The low-density electron gas in the spin-extended Hartree–Fock approximation

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Abstract. The spin-extended Hartree–Fock approximation with localized overlapping orbitals is applied to the low-density electron gas problem. A procedure is outlined which in the case of small overlap makes the energy per electron convergent when the number of electrons tends to infinity. As a first approximation the perfect pairing case is considered. It is shown that the singlet ground state energy lies in between the energies of ferromagnetic and antiferromagnetic states for any perfect pairing structure in second order in the overlap approximation.

1. Introduction

The electron gas in a homogeneous positive background field is a very useful and acknowledged reference system for various solid state electronic structure problems. However, even this simplified system cannot be solved exactly and different approximations should be used for different regimes. One interesting case is the low-density regime, which is closely related to the localization–delocalization transition in a half-filled band problem. In this regime the restricted Hartree–Fock (RHF) approximation for the ground state produces the uniform electron density distribution, and with correlations taken into account results in a Wigner crystal [1,2], with electrons strongly localized at BCC lattice sites. The Wigner crystal state was treated semiclassically [3–5] and with the quantum Monte Carlo method [6,7]. Reviews of these works can be found in papers by March and co-workers [8–10]. The quantum-mechanical approach, corresponding to the unrestricted (one-determinant) Hartree–Fock (UHF) approximation, was developed in a recent paper by van Dijk and Vertogen [11] using the quantum field technique. But the UHF method is open to criticism because, although the Hamiltonian $\hat{H}$ commutes with the total spin $\hat{S}^2$ and $\hat{S}_z$ operators, the UHF wave function is an eigenfunction of $\hat{S}_z$ and in contrast to the RHF wave function is not an eigenfunction of $\hat{S}^2$, except in some special cases. In fact the N-electron ferromagnetic state of [11] is the pure spin state and not the antiferromagnetic state, the mean value of $\hat{S}^2$ being equal to $N/2$ in the antiferromagnetic state.

The aim of the present paper is to apply to the low-density electron gas problem a better approximation—the spin-extended Hartree–Fock (EHF) method, which includes as particular cases both RHF and UHF methods. In this paper we will use one of the versions of the EHF method, namely the valence-bond (VB) method, which enables us to consider ferromagnetic, antiferromagnetic and singlet pure spin states of the electron gas within the same formalism.

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2. The wave function

Let us consider the ground state of an N-electron system and let us assume for convenience the number N of electrons to be even. In the RHF method the ground state is usually assumed to be a singlet state and one starts with $N/2$ orbitals (space orbitals)

$$\phi_l(r) \qquad l = 1, 2, \ldots, N/2. \tag{1}$$

Bloch functions in the half-filled band case, for example, proceed with N spin orbitals

$$\psi_{2l-1}(x) = \phi_l(r)\alpha(\sigma) \qquad \psi_{2l}(x) = \phi_l(r)\beta(\sigma) \qquad l = 1, 2, \ldots, N/2 \tag{2}$$

where x stands for space–spin variables, σ, and for the total wave function takes a single Slater determinant of N spin orbitals (2). This wave function is a pure singlet state. Due to one-determinant structure it is invariant under arbitrary unitary transformation of spin orbitals (2) (or space orbitals (1)). Therefore two different sets of orbitals which have different shape, but are related to each other by the unitary transformation, are physically equivalent because they correspond to the same total wave function. A well known example is the case of a completely filled band, where a set of delocalized Bloch functions and a set of localized Wannier functions are equivalent. Besides, if the spin orbitals are subject to arbitrary non-singular linear transformation, the total wave function will change only by a specific factor (normalization factor). Consequently if one has a set of non-orthogonal orbitals and linearly transforms it into a set of orthogonal orbitals, both sets will correspond to the same (apart from the normalization factor) total wave function. Therefore the orthogonality conditions on the orbitals in the RHF method are not a constraint at all. In the UHF method one starts with N space orbitals

