PHYSICAL REVIEW B VOLUME 18, NUMBER 5 1 SEPTEMBER 1978

Short-ranged correlations and the ferromagnetic electron gas

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(Received 1 May 1978)

A discussion of the various properties of pair correlation functions of a magnetic electron gas is presented. The cusp conditions obeyed by the many-electron wave functions for a pair of electrons with parallel and antiparallel spins in close proximity are expressed as derivative conditions on the corresponding parallel- and antiparallel-spin pair correlation functions. In particular, it is shown that in a fully ferromagnetic gas the parallel spin correlations determine the correlation energy whereas in the paramagnetic case, this function is of less importance in comparison to the antiparallel-spin correlation function. In the high-momentum limit, it is found that the momentum distribution of electrons is dominated by antiparallel-spin correlations in the partially magnetic case whereas in the fully ferromagnetic case, it is dominated by parallel-spin correlations but is smaller by a factor of q^{-2}. A calculation of the parallel-spin correlation function for the ferromagnetic gas in perturbation theory is presented. A model for the exchange correlation energy of the system which takes into account the exact conditions given here is proposed. Corresponding results for the two-dimensional electron gas are also stated.

I. INTRODUCTION

The nature of electron correlations in atoms and molecules has been pursued vigorously by chemists and, in solids, by physicists and these two studies have essentially proceeded independently. Only recently a meeting ground has been found in the density-functional approach. In this approach (more generally, the spin-density functional theory), one leans heavily on the properties of an interacting electron gas. This unified picture is best described in terms of pair correlation functions for parallel and antiparallel spins of the electrons. These functions are proportional to the probability that two electrons in the prescribed spin orientations be separated by some distance r. McWeeny[1] pioneered studies of these functions with electron correlations in molecules in view. Parallel-spin electrons stay away from each other because of the Pauli exclusion principle even if they are noninteracting. This has led to the concept of the "Fermi hole." On the other hand, antiparallel-spin electrons can come close to each other without violating the Pauli principle. They avoid each other only because of the Coulomb interaction between them. This led to the idea of the "Coulomb hole." These concepts have been studied by chemists for a long time,[2] and some important "cusp" properties concerning these functions were noted by them. In particular, it was recognized that the cusp behavior at short distances is important and it is for this reason that wave functions containing this proper behavior scored impressive successes.[2,3] This "cusp" behavior of the wave functions was put on a firm mathematical footing for many-electron wave functions by T. Kato.[4]

These developments went unnoticed in the study of the pair correlation functions of the electron gas. Most of all, only the paramagnetic electron gas was studied vigorously and impressive numerical work has been accomplished by Singwi and coworkers, based on a certain self-consistent scheme.[5] Geldart and co-workers,[6] and more recently Yashuhara,[7] have tried to evaluate these functions by summing a class of diagrams in a many-body perturbation theory. Most of these calculations violated the requirement that these functions be positive definite beyond a certain value of the density of the electron gas, even though the Vashishta-Singwi scheme is reasonable in the density range appropriate to solids. Kimball,[8] independent of McWeeny and Kato, derived the cusp condition for the antiparallel-spin correlation function. The main reason for confining one's attention to this function is that the lion's share of the correlation energy in the paramagnetic electron gas is due to antiparallel-spin correlations. In a recent paper, McWeeny[2] has developed a scheme for calculating the correlation energy of the paramagnetic electron gas based on the cusp condition following a similar calculation for the atoms by Colle and Salvetti.[9] The result is quite striking in that it appears to interpolate nicely between the high- and low-density regions.

