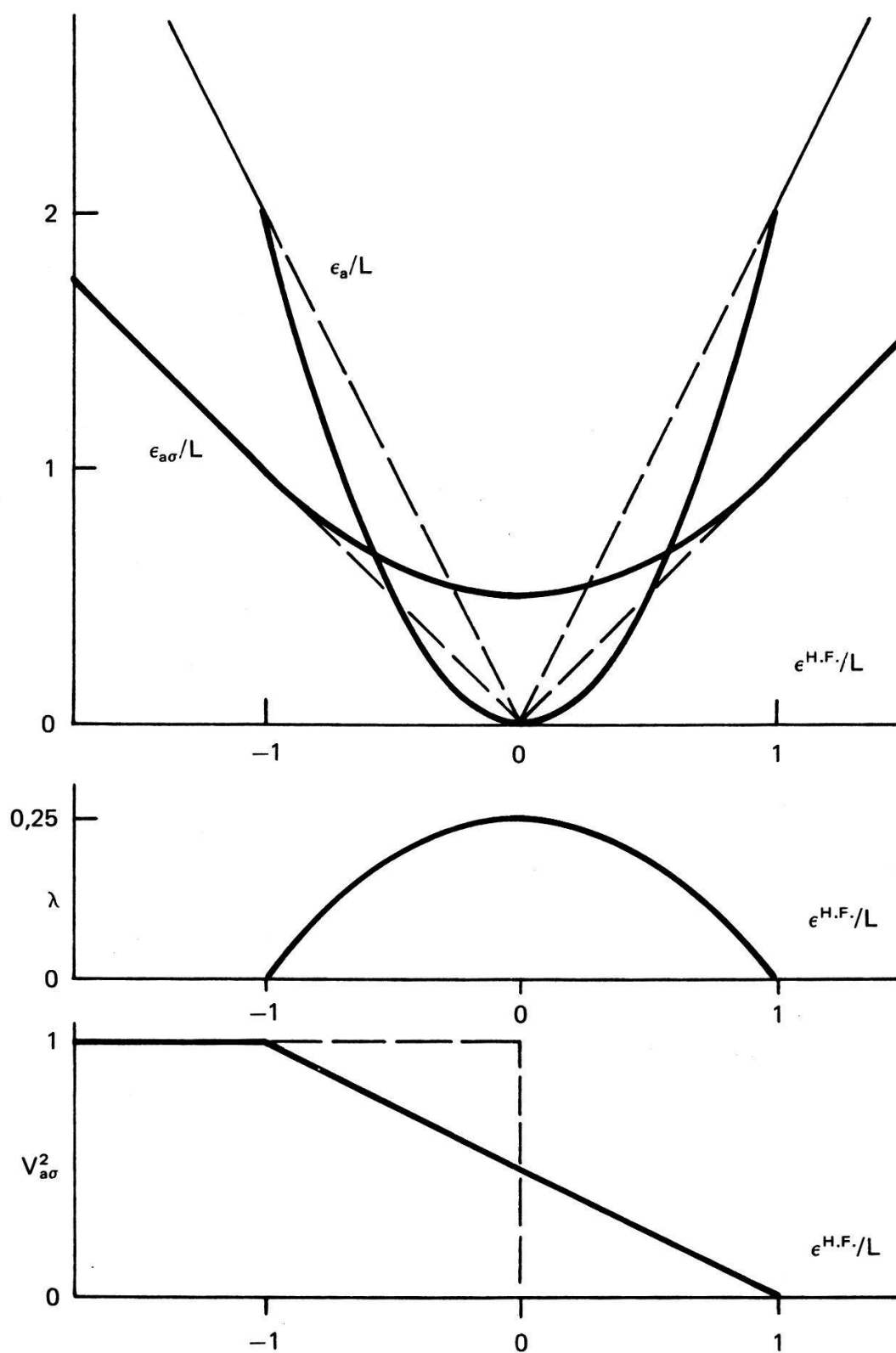
Figure 3
Single ($\epsilon_{a\sigma}$) and double (ϵ_σ) excitation energies versus Hartree-Fock energy in the non-magnetic case.