$$\phi_k(r) \qquad k = 1, 2, \ldots, N \tag{3}$$

proceeds with N spin orbitals which are $\phi_k(r)$ multiplied by either the $\alpha(\sigma)$ or the $\beta(\sigma)$ spin function and takes for the total wave function a single Slater determinant of these spin orbitals. The difference between the numbers of α and β spin functions determines the z projection of the total spin. All that was said above about the unitary and general linear transformation of spin orbitals in the RHF method is also valid in this case. At the same time the UHF total wave function is not, in general, a pure spin state, but a spin mixture. In the VB method [12] one also starts from N space orbitals (3) as in the UHF method, but employs $2N$ spin orbitals, multiplying every space orbital $\phi_k(r)$ by both $\alpha(\sigma)$ and $\beta(\sigma)$ spin functions, and constructs from them the pure spin total wave function. The best developed case in the VB method is the singlet state case, where one begins with the product of space orbitals

$$\Phi(r_1, r_2, \ldots, r_N) = \phi_1(r_1)\phi_2(r_2) \ldots \phi_N(r_N). \tag{4}$$

This N-electron space function with no permutation symmetry gives rise to an N-electron singlet wave function by coupling electrons pairwise (binding them) with the two-electron singlet spin function

$$\chi(\sigma, \sigma') = (1/\sqrt{2})\{\alpha(\sigma)\beta(\sigma') - \beta(\sigma)\alpha(\sigma')\}. \tag{5}$$

Then the singlet N-electron spin function takes the form

$$\Theta_k(\sigma_1, \sigma_2, \ldots, \sigma_N) = \prod_{i,j} \chi(\sigma_i, \sigma_j) \tag{6}$$

where the product is over all pairs ('bonds'). The function (6) has an index k because there are $(N-1)!!$ different spin-paired structures for N electrons. Each structure gives rise to a particular function Θ_k though only $N!/(N/2)!(N/2+1)!$ of them are linearly independent [13]. Antisymmetrizing the product of (4) and (6) one obtains functions

$$\Psi_k(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \sum_P \epsilon(P) \hat{P} \Phi(r_1, \ldots, r_N) \Theta_k(\sigma_1, \ldots, \sigma_N). \qquad (7)$$

Here $\hat{P}$ is the permutation operator which can be written as a product of permutation operators $\hat{P}_r$ for space and $\hat{P}_\sigma$ for spin variables; $\epsilon(P)$ is the sign of the permutation and the summation is over all possible permutations. Then the total wave function of the system can be written as a linear combination of linearly independent functions Ψ_k

$$\Psi(x_1, \ldots, x_N) = \sum_k C_k \Psi_k(x_1, \ldots, x_N). \qquad (8)$$

As an approximation one often uses only one basis function Ψ_k corresponding to a particular spin-paired structure (6), for example, corresponding to the lowest value of energy. This is known as the perfect-pairing approximation. It simplifies calculations but it is an additional approximation to the finite basis set (3) approximation. The obtained basis (7) and total (8) wave functions of the VB method are not single Slater determinants, as the wave functions in the RHF and URF methods are, but a linear combination of determinants. So the VB wave function is not invariant under the linear transformation of orbitals because it consists of $2N$ spin orbitals, and each determinant contains only N of them. Therefore different sets of orbitals, related to each other by a linear transformation, correspond to the different total wave functions. This forces one to employ non-orthogonal orbitals in the VB method, because orthogonalization will be now an additional constraint imposed on the wave function. At the same time non-orthogonal orbitals are more difficult to deal with, because they lead to $O(N^2)$, $O(N^3)$, and so on, terms in matrix elements, that is to terms which increase as N^2, N^3 and so on when N tends to infinity. In the present paper it will be shown how to avoid this difficulty in the case of small overlap. The wave function of the RHF singlet state and wave functions of ferromagnetic and antiferromagnetic UHF states can be considered as particular cases of the VB wave function. Indeed, if we employ non-orthogonal orbitals (3), select a spin-paired structure (6) and equate space orbitals belonging to the same pair

$$\phi_i(r) = \phi_j(r) \qquad (9)$$

the function (7) will be exactly the RHF singlet wave function. This function does not depend on the selected spin-pairing structure. From this one can conclude that the VB wave function is better than the RHF wave function because it contains twice as many space orbitals. The wave function of the ferromagnetic state can also be written as (7) if for the spin function one takes

$$\Theta_{\mathrm{FM}}(\sigma_1, \ldots, \sigma_N) = \alpha(\sigma_1)\alpha(\sigma_2) \ldots \alpha(\sigma_{N-1})\alpha(\sigma_N) \qquad (10)$$

This is a pure spin state with maximum possible total spin and spin z projection.