Recently Gunnarson *et al.*[10] have suggested a method of incorporating the pair correlation functions directly into a density-functional theory. It is unfortunate that not even the energy density of

the magnetic electron gas is accurately known. The advantage of the approach taken by McWeeny, Kato, and Kimball is that many conclusions about short-range correlations can be applied to real systems with only minor modifications. In the fully magnetized electron gas, in contrast to the paramagnetic situation, the parallel-spin correlations determine the correlation energy. Only one theoretical attempt to study the correlations in a magnetic electron gas by generalizing the paramagnetic studies exists.[11] There is also a calculation of the ground-state energy in the ring-diagram approximation.[12] The use of the pair correlation function directly in a density-functional theory for the inhomogeneous magnetic systems has been suggested by Rajagopal and von Barth.[13]

The purpose of the present paper is to develop some exact statements concerning the pair correlation functions of a magnetic electron gas. After defining these functions, certain consequences follow almost immediately. By considering the nature of the many-electron wave functions in some detail when two electrons are close to each other, we develop the cusp conditions for these functions for parallel- and antiparallel-spin pairs. The antiparallel case was derived earlier by Kimball.[8] The result for the parallel case is new. These results are given in Sec. II. Recently, there has been a great deal of interest in the two-dimensional electron gas. The corresponding results for the various pair correlation functions in two dimensions are also given in Sec. II. Those results for the paramagnetic gas are given in Ref. 14. In Sec. III, it is shown that several quantities are related to the curvature of the ferromagnetic-electron-gas correlation function at zero separation. In particular, the third derivative of this function as the interparticle separation goes to zero, the corresponding structure factor for the parallel spins, and the momentum distribution function for large wavelengths are all simply related to the curvature at zero separation. The form of the parallel-spin correlation function for small distances is estimated from a high-density expansion in the same section. In Sec. IV, we summarize the results. We also develop a "model" for the pair correlation functions. McWeeny[2] has noted that such a model for the correlation function can be used to obtain the correlation energy. We suggest an alternative method for calculating this energy.

II. PAIR-CORRELATION FUNCTIONS FOR THE MAGNETIC ELECTRON GAS

The description of the systems of interacting electrons is best given by means of the second-quantized operators $\Psi_\sigma(\vec{r})$ and $\Psi_\sigma^\dagger(\vec{r})$, denoting the destruction and creation of electrons at position $\vec{r}$ with spin σ. These operators obey the usual equal time anticommutation relations. We will confine our discussion to zero temperature, for convenience. Let $n_\sigma(\vec{r}_1)$ denote the number density of electrons in the spin state σ_1, at $\vec{r}$ given by $n_{\sigma_1}(\vec{r}_1) = \langle \Phi | \Psi_{\sigma_1}^\dagger(\vec{r}_1)\Psi_{\sigma_1}(\vec{r}_1) | \Phi \rangle$ where $\Phi(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N)$ is the normalized N-electron ground-state wave function of the system of total number of electrons N (Φ for short). The pair correlation functions $g_{\sigma_1\sigma_2}(\vec{r}_1, \vec{r}_2)$ for the electron gas are defined by

$$n_{\sigma_1}(\vec{r}_1)n_{\sigma_2}(\vec{r}_2)g_{\sigma_1\sigma_2}(\vec{r}_1, \vec{r}_2) = \langle \Phi | \Psi_{\sigma_1}^\dagger(\vec{r}_1)\Psi_{\sigma_2}^\dagger(\vec{r}_2)\Psi_{\sigma_2}(\vec{r}_2)\Psi_{\sigma_1}(\vec{r}_1) | \Phi \rangle \quad (1)$$

and $g_{\sigma_1\sigma_2}(\vec{r}_2, \vec{r}_2)$ is the probability that if an electron of spin σ_1 is at $\vec{r}_1$, there will be another one of spin σ_2 at $\vec{r}_2$. In the electron gas, because of homogeneity of the system, $n_{\sigma_1}(\vec{r}_1)$ is independent of $\vec{r}_1$ and $g_{\sigma_1\sigma_2}(\vec{r}_1, \vec{r}_2)$ depends only on the distance between the two electrons, $|\vec{r}_1 - \vec{r}_2|$. From this definition and the fact that the operators obey anticommutation rules, we have the following properties (which do not depend on the homogeneity property of our system):

