Dynamical and Statistical Correlations in an Electron Gas*

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In the Cowan-Kirkwood treatment of an electron gas, one particle is singled out and the relative motion described. The density for the new problem is then related to the pair function for the original. Two effects omitted from this model, the considerable velocity of the chosen particle and its statistical interaction with the remainder, are included in the present treatment. The pair function is considerably altered in detail but a calculation at a typical metallic density indicates that the two effects compensate energetically. This explains the success of the simple Cowan-Kirkwood treatment in this region. There are reasons why the present formulation should have a wider range of applicability than the original method.

I. INTRODUCTION

A FEW years ago Cowan and Kirkwood[1] (C.K.) proposed an interesting method for calculating correlation effects in an electron gas. Theirs was essentially the Debye–Hückel technique of selecting some one particle from the gas and calculating the distribution of the other particles around it to obtain a pair distribution function. The model adopted was of a static point charge (without statistical properties) interacting with a gas of electrons, a model that has been used for the vacancy problem.[2]

It would appear, therefore, that the deficiencies of the method are twofold. Firstly, the electron singled out is assumed static, whereas a typical particle will possess a substantial fraction of the Fermi velocity. This clearly corresponds to an omission of backflow— a concept that has recently been applied to electronic systems.[3] Secondly, no account is taken of the statistical hole surrounding the selected particle for in the limit of vanishing coupling, the Coulombically produced C.K. hole disappears entirely. Our purpose here is to propose a remedy for these defects and understand the success of the C.K. method at metallic densities.

The reason for this success is easily stated at this stage. Consider the changes in pair function corresponding to the dynamical and statistical effects referred to above. On allowing the selected particle to have an appreciable velocity, closer encounters with other particles become possible resulting in an aggregate shift in the charge cloud towards the origin. However, on taking into account the exchange effect the parallel spin electrons are repelled. The forms of the two electron clouds are altered in detail but energetically the two shifts approximately cancel.

Section 2 is devoted to a precise formulation of the intuitive idea of C.K., Sec. 3 to the establishing of a suitable approximate method, Secs. 4 and 5 to obtaining some semiquantitative results, and Sec. 6 to a brief discussion.

2. RELATIVE COORDINATES

For convenience let us consider a unit density gas characterized by the Hamiltonian

$$H_0 = -\tfrac{1}{2} \sum_{i=1}^{N} \nabla_{r_i}^2 + \lambda \sum_{i<j} \frac{1}{|r_i - r_j|}. \tag{1}$$

This is readily converted into the electron gas problem[4] at any prescribed density by suitable choice of λ. Selecting one particle, that at r_1, say, for special consideration, we make the change of variable

$$\xi_1 = \frac{1}{N} \sum_{i=1}^{N} r_i, \quad \xi_i = r_i - r_1 \ (i>1). \tag{2}$$

Then (1) becomes

$$H_0 = -(1/2N)\nabla_{\xi_1}^2 + H, \tag{3}$$

where H is an operator in $N-1$ variables only and given by

$$H = -\sum_{2 \le i \le j \le N} \nabla_{\xi_i} \cdot \nabla_{\xi_j} + \lambda \sum_{i=2}^{N} \frac{1}{\xi_i} + \lambda \sum_{i<j} \frac{1}{|\xi_i - \xi_j|}. \tag{4}$$