To write down the wave function of the antiferromagnetic state one has to divide the set $\mathcal{L} = \{1, 2, \ldots, N\}$ into two subsets $\mathcal{L}_1$ and $\mathcal{L}_2$ with equal numbers of points and employ the spin function

$$\Theta_{\mathrm{AFM}}(\sigma_1, \ldots, \sigma_N) = \prod_{k=1}^{N} \eta_k(\sigma_k) \qquad (11)$$

where

$$\eta_k(\sigma) = \begin{cases} \alpha(\sigma) & k \in \mathcal{L}_1 \\ \beta(\sigma) & k \in \mathcal{L}_2. \end{cases} \tag{12}$$

The function Θ_{AFM} is a spin mixture with zero z projection of the total spin.

3. The energy expression

Let us consider the low-density electron gas and its ground singlet state. The wave function (8) of the VB method seems suitable for this case, because it naturally reflects the Wigner crystal localization picture. Let $\phi(r)$

$$\int |\phi(r)|^2 \, dr = 1 \tag{13}$$

be some appropriate one-electron function, localized and normalized to unity. Translation of this function into N sites R_j of lattice results in the set of N space orbitals

$$\phi_j(r) = \phi(r - R_j). \tag{14}$$

We label the lattice sites by the integer j, and we ascribe the site number to the function localized around it. These orbitals in general are not orthogonal to each other and we will use the following notation

$$S_{ij} = \int \phi_i^*(r)\phi_j(r) \, dr \tag{15}$$

for the overlap integral.

If one employs the function (8) the usual system of linear equations for coefficients C_k immediately follows

$$\sum_m \{\langle \Psi_l | \hat{H} | \Psi_m \rangle - W \langle \Psi_l | \Psi_m \rangle\} C_m = 0. \tag{16}$$

For basis functions (7) and for an arbitrary operator $\hat{A}(r_1, \ldots, r_N)$ which is spinless and symmetrical in its arguments one can write

$$\langle \Psi_l | \hat{A} | \Psi_m \rangle = \sum_P \epsilon(P) G_{lm}(P) \int \phi_1^*(r_1)\phi_2^*(r_2), \ldots, \phi_N^*(r_N) \hat{A}(r_1, r_2, \ldots, r_N)$$

$$\times \hat{P}_r \phi_1(r_1)\phi_2(r_2), \ldots, \phi_N(r_N) \, dr_1 \, dr_2, \ldots, dr_N \tag{17}$$

where

$$G_{lm}(P) = \int \Theta_l(\sigma_1, \ldots, \sigma_N) \hat{P}_\sigma \Theta_m(\sigma_1, \ldots, \sigma_N) \, d\sigma_1, \ldots, d\sigma_N. \tag{18}$$

It is well known that because orbitals $\phi_l(r)$ are not orthogonal the matrix element (17) will contain $O(N^2)$, $O(N^3)$ etc terms (even for a one-electron operator) due to the non-linked clusters. Therefore direct calculation of (16) becomes impracticable even for moderate N

and it is extremely difficult to recognize that the ratio W/N tends to a certain finite value when N tends to infinity. However, one can transform the set of linearly independent functions Ψ_k into a set of orthonormal functions $\Psi_k^{(0)}$ using the Löwdin equation [14]

$$\Psi_l^{(0)} = \sum_m \{\mathbf{T}^{-1/2}\mathbf{B}\}_{ml}\Psi_m \tag{19}$$

where $\mathbf{T}$ is the matrix of scalar products

$$\mathbf{T}_{lm} = \langle\Psi_l|\Psi_m\rangle \tag{20}$$

and $\mathbf{B}$ is an arbitrary unitary matrix. With functions $\Psi_k^{(0)}$ the system (16) reads

$$\sum_m \{\langle\Psi_l^{(0)}|\hat{H}|\Psi_m^{(0)}\rangle - W\delta_{lm}\}C_m^{(0)} = 0. \tag{21}$$

For every matrix element in (21) it is possible to develop the series in powers of overlap, which will contain no ambiguous $O(N^2)$, $O(N^3)$ etc terms. This series, of course, will be useful only for small overlap, which is the case for a low-density gas near the Wigner crystal state.