$$\text{(A)}\quad g_{\sigma_1\sigma_2}(\vec{r}_1, \vec{r}_2) \geq 0, \quad (2)$$

$$\text{(B)}\quad g_{\sigma\sigma}(\vec{r}, \vec{r}) = 0 \quad \text{(Pauli exclusion principle)}, \quad (3a)$$

and

$$g_{\sigma_1\sigma_2}(\vec{r}_1, \vec{r}_1) \geq 0 \quad \text{for } \sigma_1 \neq \sigma_2, \quad (3b)$$

$$\text{(C)}\quad g_{\sigma_1\sigma_2}(\vec{r}_1, \vec{r}_2) = g_{\sigma_2\sigma_1}(\vec{r}_2, \vec{r}_1). \quad (4)$$

The symmetry of the correlation function with respect to the exchange of particles follows from Eq. (1) and the commutation relations for $\Psi^\dagger\Psi$ and $\Psi^\dagger\Psi$:

$$\text{(D)}\quad \int d\vec{r}_2\, n_{\sigma_2}(\vec{r}_2)[g_{\sigma_1\sigma_2}(\vec{r}_1, \vec{r}_2) - 1] = -\delta_{\sigma_1\sigma_2}. \quad (5)$$

This last property follows directly by integrating both sides of Eq. (1) appropriately and using the fact that the ground state of the system has a fixed number of particles in the spin state σ. An equivalent expression with $(\vec{r}_1, \sigma_1)$ and $(\vec{r}_2, \sigma_2)$ interchanged follows from the exchange symmetry of g. All of the above properties are consequences of the definition of g [Eq. (1)]. They are valid for any Fermi systems and are independent of the dimensionality.

The following two conditions are special to the case of Fermions interacting in a pairwise Coulomb interaction and in three dimensions (e.g., electrons). Let $\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$ and $\vec{r} = \vec{r}_1 - \vec{r}_2$. Then, by definition, $g_{\sigma_1\sigma_2}(\vec{r}, \vec{R}) = g_{\sigma_1\sigma_2}(\vec{r}_1, \vec{r}_2)$. Now we have

(E) $g_{\sigma\sigma}(\vec{r}=0,\vec{R})=0$, (6)

$$\frac{\partial}{\partial|\vec{r}|}\, g_{\sigma\sigma}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}=0\ , \tag{7a}$$

$$\frac{\partial^2}{\partial|\vec{r}|^2}\, g_{\sigma\sigma}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}=\frac{2}{3}\frac{a_0}{\lambda}\frac{\partial^3}{\partial|\vec{r}|^3}(\vec{r},\vec{R})\Big|_{\vec{r}\to 0}\ , \tag{7b}$$

where λ is the dimensionless strength of the electron-electron interaction and a_0 is the usual Bohr radius.

(F) For $\sigma_1\neq\sigma_2$,

$$g_{\sigma_1\sigma_2}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}=\frac{a_0}{\lambda}\frac{\partial}{\partial|\vec{r}|}\, g_{\sigma_1\sigma_2}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}\ . \tag{8}$$

These relations are exact consequences of solving the many-electron Schrödinger equation for a fixed configuration of all but a pair of electrons in the system, when the pair comes close to each other. Under these conditions, the ground-state wave function can be determined quite accurately as was done by Kato and by Kimball. Equations (6)–(8) were known to Kato, but (7b) is new. Kimball expressed the cusp conditions [Eq. (8)] in terms of pair correlation functions and, furthermore, related it to the large wave vector behavior of structure factor, as well as to that of the momentum distribution function. Equations (6) and (7a) are consequences of the fact that Φ is antisymmetric under the interchange of $\vec{r}_1$ and $\vec{r}_2$ and in fact, by considerations such as that of Kato and Kimball, for $|\vec{r}|\to 0$, we need only to solve the Schrödinger equation for a pair of electrons with angular momentum unity:

$$\Phi(\vec{r},\vec{R};\sigma,\sigma,\ldots)\cong A|\vec{r}|\,[1+(\lambda/4a_0)|\vec{r}|\,]\ , \tag{9}$$

where A is a constant.