The effect of this transformation on $\Psi_0(r_1, \cdots, r_N, \sigma_1, \cdots, \sigma_N)$, the ground-state wave function associated with (1), is to redescribe it as $N^{-1/2}\Psi(\xi_2, \cdots \xi_N, \sigma_1, \cdots, N)$, whence

$$\int |\Psi_0(r_1, \cdots r_N, \sigma_1, \cdots \sigma_N)|^2 d\sigma_1 \cdots d\sigma_N dr_3 \cdots dr_N$$

$$= \int |N^{-1/2}\Psi(\xi_2, \cdots, \xi_N, \sigma_1, \cdots \sigma_N)|^2 d\sigma_1 \cdots$$

$$d\sigma_N d\xi_3 \cdots d\xi_N. \tag{5}$$

This may be rewritten[4]

$$2P(r_1 r_2) = \bar{\rho}(\xi_2), \tag{6}$$

[1] R. D. Cowan and J. G. Kirkwood, Phys. Rev. 111, 1460 (1958).
[2] L. C. R. Alfred and N. H. March, Phys. Rev. 103, 877 (1956); Phil. Mag. 2, 985 (1957). N. H. March and A. M. Murray, Proc. Roy. Soc. (London) A256, 400 (1960); A261, 119 (1961); A266, 559 (1962). G. K. Corless and N. H. March, Phil. Mag. 6, 1285 (1961).
[3] J. Bardeen and J. R. Schrieffer, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. III, pp. 186, 187. D. Pines and J. R. Schrieffer, Nuovo Cimento 10, 496 (1958).
[4] W. H. Young and N. H. March, Proc. Roy. Soc. (London) A256, 62 (1960).

where $2P(\mathbf{r}_1\mathbf{r}_2)$ is the pair function for the original wave function, while $\bar{\rho}(\xi_2)$ is the sum over σ_1 of the spinless density for the new wave function Ψ in the $N-1$ spatial coordinates $\xi_2, \cdots, \xi_N$, i.e.,

$$\bar{\rho}(\xi_2) = \int \rho(\xi_2)d\sigma_1, \tag{7}$$

where

$$\rho(\xi_2) = (N-1)\int |\Psi(\xi_2,\cdots,\xi_N,\sigma_1,\cdots\sigma_N)|^2 d\sigma_2 \cdots$$
$$d\sigma_N d\xi_3 \cdots d\xi_N. \tag{8}$$

Equation (6), embodying a relationship between the original pair function and the new density, would appear to be a proper formulation of the C.K. idea. Note, however, the form of the kinetic energy in (4) clearly taking into account the relative motion. By using a conventional Thomas–Fermi (T.F.) form for the kinetic energy for the reduced problem C.K. omit this dynamical effect and obtain pair functions which should be most appropriate for the electrons with zero wave number.

3. APPROXIMATE PAIR FUNCTION

We now wish to use the above exact formalism as a basis for approximate computation. To see how this can be done consider the case $\lambda=0$, when exact solutions are known. The wave function Ψ_0 in this case is just the usual determinant of plane wave states,

$$(N!)^{-1/2} \det| \varphi_{\mathbf{k}_1}(\mathbf{r}_1)\chi_{1/2}(\sigma_1) \varphi_{\mathbf{k}_2}(\mathbf{r}_2)\chi_{1/2}(\sigma_2)\cdots$$
$$\varphi_{\mathbf{k}_{N/2}}\chi_{1/2}(\sigma_{N/2}) \varphi_{\mathbf{k}_1}(\mathbf{r}_{N/2}+1)\chi_{-1/2}(\sigma_{N/2+1})\cdots$$
$$\varphi_{\mathbf{k}_{N/2}}(\mathbf{r}_N)\chi_{-1/2}(\sigma_N)|, \tag{9}$$

where

$$\varphi_{\mathbf{k}}(\mathbf{r}) = N^{-1/2} \exp(2\pi i \mathbf{k}\cdot\mathbf{r}/N^{1/3}), \tag{10}$$

the $\mathbf{k}$ being vectors with integer components. Then, using the result that the sum over all momenta is zero, we obtain for the corresponding Ψ the expression

$$[(N-1)!]^{1/2} \det| \varphi_{\mathbf{k}_1}(0)\chi_{1/2}(\sigma_1) \varphi_{\mathbf{k}_2}(\xi_2)\chi_{1/2}(\sigma_2)\cdots$$
$$\varphi_{\mathbf{k}_{N/2}}(\xi_N)\chi_{-1/2}(\sigma_N)|. \tag{11}$$

To illustrate (6) the density for the wave function (11) is readily calculated. One obtains

$$\bar{\rho}(\xi_2) = 1 - \tfrac{1}{2}l^2(\xi_2), \tag{12}$$

where

$$l(\xi) = 3(\sin\zeta - \zeta \cos\zeta)/\zeta^3, \quad \zeta = (3\pi^2)^{1/3}\xi, \tag{13}$$

and this is just the pair function for the original problem.