In this paper we will consider the simplest case of perfect pairing. The general case will be discussed in our next paper. In the perfect pairing approximation with selected spin-pairing structure, say Ψ_l, only one equation is left in the system (21) which gives

$$W = \langle\Psi_l|\hat{H}|\Psi_l\rangle/\langle\Psi_l|\Psi_l\rangle. \tag{22}$$

To develop a series let us define for any spinless operator $\hat{A}$ the function $\mathcal{A}(t)$ of real variable t

$$\mathcal{A}(t) = \sum_P \epsilon(P)t^{n(P)}G_{ll}(P) \int \phi_1^*(r_1)\ldots\phi_N^*(r_N)\hat{A}(r_1,\ldots,r_N)$$

$$\times \hat{P}_r\phi_1(r_1)\ldots\phi_N(r_N)\,dr_1,\ldots,dr_N \tag{23}$$

where $n(P)$ is the exchange parameter which shows how many pairs of different orbitals depending on the same variable are in the integrand for that particular permutation P. For example, if P is a transposition P_{ij} then $n(P) = 2$, if P is a cycle permutation of any three indexes i, j, k then $n(P) = 3$, etc. According to the definition (23), one has

$$\langle\Psi_l|\hat{A}|\Psi_l\rangle = \mathcal{A}(1). \tag{24}$$

Now we will define three functions $\mathcal{H}(t)$ for $\hat{A} = \hat{H}$, $\mathcal{N}(t)$ for $\hat{A} = \hat{I}$, and $\mathcal{W}(t)$ as the ratio

$$\mathcal{W}(t) = \mathcal{H}(t)/\mathcal{N}(t). \tag{25}$$

Expanding $\mathcal{W}(t)$ as a Taylor series of t, we obtain

$$W = \mathcal{W}(1) = \mathcal{W}(0) + \mathcal{W}'(0) + \tfrac{1}{2}\mathcal{W}''(0) + \cdots. \tag{26}$$

It is not difficult to calculate derivatives and take their values at $t = 0$. We will restrict ourselves here to the smallest possible value of the exchange parameter $n = 2$, that is,

in the summation over permutations we will take only the identity permutation and all transpositions P_{ij}. This corresponds to second order in the overlap approximation which was used in [11]. For the identity permutation $G_{ll}(I) = 1$ and for transpositions we will use the short notation

$$G^{ij} = G_{ll}(P_{ij}). \tag{27}$$

As a result we have

$$\mathcal{N}(0) = 1 \tag{28a}$$

$$\mathcal{N}'(0) = 0 \tag{28b}$$

$$\mathcal{N}''(0) = -\sum_{i,j=1}^{N}{}' S_{ij} S_{ji} G^{ij} \tag{28c}$$

$$\mathcal{H}(0) = W_{\mathrm{b}} + \sum_{i=1}^{N} \langle i|h|i \rangle + \tfrac{1}{2} \sum_{i,j=1}^{N}{}' \langle ij|g|ij \rangle \tag{29a}$$

$$\mathcal{H}'(0) = 0 \tag{29b}$$

$$\mathcal{H}''(0) = -\sum_{i,j=1}^{N}{}' G^{ij} \{ \langle i|h|j \rangle S_{ji} + S_{ij} \langle j|h|i \rangle \} - \sum_{i,j,k=1}^{N}{}' G^{ij} S_{ij} S_{ji} \langle k|h|k \rangle$$

$$- \sum_{i,j=1}^{N}{}' G^{ij} \langle ij|g|ji \rangle - \sum_{i,j,k=1}^{N}{}' G^{ij} \{ \langle ik|g|jk \rangle S_{ji} + S_{ij} \langle jk|g|ik \rangle \}$$

$$- \tfrac{1}{2} \sum_{i,j,k,l=1}^{N}{}' G^{ij} S_{ij} S_{ji} \langle kl|g|kl \rangle - \sum_{i,j=1}^{N}{}' S_{ij} S_{ji} G^{ij} W_{\mathrm{b}} \tag{29c}$$

$$\mathcal{W}(0) = \mathcal{H}(0) \tag{30a}$$

$$\mathcal{W}'(0) = 0 \tag{30b}$$

$$\mathcal{W}''(0) = \mathcal{H}''(0) - \mathcal{H}(0)\mathcal{N}''(0) \tag{30c}$$

where a prime by the sum means that the two indexes are not equal. W_{b} is the self-energy of the background. It mimics the atomic core interaction energy in a solid and should be included to ensure the charge neutrality of the system. Brackets $\langle i|h|k \rangle$ and $\langle ij|g|kl \rangle$ are usual notations for matrix elements of one-electron and two-electron operators.