On the other hand, for $\sigma_1\neq\sigma_2$, we need only consider the state of zero angular momentum for the pair:

$$\Phi(\vec{r},\vec{R};\sigma_1,\sigma_2;\ldots)\cong B(1+(\lambda/a_0)|\vec{r}|), \quad \sigma_1\neq\sigma_2\ , \tag{10}$$

where B is some constant.

For the two-dimensional electron system,[14] the (E) and (F) are replaced by

(E′) $g^{(2)}_{\sigma\sigma}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}=0$, (11a)

$$\frac{\partial}{\partial|\vec{r}|}\, g^{(2)}_{\sigma\sigma}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}=0\ , \tag{11b}$$

$$\frac{\partial^2}{\partial|\vec{r}|^2}\, g^{(2)}_{\sigma\sigma}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}=\frac{a_0}{2\lambda}\frac{\partial^3}{\partial|\vec{r}|^3}\, g^{(2)}_{\sigma\sigma}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}\ , \tag{11c}$$

(F′) $$g^{(2)}_{\sigma_1\sigma_2}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}=\frac{a_0}{2\lambda}\frac{\partial}{\partial|\vec{r}|}\, g^{(2)}_{\sigma_1\sigma_2}(\vec{r},\vec{R})\Big|_{|\vec{r}|\to 0}\ . \tag{12}$$

The superscript (2) in the above refers to two dimensions and all the vectors are two-dimensional. The corresponding statements on the wave functions are

$$\Phi^{(2)}(\vec{r},\vec{R};\sigma,\sigma;\ldots)\cong A^{(2)}|\vec{r}|\left(1+\frac{\lambda}{3a_0}|\vec{r}|\right)\ , \tag{13}$$

and

$$\Phi^{(2)}(\vec{r},\vec{R};\sigma_1,\sigma_2;\ldots)\cong B^{(2)}\left(1+\frac{\lambda}{a_0}|\vec{r}|\right), \quad \sigma_1\neq\sigma_2\ . \tag{14}$$

These are all the results that can be stated in an exact manner. In Sec. III, we shall deal with some approximation schemes with the hope of obtaining some information about the detailed nature of these pair correlation functions.

III. CUSP CONDITIONS AND SOME APPROXIMATE CALCULATIONS OF $g_{\sigma_1\sigma_2}(\vec{r}_1,\vec{r}_2)$

We first show a connection between the cusp conditions (E) and (F) of Sec. II with the short-wavelength behavior of the structure factor and momentum-distribution functions. These functions are related to physical scattering processes, as is well known. We follow Ref. 8(b) in estimating these results. For uniform systems, $g(\vec{r},\vec{R})\to g(r)$,

$$g_{\sigma_1\sigma_2}(r)-1=\frac{1}{n}\int e^{i\vec{q}\cdot\vec{r}}[S_{\sigma_1\sigma_2}(q)-1]\,\frac{d^3q}{(2\pi)^3}\ . \tag{15}$$

Here the wave vector q is measured in units of k_F. The relation between $S_{\sigma_1\sigma_2}(q)$ $(\sigma_1\neq\sigma_2)$ for large q and $g(r)$ was given earlier[8(b)] and it is

$$\frac{3\pi a_0}{8K_F^3}\lim_{q\to\infty}\{q^4[S_{\sigma_1\sigma_2}(q)-1]\}=g_{\sigma_1\sigma_2}(0), \quad (\sigma_1\neq\sigma_2)\ . \tag{16}$$

Similar arguments[8(b)] give us another relationship

$$\frac{\pi a_0}{8K_F^3}\lim_{q\to\infty}\{q^6[S_{\sigma\sigma}(q)-1]\}=g''_{\sigma\sigma}(0)\ . \tag{17}$$