Now suppose the particles interact. We will assume that (11) may be replaced by

$$\Psi = [A(N-1)!]^{-1/2} \det|\phi_{\mathbf{k}_1}(\xi_1)\chi_{1/2}(\sigma_1)\phi_{\mathbf{k}_2}(\xi_2)\chi_{1/2}(\sigma_2)\cdots$$
$$\phi_{\mathbf{k}_{N/2}}(\xi_N)\chi_{-1/2}(\sigma_N)|, \tag{14}$$

for the purpose of computing via (6), (7), and (8) an approximate pair function. The differences between (11)

and (14) will be noted. The plane wave states have been replaced by general states and A is a constant which preserves normalization under this change. The quantity ξ_1, not to be confused with the center of gravity coordinate of Eq. (2), is identically zero, but its formal introduction is convenient as we shall see.

With regard to the fundamental status of (14), in terms of its original $\mathbf{r}$, σ variables it is antisymmetric with respect to interchange of particles 2, 3, $\cdots$, N among themselves but not with respect to particle 1 and any of the others. On the other hand, Ψ vanishes if any other particle takes on the coordinates of particle 1. Thus, (14) provides some description of the statistical effect we seek, a description which is exact at zero coupling.

The calculation of $\bar{\rho}$ is facilitated by observing that $(AN)^{-1/2}\Psi$ is formally a conventional Slater determinant in N variables with pair function

$$\frac{N(N-1)}{2} \int |(AN)^{-1/2}\Psi(\xi_1,\cdots\xi_N,\sigma_1,\cdots\sigma_N)|^2 d\sigma_1 \cdots$$
$$d\sigma_N d\xi_3 \cdots d\xi_N = \tfrac{1}{2}\{n(\xi_1)n(\xi_2) - \tfrac{1}{2}|\gamma(\xi_1|\xi_2)|^2\}, \tag{15}$$

where

$$\gamma(\xi_1|\xi_2) = 2 \sum_{\text{occ. } \mathbf{k}} \phi_{\mathbf{k}}^*(\xi_1)\phi_{\mathbf{k}}(\xi_2), \quad n(\xi) = \gamma(\xi|\xi). \tag{16}$$

The function $\gamma(\xi_1|\xi_2)$ will be recognized as a density matrix associated with the ϕ orbitals, while n is the corresponding density. Comparison with (7) and (8) gives, on putting $\xi_1=0$, the result

$$\bar{\rho}(\xi) = A[n(0)n(\xi) - \tfrac{1}{2}|\gamma(0|\xi)|^2]. \tag{17}$$

Integration (17) gives the normalization requirement

$$An(0) = 1, \tag{18}$$

and so (17) finally reduces to

$$\bar{\rho}(\xi) = n(\xi) - |\gamma(0|\xi)|^2/2n(0). \tag{19}$$

In the C.K. method, one uses an $N-1$ particle determinant given by the cofactor of any element in ξ_1, in (14). Such a choice omits the important exchange term from (19). The linear combination of N such cofactors given by (14) is necessary to produce this term.

Our proposed scheme is now fairly well defined. H, given by (4), is to be the fundamental Hamiltonian, while Ψ given by (14) is to be the trial wave function. Certain novel problems, however, occur in the variational calculation and we will find it convenient to work in the particularly simple T.F. approximation, following C.K., recognizing in the light of experience gained in the vacancy problem[2] that the finer detail in the pair function will be absent. The next section then is concerned with writing some of the expressions we need in terms of this approximation.