$$\langle i|h|j \rangle = \int \phi_i^*(r) \{ -\tfrac{1}{2}\Delta + V(r) \} \phi_i(r) \, dr \tag{31}$$

$$\langle ij|g|kl \rangle = \int \phi_i^*(r_1) \phi_j^*(r_2) \frac{1}{|r_1 - r_2|} \phi_k(r) \phi_l(r) \, dr_1 \, dr_2 \tag{32}$$

where $V(r)$ is the energy of an electron in the background field.

The second and fifth sums in the right hand side of (29c) are $O(N^2)$ terms, because indices i, j do not couple with k and l, but in (30c) these terms cancel. Simultaneously

terms containing W_b cancel in (30c) also, as expected. It is possible to verify that the same takes place in the third and (more cumbersome) fourth orders in overlap.

Now the energy expression can be obtained up to second order in the overlap. But first let us separate and combine together the slowest decaying terms. Adding and subtracting $1/R_{ij}$ from $\langle ij|g|ij\rangle$, $(R_{ij} = |R_i - R_j|)$ using the evident relation

$$\int \phi_i^*(r)V(r)\phi_i(r)\,dr = \int \phi_i^*(r)[V(r) - V(R_i)]\phi_i(r)\,dr + V(R_i) \tag{33}$$

and grouping terms one can obtain

$$W = W_1 + W_{\text{vib}} + W_{\text{ec}} + W_{\text{xc}}. \tag{34}$$

Any of these energies is an $O(N)$ term and therefore one can define the energy per electron

$$w_k = \lim_{N\to\infty} \frac{W_k}{N} \tag{35}$$

where k is 1, vib, ec or xc.

In equation (34)

$$W_1 = W_b + \sum_{i=1}^{N} V(R_i) + \frac{1}{2}\sum_{i,j=1}^{N}{}' \frac{1}{R_{ij}} \tag{36}$$

is the collection of the slowest decaying terms and it is exactly the energy of the static Wigner lattice. Therefore the energy per electron due to this term is

$$w_l = -M/r_s \tag{37}$$

where r_s is the usual homogeneous gas parameter $(4\pi r_s^3/3 = V/N)$ and M is a constant depending on the particular lattice.

The next term

$$W_{\text{vib}} = \sum_{i=1}^{N} \int \phi_i^*(r)[-\tfrac{1}{2}\Delta + V(r) - V(R_i)]\phi_i(r)\,dr \tag{38}$$

is apparently an $O(N)$ term. In accordance with (14) one has

$$w_{\text{vib}} = \int \phi(r)\left[-\frac{1}{2}\Delta + \frac{1}{2r_s^3}r^2\right]\phi(r)\,dr \tag{39}$$

which is the energy of a three-dimensional quantum harmonic oscillator.

The next term in (34)

$$W_{\text{ec}} = \frac{1}{2}\sum_{i,j=1}^{N}{}'\left[\langle ij|g|ij\rangle - \frac{1}{R_{ij}}\right] \tag{40}$$

is the electrostatic correction, that is the difference between the Hartree electrostatic interaction energy of localized electrons and that of point charges at lattice sites. The members of this sum decay rapidly with increasing R_{ij}. Therefore this sum is $O(N)$ and

$$w_{\text{ec}} = \frac{1}{2}\sum_{i\neq 0}\left[\int \frac{|\phi(r)|^2|\phi(r' - R_i)|^2}{|r - r'|}\,dr\,dr' - \frac{1}{R_i}\right] \tag{41}$$

where the sum is rapidly convergent.