The momentum distribution function $n_\sigma(K)$ for an electron of spin σ, and momentum K, is given by

$$n_\sigma(K)=\frac{N}{V}\int e^{i\vec{K}\cdot(\vec{r}-\vec{r}')}\Phi^*(\vec{r},\sigma,\vec{r}_2,\sigma_2,\dots)\Phi(\vec{r}',\sigma,\vec{r}_2,\sigma_2,\dots)\,d\vec{r}\,d\vec{r}'\prod_{i=2}^{N}dx_i$$

$$=\frac{N}{V}\int e^{\vec{K}\cdot(\vec{r}-\vec{r}')}[\Phi^*(r,\sigma,\vec{r}_2,\sigma\dots)\Phi(\vec{r}',\sigma,\vec{r}_2,\sigma,\dots)$$

$$+\Phi^*(r,\sigma,\vec{r}_2,-\sigma,\dots)\Phi(\vec{r}',\sigma,\vec{r}_2,-\sigma,\dots)]\,d\vec{r}\,d\vec{r}'d\vec{r}_2\prod_{i=3}^{N}dx_i \tag{18}$$

where

$$dx_1=\sum_{\sigma_1}d\vec{r}_1\ .$$

Correspondingly the definition $g_{\sigma_1\sigma_2}$ in terms of the wave function is

$$n_{\sigma_1}n_{\sigma_2}g_{\sigma_1\sigma_2}(\vec{r}_1,\vec{r}_2)$$

$$=N(N-1)\int\Phi^*(r_1,\sigma_1,r_2,\sigma_2,\dots)$$

$$\times\Phi(r_1,\sigma_1,r_2,\sigma_2,\dots)\prod_{i=3}^{N}dx_i \tag{19}$$

Combining Eqs. (18) and (19) and (9) and (10) we obtain

$$n_\sigma(K)_{K\to\infty}\to\frac{K_F^3}{3V}\left(\frac{16\pi}{a_0}\right)^2 g''_{\sigma\sigma}(0)\,\frac{1}{K^{10}}\ , \tag{20}$$

for the saturated ferromagnet, and

$$n_\sigma(K)_{K\to\infty}\to\frac{K_F^3(1-\zeta^2)}{V}\left(\frac{8\pi}{a_0}\right)^2 g_{\sigma,-\sigma}(0)\,\frac{1}{K^8}\ , \tag{21}$$

for the unsaturated ferromagnet, $0<\zeta<1$.

Here ζ is the relative magnetization. Equation (21) shows that the dominating quantity in $n_\sigma(K)$ for large K is the antiparallel-spin correlation function if one has a partially magnetic state. In view of the behavior of the parallel-spin correlation function for small separations of electrons, this behavior is not surprising.

The functions $g_{\sigma_1\sigma_2}$ can be calculated in terms of the many-body perturbation theory. Such attempts, in the case of paramagnetic electron gas, have not been very fruitful.[6] One may develop self-consistent schemes of calculating these as was done by Singwi and his co-workers.[5] The precise short-range behavior of these functions obtained here are not easy to maintain in these theories and we shall briefly indicate this aspect here. One, therefore, may resort to proposing "model" pair correlation functions which obey at least all the exact statements (A)–(F) given above and compute quantities of interest from that. We shall briefly examine one such suggestion in Sec. IV.

In the Hartree-Fock (HF) approximation, it is easy to note that $g_{\sigma_1\sigma_2}(r)$ can be explicitly given:

$$g_{\sigma_1\sigma_2}(r)=1-9\delta_{\sigma_1\sigma_2}\left(\frac{\sin K_{F\sigma_1}r-K_{F\sigma_1}r\cos K_{F\sigma_1}r}{K_{F\sigma_1}^3r^3}\right)^2 . \tag{22}$$

Here $\delta_{\sigma_1\sigma_2}$ is the usual Kronecker symbol and $K_{F\sigma_1}$ is the Fermi momentum of spin σ_1 related to n_{σ_1} via

$$n_{\sigma_1}=K_{F\sigma_1}^3/6\pi^2=K_F^3(1+\sigma_1\zeta)/6\pi^2)\ . \tag{23}$$

It is customary to define the total number by

$$n=n_\uparrow+n_\downarrow=K_F^3/3\pi^2\ . \tag{23'}$$

This approximation takes proper account of the Pauli principle and hence the relations (A)–(D) are obeyed as well as (6), (7a) of (E). However, Eqs. (7b) and (8) are not obeyed because the approximation fails to take into account the Coulomb repulsion between two electrons. More precisely, from Eq. (22) we see that $g_{\sigma_1\sigma_2}(r)=1$ for $\sigma_1\neq\sigma_2$ for all r, showing that the "Coulomb hole" does not exist in the HF scheme.