4. APPLICATION OF THE T. F. METHOD

We wish to express the ϕ_k of the previous section in terms of the density function n. To do this we make the usual T.F. assumption[5] that around ξ, we can approximate $\phi_k(\xi)$ by a plane wave appropriate to density $n(\xi)$. In other words,

$$\phi_k(\xi) = L^{-3/2} \exp(2\pi i \mathbf{k}\cdot\xi/L), \quad N/L^3 = n(\xi). \quad (20)$$

On using the latter in (16) the density matrix becomes

$$\gamma(\xi_1 | \xi_2)$$
$$= [n(\xi_1)n(\xi_2)]^{1/2} l\{[n(\xi_1)]^{1/3}\xi_1 - [n(\xi_2)]^{1/3}\xi_2\}, \quad (21)$$

and so (19) becomes

$$\bar{p}(\xi) = n(\xi) - \tfrac{1}{2}n(\xi)l^2\{[n(\xi)]^{1/3}\xi\}. \quad (22)$$

It is now convenient to derive an expression in the T.F. approximation for the expectation value of the kinetic energy part of H with respect to the Hartree product formed from the diagonal elements of (14). A little computation shows this to be

$$T = -\sum_k \int \phi_k{}^* \nabla^2 \phi_k d\tau + \tfrac{1}{2}\sum_k \left(\int \phi_k{}^* \nabla \phi_k d\tau\right)^2, \quad (23)$$

an energy differing from that pertaining to a static charge model by the positive quantity

$$\frac{1}{2}\sum_k \int \phi_k{}^* \left[\frac{\nabla}{i} - \int \phi_k{}^* \frac{\nabla}{i}\phi_k d\tau\right]^2 \phi_k d\tau. \quad (24)$$

It is this positive definiteness which will produce the shift in pair function towards the origin expected on dynamical grounds. Substituting the orbitals (20) into (23) leads under the usual T.F. assumption of slowly varying density to the kinetic energy

$$T = \frac{6}{5}E_F \int n^{5/3}d\tau - \frac{3}{5}E_F \int n^{4/3}d\tau, \quad E_F = (3\pi^2)^{2/3}/2. \quad (25)$$

5. ESTIMATION OF n

Our principal aim in this work is to understand the reasons for the success of C.K. rather than to carry through fully quantitative calculations. With this primary purpose in mind we have concentrated on the pair function (22) as a suitable indicator and calculated the unknown n in a somewhat crude but, for our immediate needs, adequate approximation.

The method of finding n which might, perhaps, first come to mind does not lead to quantitatively satisfactory results. It is, however, not without interest and is therefore briefly discussed. This is to use variationally the Hartree product formed from the diagonal terms of (14) and introduced in the previous section. The
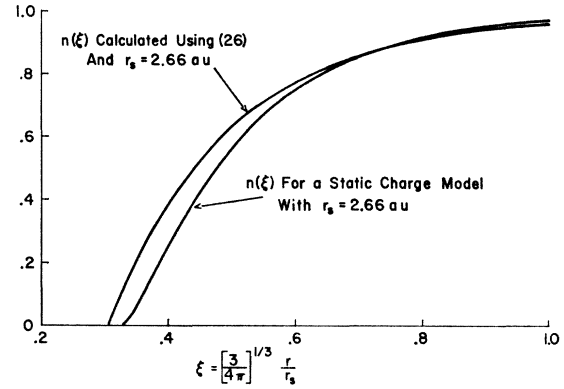

FIG. 1. Profiles of the charge densities as seen from one electron using the dynamic and static charge models. The exchange hole has been neglected in these calculations. The conventional electron separation parameter r_s is taken to be 2.66 a.u. (atomic units).