There is a one to one correspondence between the states $|\psi\rangle$, $|a\uparrow, \psi\rangle$, $|a\downarrow, \psi\rangle$, $|a, \psi\rangle$ and the Hartree-Fock ground state, single excitations (holes below the Fermi level, particles above) and the double excitation. In general the excitations carry a current. Strangely the double excitations should play a role in the low temperature specific heat and transport problems. These questions demand an evaluation of the self-consistency problem at finite temperatures.

8. Possible Applications

The exchange integral between states of a metallic electron band may typically be of order $J \approx 3 \text{eV}$ (for atomic volume) and the density of states $\nu \approx 0.3 \text{ eV}^{-1}$, so that $J\nu \approx 1 < 3$. In the $3d$ shells of transition metals values as high as $\nu = 2 \text{ eV}^{-1}$ occur and $J\nu > 3$ seems realistic. While it would be premature to predict an applicability of the theory, some empirical facts should be noted.

a) The $3d$ band width as measured by the ESCA [7] method is about 3 eV for nickel and 5 eV for rhodium. Band structure calculations [8] give about 5 eV for Ni. In the photo-emission process an external field creates a one particle excitation (hole) and an electron in a higher band. If the hole lies in the coherence range, the gap energy has to be furnished, which makes it appear to lie deeper. The band width is squeezed on the observed $\epsilon_{a\sigma}$ scale. This explanation requires $2L\lambda \approx 2$ eV or $L \approx 4$ eV. From (37) $L \approx J\nu\lambda\Delta\epsilon^{\text{H.F.}}$ where $\Delta\epsilon^{\text{H.F.}}$ is the range of coherence. The values $J = 3$ eV, $\nu = 2 \text{ eV}^{-1}$, $\lambda = 1/4$ lead to $\Delta\epsilon^{\text{H.F.}} = 2.6$ eV, which is possible. If Ni is in the coherent state, while Rh is not, then in the Ni–Rh alloy system a phase change should occur, at which the apparent band width jumps.

b) The small magnetization of Ni interpreted by the Stoner-Wohlfarth [9] theory corresponds to a shift between the up spin and down spin bands of 0.5 eV only. This small number requires an extremely dramatic screening effect. On the other hand a small magnetization is a natural consequence of the spin coherent state.

c) Lowde and Windsor [10] found in a detailed analysis, that the neutron scattering cross section presents a larger parallel spin correlation than accounted for by current theories. Since the spin coherence is driven by the operator (32), a considerable parallel spin correlation should result in this state.

d) Busch, Siegmann and Campagna [11] have measured the polarization of photo-emitted electrons from Fe, Co and Ni. In all cases the polarization corresponds to that of the majority (up spin) carriers. Similar results were obtained [12] by tunnelling into superconductors. In the Stoner-Wohlfarth theory the polarization is at low photon energies given by the relation of the up spin to the down spin Fermi surfaces. In Ni and Co the up spin bands are nearly full; the corresponding Fermi surfaces are small and erroneously a negative polarization is predicted.

When a magnetization distribution such as that of Figure 1 is plotted against the observed energy scale $\epsilon_{a\sigma}$, a positive polarization is expected, which diminishes somewhat as the photon energy is increased over the width into which the coherence region is compressed, say 1 eV. Qualitatively this agrees with observation; the argument is, however, not backed by detailed numerical calculations.

The problem of the spin polarization of photo-electrons has stimulated various explanations [13–15] and it was also the motivation for the present work. While there is a consensus that collective effects quantitatively modify the band theory, this work proposes that exchange can drive a system into a spin coherent phase.

e) A difficulty of the present theory lies in the small gap of the double excitations in the ferromagnetic state. The observed specific heat and the transport properties demand a spectrum with a gapless continuum. This suggests that if the coherent ground state is a useful approximation, there might be more subtle excitations than those which reverse the magnetization of an orbital.

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