The HF approximation may be thought of as the lowest-order approximation in a perturbation theory of the electron interactions. In first order one obtains:

$$n_{\sigma_1}n_{\sigma_2}g^{(1)}_{\sigma_1\sigma_2}(r)=\lambda\sum_{K_1K_2q}e^{i\vec{q}\cdot\vec{r}}\,\frac{V(q)-\delta_{\sigma_1\sigma_2}V(\vec{q}-\vec{K}_1-\vec{K}_2)}{\epsilon_{K_1}-\epsilon_{K_2}-\epsilon_{\vec{K}_2+\vec{q}}-\epsilon_{\vec{K}_2-\vec{q}}}\,f_{\sigma_1}(K_1)f_{\sigma_2}(K_2)\,[1-f_{\sigma_1}(\vec{K}_1+\vec{q})][1-f_{\sigma_2}(\vec{K}_2-\vec{q})]\ , \tag{24}$$

where $f_\sigma(K)$ is the usual Fermi function for electrons of spin σ, and wave vector K. The momentum summations are written so that Eq. (24) is applicable to three- and two-dimensional cases. $V(q)$ is the Fourier transform of the Coulomb potential and is $4\pi e^2/q^2$ in three dimensions and $2\pi e^2/q$ in two dimensions. ϵ_K is the one-electron energy $K^2/2m$. The higher-order terms in the perturbation series quickly become highly complicated (see Sec. IV however).

We will now consider the fully magnetized electron gas because it brings out the main features of the parallel-spin correlations in a clear fashion. In this case, unlike in the paramagnetic case, the system behaves more like a noninteracting system. This is because of the efficiency of the Pauli principle in minimizing the potential energy so that additional correlations are small. First of all, let us note that for $r=0$, $g_{\sigma\sigma}^{(1)}(r)$ is zero. Next, we note that the lowest-order correction to $g_{\sigma\sigma}''$ is relatively small. The two primes denote differentiation two times with respect to r. From Eq. (22), we have

$$g_{\uparrow\uparrow}'' = \tfrac{2}{5} K_{F\uparrow}^2 . \tag{25}$$

From Eq. (24), we have, on scaling all momenta by $K_{F\uparrow} = 2^{1/3} K_F$

$$g_{\uparrow\uparrow}^{(1)''}(0) = \frac{2}{5} K_{F\uparrow}^2 \frac{45\alpha r_s}{64\pi^4} \frac{1}{2^{1/3}} \times \int\int_R \int \frac{d^3x_1\, d^3x_2\, d^3y}{\vec{y}\cdot(\vec{y}+\vec{x}_1-\vec{x}_2)} \times \left(1 - \frac{y^2}{|\vec{y}+\vec{x}_1-\vec{x}_2|^2}\right), \tag{26}$$

where R is the region of integration specified by

$$|\vec{x}_1|<1, \quad |\vec{x}_2|<1, \quad |\vec{x}_1+\vec{y}|>1, \text{ and } |\vec{x}_2-\vec{y}|>1. \tag{27}$$

The integral was done on a computer and we obtain

$$g_{\uparrow\uparrow}''(0) = \frac{2}{5} K_{F\uparrow}^2 \left(1 - \frac{r_s}{2.9}\right). \tag{28}$$

In Sec. IV, we shall summarize our results and indicate in what ways we can perhaps gain some insight into the correlation energy of the ferromagnetic electron system.