Finally,

$$W_{xc} = \frac{1}{2} \sum_{i,j=1}^{N}{}' K_{ij} G^{ij} \tag{42}$$

is the exchange-correlation energy, where

$$K_{ij} = -\langle ij|g|ji\rangle - S_{ij}\left[\langle j|h|i\rangle + \sum_{k \neq i,j}\langle jk|g|ik\rangle\right] - \left[\langle i|h|j\rangle + \sum_{k \neq i,j}\langle ik|g|jk\rangle\right]S_{ji}$$

$$+ S_{ij}S_{ji}\left[\langle i|h|i\rangle + \sum_{k \neq i}\langle ik|g|ik\rangle + \langle j|h|j\rangle + \sum_{k \neq j}\langle jk|g|jk\rangle - \langle ij|g|ij\rangle\right] \tag{43}$$

In (43) the first term is the direct exchange. The matrix element in it is usually positive at large R_{ij}. All other terms are due to the orbitals' non-orthogonality and it is well known that these terms govern the value and sign of K_{ij}. The exchange-correlation term W_{xc} is $O(N)$. Indeed, indices ij in the right-hand side of (43) are linked by overlap, so K_{ij} rapidly decreases with increasing R_{ij}. The summation over k does not change the order of magnitude because of the relation

$$\langle i|h|i\rangle + \sum_{k \neq i}\langle ik|g|ik\rangle = \int |\phi_i(r)|^2\left(V(r) + \sum_{k \neq i}\int \frac{|\phi_k(r')|^2}{|r - r'|}\,dr'\right)dr \tag{44}$$

and the similar relation with indices ij. The quantity in the brackets in (44) is the potential energy of an electron in the positive background field and that of all other electrons and is finite. To evaluate the exchange-correlation energy w_{xc} per electron it is necessary to specify the pairing structure and calculate all G^{ij}.

There is a well developed Rumers diagram technique [12] for calculating integrals (18) in general, but for transpositions the calculations of G^{ij} are easy and can be done at once. If i and j belong to the same pair, then transposition results in a sign change only. If i and j belong to a different pairs then

$$G^{ij} = \int \chi(\sigma_i, \sigma_k)\chi(\sigma_j, \sigma_l)\chi(\sigma_j, \sigma_k)\chi(\sigma_i, \sigma_l)\,d\sigma_i\,d\sigma_j\,d\sigma_k\,d\sigma_l = \frac{1}{2}. \tag{45}$$

As a result we have

$$G^{ij} = \begin{cases} -1 & \text{if } i, j \text{ are in the same pair} \\ \frac{1}{2} & \text{if } i, j \text{ are in different pairs.} \end{cases} \tag{46}$$

It is evident that for ferromagnetic and antiferromagnetic cases the energy constituents W_1, W_{vib}, and W_{ec} are the same as in the singlet state. The difference is in W_{xc} because of the different values of G^{ij}. In the ferromagnetic case the function Θ_{FM} is completely symmetric and therefore

$$G^{ij}_{FM} = 1. \tag{47}$$

In the antiferromagnetic case it follows from (11) immediately that

$$G^{ij}_{AFM} = \begin{cases} 1 & \text{if } i, j \text{ are in the same sublattice} \\ 0 & \text{if } i, j \text{ are in different sublattices.} \end{cases} \tag{48}$$

4. Discussion

It is consistent with second order in the overlap approximation to employ the ground state three-dimensional harmonic oscillator wave function as orbital $\phi(r)$ (13) and to retain the nearest neighbours (NNs) only in the sum over pairs in the electrostatic correction W_{ec} (40) and the exchange-correlation energy W_{xc} (42). In this case

$$K_{ij} = \begin{cases} K & ij \text{ are nearest neighbours} \\ 0 & \text{otherwise} \end{cases} \tag{49}$$

and the energy expression can be written as

$$W = W_0 + \tfrac{1}{2}K \sum_{ij}^{NN} G^{ij} \tag{50}$$

where $W_0 = W_1 + W_{vib} + W_{ec}$, and the sum is over NN pairs.