appropriate energy to be varied is

$$T + \lambda \int \frac{n}{\xi}d\tau + \frac{\lambda}{2}\int \frac{n(\xi_1)n(\xi_2)}{|\xi_1 - \xi_2|}d\tau_1 d\tau_2, \quad (26)$$

and this has been done by adapting a method due to Alfred and March.[2,5] Details are given in the Appendix. The graph for n for $\lambda = 4.288$ a.u. (corresponding to a choice of 2.66 a.u. for the conventional parameter r_s) is shown in Fig. 1. For comparison purposes the corresponding result for a static charge model is also drawn and the expected shift in the ambient charge cloud is noted. On substituting for n in (22) one obtains a pair function of qualitatively correct form but on calculating the electron gas potential energy per particle in Ry from[6]

$$-\lambda^{-1}\int_0^\infty (1-\bar{p})4\pi\xi d\xi, \quad (27)$$

one obtains a value which is probably[7] more than two times too large in absolute value. Nonetheless, even this rough model appears to have more fundamental status than the static charge picture and it is interesting to compare the screening constants predicted by the two methods for the interelectronic potential for large separations. These turn out (see the Appendix) to be directly determined by the quadratic term in the expansion of the kinetic energy density in terms of the displaced charge. When $n^{5/3}$ is replaced by $2n^{5/3} - n^{4/3}$ this has the effect of reducing the screening factor from $0.814r_s{}^{1/2}$ to $0.644r_s{}^{1/2}$ times the Fermi momentum agreeing more closely with the presumably[8] more accurate Bohm–Pines[9] value of $0.353r_s{}^{1/2}$.

[5] N. H. March, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 1.

[6] N. H. March and W. H. Young, Phil. Mag. 4, 384 (1959).
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[9] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. I, p. 367.
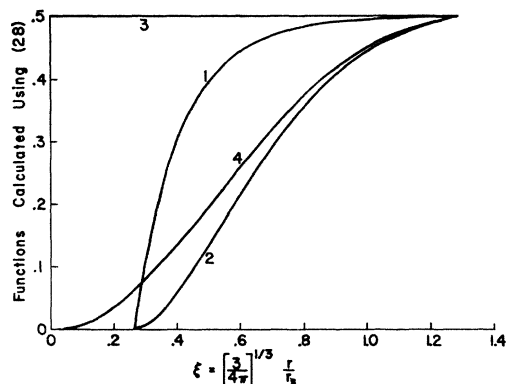
FIG. 2. Profiles of the charge densities as seen from one electron using the dynamic model with the exchange hole taken into account. Curves 1 and 2 refer, respectively, to electrons with spins antiparallel and parallel to that at the origin for $r_s = 2.66$ a.u. For comparison purposes curves 3 and 4, the corresponding free fermion results, have been drawn.

The quantitative failure of the above method is easily understood. The statistical effect is not a correction to the dynamical effect but is energetically competive with it. This calls for the full variational use of the wave function (14) rather than just its diagonal part. It is not difficult to evaluate the various energy contributions if we recall the observation preceding (15). For example, the density determining the potential energy of interaction of the surrounding electrons with that at the origin is given by (19). The other contributions are more complicated and will not be written down. However, from the point of view of the variational method we can isolate the more significant terms and obtain an improved estimate of n over that given by (26). Of course, one would ultimately hope to do better than the following but for immediate purposes the approximation is adequate.

Let us assume that the stable configuration is largely decided by the behavior of the electrons of spin opposite to that at the origin interacting with the origin, with each other, and with the opposite spin cloud. One may approximate to the energy of such an electronic system by modifying (26) to read

$$\frac{T}{2}+\frac{\lambda}{2}\int \frac{n}{\xi}d\tau+\frac{\lambda}{2}\int \frac{n(\xi_1)n(\xi_2)}{|\xi_1-\xi_2|}d\tau_1 d\tau_2. \qquad (28)$$