IV. SUMMARY AND CONCLUDING REMARKS

We have examined the consequences of the behavior of the many-electron wave function where a pair of electrons are in proximity as a means of obtaining information concerning the short-range properties of the pair correlations in a magnetic electron gas. These considerations are generalizations of the corresponding results for the paramagnetic case. We have also presented the results for a two-dimensional electron gas. In particular, in the paramagnetic case, the anti parallel-spin correlations play a paramount part since the parallel-spin correlations are of relatively little consequence because of Pauli exclusion principle. In the fully magnetized electron gas, on the other hand, the correlations are among the parallel spins, and this we have studied in some detail. In the partially magnetized case, both of these correlations play a part with antiparallel-spin interactions contributing a lion's share. This is seen for example in the asymptotic dependence of the momentum distribution function, $n_\sigma(K)$ of Eq. (21). The limit of large-wave-vector form of the structure factor for parallel spins is seen to be smaller by a factor q^{-2} compared to the corresponding behavior of the structure factor for the antiparallel spins. We have calculated the pair correlation function in lowest-order perturbation theory of the interactions in Eq. (24). A calculation of the contributions of ring-diagrams can be made[15] and the answer is given here without derivation:

$$g_{\sigma_1\sigma_2}^{(\mathrm{ring})}(r) = g_{\sigma_1\sigma_2}^{\mathrm{HF}}(r) + \frac{1}{n_{\sigma_1} n_{\sigma_2}} \int \frac{d^4q\, e^{i\vec{q}\cdot\vec{r}}}{(2\pi)^4} \int \frac{d^4K_1}{(2\pi)^4} \int \frac{d^4K_2}{(2\pi)^4} \left[V_s(q) - \delta_{\sigma_1\sigma_2} V_s(K_1-K_2-q)\right] \times G_{\sigma_1}(K_1+q) G_{\sigma_2}(K_2-q) G_{\sigma_2}(K_2) G_{\sigma_1}(K_1), \tag{29}$$

where $G_\sigma(k)$ is the one-electron Green's function for spin σ, and $V_s(q)$ is the Coulomb interaction $V(q)$, among electrons screened by the random-phase-approximation dynamical dielectric function $\epsilon(q)$. The frequency integration q_0 now must take account of the frequency dependence of V_s. The explicit calculation of this quantity is numerically complicated. It should be noted that Eq. (29) obeys the conditions that $g_{\sigma\sigma}(0)=0$. In diagrammatic language, we see that in order to obtain this proper behavior, we must consider not only ring diagrams represented by the second term in Eq. (29), but we should also add contributions from one-exchange–many-ring diagrams, the third term in Eq. (29). This illustrates one of the difficulties in applying the perturbation theory in a straightforward way. Other vertex corrections, such as those given in the paramagnetic case,[6] can be worked out following the methods of Ref. 11, but we shall not present them here. Our point here is only to show that extra care is required in dealing with such a theory.

We would like to briefly outline here one of the most important uses of the pair correlation functions, namely, the calculation of the exchange-correlation energy, denoted by E_{xc}, of the many-electron system which may be used in the spin-density-functional formalism. The general ex-

pression for E_{xc} is[13] (energy per particle)

$$\frac{E_{xc}}{N} = \frac{e^2}{2} \sum_{\sigma_1\sigma_2} n_{\sigma_1} n_{\sigma_2} \int \frac{d\vec{r}}{|\vec{r}|} \times \int_0^1 d\lambda [\, g_{\sigma_1\sigma_2}(r,\lambda) - 1], \tag{30}$$

where $g_{\sigma_1\sigma_2}(r,\lambda)$ is the pair correlation function for an electron gas with electron interactions having a strength, λ. In this form, the contribution to E_{xc} from the calculation of the expectations value of the kinetic energy is properly taken into account. McWeeny[2] and Colle and Salvetti[9] assume the wave function for the interacting system in the form of a product of that of the noninteracting system and a correlation factor, which takes into proper account the cusp behavior, Eqs. (13) and (14). They then assume that the contribution to E_{xc} from the kinetic energy term is approximately zero. Thus, we directly employ a "model" for $g_{\sigma_1\sigma_2}(r,\lambda)$ which obeys all the constraints (A)–(F). We have done this for both two- and three-dimensional cases. We present here the main idea. We find in three dimensions,