In the ferromagnetic case all G^{ij} are equal to 1. Consequently

$$w_{FM} = w_0 + \tfrac{1}{2}nK \tag{51}$$

where n is the number of neighbours nearest to a given lattice site. In the antiferromagnetic state NNs belong to different sublattices and therefore $W_{xc} = 0$. Hence

$$w_{AFM} = w_0. \tag{52}$$

The energy of the singlet state depends on the particular pairing structure. One structure can be constructed by selecting a pair of NNs, coupling them with a singlet function and translating this 'bond' onto the whole crystal. In this case one of the neighbours nearest to a given one belongs to the same pair and $n - 1$ neighbours belong to different pairs. Therefore

$$w_S^{(1)} = w_0 + \tfrac{1}{4}(n - 3)K. \tag{53}$$

There are n pairing structures with $w_S^{(1)}$ energy.

Another structure can be constructed in a similar way but with a pair of second (or next) nearest neighbours (SNN) selected. In this case all the NN belong to different pairs. Hence

$$w_S^{(2)} = w_0 + \tfrac{1}{4}nK. \tag{54}$$

In this pairing structure 'bond' has no direct physical meaning because we take into account the NN overlap only but couple SNN sites. However, making use of the linear dependence of different pairing structures mentioned in section 2 one can express the structure with SNN coupling as a linear combination of several structures with NN coupling. So the SNN structure corresponds in a sense to a resonating valence bond state. Further still one can express the SNN structure as a structure where NNs are coupled but with mixed singlet–singlet and triplet–triplet coupling and not the pure singlet–singlet situation. Any structure which is due to the translation of the 'bond' between neighbours which are not nearest, and has the same number of 'bonds', corresponds to the same $w_S^{(2)}$ energy. So in the infinite lattice there are an infinite number of states with the energy $w_S^{(2)}$.

The obtained energies are evidently extreme ones for the singlet state—there is no singlet pairing structure with energy outside the $[w_S^{(1)}, w_S^{(2)}]$ region (within the approximations used). At the same time it is possible to construct a pairing structure with the energy in between $w_s^{(1)}$ and $w_S^{(2)}$ by breaking up the translation symmetry of the pairing structure (not the translation symmetry of the lattice). To do so one has, for example, to start with the first structure described above, to select a finite NN chain, and without changing the total number of 'bonds' to lessen the number of NN 'bonds' by 'rebonding' the sites crosswise. There is an infinite number of such structures with different energy and starting from the first structure one can gradually arrive at the second structure 'rebonding' one pair of 'bonds' at a time. Consequently there is a whole energy band of singlet states between $w_S^{(1)}$ and $w_S^{(2)}$.

From equations (51)–(54) one can see that in the perfect pairing approximation the energy of any singlet state is in between the energies of the ferromagnetic and antiferromagnetic states. As it occurs [11] except for very low densities the antiferromagnetic state has the lowest energy, hence K is positive. In this case the lowest singlet energy is $w_s^{(1)}$ which is higher than the energy of the antiferromagnetic state. The singlet energy can be lowered by going beyond the perfect pairing approximation to the general one (16). However to decide whether it will make the ground state of the electron gas a singlet, it is necessary to complete further computations which are in progress now.

Acknowledgments

References

[1]   Wigner E 1934 *Phys. Rev.* **46** 1002
[2]   Wigner E 1938 *Trans. Faraday Soc.* **34** 678
[3]   Coldwell-Horsfall R A and Maradudin A A 1960 *J. Math. Phys.* **1** 395
[4]   Carr W J 1961 *Phys. Rev.* **122** 1437
[5]   Carr W J, Coldwell-Horsfall R A and Fein A E 1961 *Phys. Rev.* **124** 747
[6]   Ceperley D M 1978 *Phys. Rev.* **18** 3126
[7]   Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[8]   Care C M and March N H 1975 *Adv. Phys.* **24** 101
[9]   Herman F and March N H 1984 *Solid State Commun.* **50** 725
[10] Lea M J and March N H 1989 *Int. J. Quant. Chem. Quant. Chem. Symp.* N **23** 717
[11] van Dijk L G J and Vertogen G 1991 *J. Phys.: Condens. Matter* **3** 7763
[12] McWeeny R 1989 *Methods of Molecular Quantum Mechanics* (New York: Academic)
[13] Wigner E 1959 *Group Theory and its Applications to the Quantum Mechanics of Atomic Spectra* (New York: Academic)
[14] Löwdin P O 1948 *Thesis* Uppsala