$$g_{\sigma\sigma}(r,\lambda) = g^{\mathrm{HF}}_{\sigma\sigma}(r)\left\{1 + e^{-\beta^2_{\sigma\sigma} r^2}\left[1 + \alpha_{\sigma\sigma}(\lambda)\left(1 + \frac{\lambda r}{2a_0}\right)\right]\right\}, \tag{31}$$

$$g_{\uparrow\downarrow}(r;\lambda) = g^{\mathrm{HF}}_{\uparrow\downarrow}(r)\left\{1 + e^{-\beta_{\uparrow\downarrow} 2r^2}\left[-1 + \alpha_{\uparrow\downarrow}(\lambda)\left(1 + \frac{\lambda r}{a_0}\right)\right]\right\}. \tag{32}$$

$\beta_{\sigma\sigma'}$ and $\alpha_{\sigma\sigma'}$ are constants to be chosen in order to obey all the conditions (A)–(F). With Colle and Salvetti,[9] we may interpret $\beta_{\sigma\sigma'}$ as a measure of the *size* of correlation, $\beta_{\sigma\sigma}$ that of Fermi hole of spin σ and $\beta_{\uparrow\downarrow}$ that of Coulomb hole. Assume the $\beta_{\sigma\sigma'}$'s are independent of λ. Equations (31) and (32) were chosen in order to obey the cusp behaviors. The sum rules, Eq. (4), give us a connection between $\beta_{\sigma\sigma'}$ and $\alpha_{\sigma\sigma'}$ for fixed σ, σ'. We have, in this model three parameters as yet undetermined. Thus we note,

$$\alpha_{\sigma\sigma}(\lambda) = \frac{I_0(\beta_{\sigma\sigma})}{I_0(\beta_{\sigma\sigma}) + \lambda/2a_0 I_1(\beta_{\sigma\sigma})}, \tag{33}$$

$$\alpha_{\uparrow\downarrow}(\lambda) = \frac{\frac{1}{2}\sqrt{\pi}\,\beta_{\uparrow\downarrow}}{\frac{1}{2}\sqrt{\pi}\,\beta_{\uparrow\downarrow} + \lambda/a_0}, \tag{34}$$

where

$$I_n(\beta_{\sigma\sigma}) = \int d^3r\, g^{\mathrm{HF}}_{\sigma\sigma}(r) e^{-\beta^2_{\sigma\sigma} r^2} r^n, \quad (n = 0.1). \tag{35}$$

All the integrals can be done analytically by elementary integration as well as the subsequent λ integrations. In the two-dimensional case, similar expressions are obtained. In the paramagnetic case, McWeeny[2] used a similar idea but without the λ-integration trick, where only the antiparallel-spin contributions are *assumed* to be important in the model in which case one has only one parameter to determine. This is done by McWeeny[2] by fitting β such that the correlation energy of the Helium atom is obtained correctly. Such a fit was used by Colle and Salvetti[9] who made a model for calculating correlation energies of atoms with impressive success. In McWeeny's calculation,[2] this choice of β gave him an expression for correlation energy of the electron gas which fitted remarkably well the high- and low-density limits as well as provided a smooth interpolation between these limits. In the partially magnetic case, we need three constants. In the fully magnetized case, we again need only one constant which may be fitted by considering the correlation energy of the lithium atom. We hope that such model building based on correlation functions will yield important results in the future.

ACKNOWLEDGMENTS

One of us (A.K.R.) thanks the theory group at IBM, Thomas J. Watson Research Laboratory for their warm hospitality. It is also a pleasure to place on record special thanks to Dr. J. Janak for several discussions on the subject matter discussed in this paper.

*On Sabbatical leave from Louisiana State University, Baton Rouge, La. 70803 (during the academic year 1977–1978).

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