It is supposed that all other terms of $(\Psi,H\Psi)$ are relatively insensitive to variation of n because of the presence of exchange-type terms of the kind displayed in (19) for example. Expression (28) leads to a revised n curve for $\lambda = 4.288$ a.u. shown in Fig. 2. The contributions from like and unlike spins are of interest and are displayed separately. Their contributions in Ry to the potential energy (27) are found numerically to be $-0.39(5)$ and $-0.14(7)$, respectively, yielding a total correlation potential energy of $-0.19(8)$. This is still

possibly a little too low (algebraically),[7] but in view of our approximations not discouragingly so, particularly as the possibility of greater uncoupling of the two charge clouds exists by removal of the double occupancy restriction in (14).

CONCLUSIONS

We have seen how the C.K. method, though successful at metallic densities, omitted two important effects. By introducing a moving rather than a static charge model one tends to get a shift in the charge cloud around any given particle towards that particle. By an introduction of exchange, however, one obtains a repulsion of the like-spin cloud. The two mechanisms together produce detailed changes in the pair distribution function but approximately cancel energetically.

The work above constitutes an improved formulation of the C.K. method. We have shown that good results should be obtained at intermediate densities. Calculations of correlation energies in this region will be reported in due course. Furthermore, since the present work gives the exact pair function in the case $\lambda = 0$, it is reasonable to expect that our method may be useful even at high densities when the C.K. formulation breaks down.

Finally, it is hoped that the method will prove to be of use in many-body theory generally. For example, the idea of singling out one particle for special study as above while treating the interactions between the remainder in an average way is particularly appealing as a means of eliminating the divergency difficulties from the hard-core problem.

ACKNOWLEDGMENTS

APPENDIX

Let us consider the problem presented by the minimization of (26). That corresponding to (28) is essentially equivalent. There are two initial difficulties. The first, concerning the divergence of the integrals, is easily removed by introducing the displaced charge $\rho = 1 - n$ and focusing attention on departures from the plane wave situation. The change in energy is then

finite and is given by

$$\Delta = \frac{6}{5} E_F \int \{(1-\rho)^{5/3}-1\} d\tau - \frac{3}{5} E_F \int \{(1-\rho)^{4/3}-1\} d\tau$$

$$-\lambda \int \frac{\rho}{\xi} d\tau + \frac{\lambda}{2} \int \frac{\rho(\xi_1)\rho(\xi_2)}{|\xi_1-\xi_2|} d\tau_1 d\tau_2. \quad (A1)$$

The second difficulty is concerned with normalization. We were careful to choose A through (18) to give correct normalization in (14). The quantity ρ, therefore, is normalized to zero. That the curves shown in the diagrams do not appear so is illusory since they may alter by $O(N^{-1})$ to ensure correct normalization without showing up graphically or contributing differently to the potential energy per particle as $N \to \infty$. More precisely, let ρ_0 be any function with finite normalization. Then ρ defined by

$$\rho = \rho_0 - N^{-1} \int \rho_0 d\tau \quad (A2)$$

integrates to zero and so is suitable for use in (A1). Substituting and taking the limit $N \to \infty$ gives

$$\Delta = \frac{6}{5} E_F \int \left\{ (1-\rho_0)^{5/3} - 1 + \frac{5}{3}\rho_0 \right\} d\tau$$

$$-\frac{3}{5} E_F \int \left[(1-\rho_0)^{4/3} - 1 + \frac{4}{3}\rho_0 \right] d\tau$$

$$-\lambda \int \frac{\rho_0}{\xi} d\tau + \frac{\lambda}{2} \int \frac{\rho_0(\xi_1)\rho_0(\xi_2)}{|\xi_1-\xi_2|} d\tau_1 d\tau_2. \quad (A3)$$

Unrestricted minimization of the latter now leads to

the Euler equation

$$-2(1-\rho_0)^{2/3} + \frac{4}{5}(1-\rho_0)^{1/3} + 6/5 + \lambda U/E_F = 0, \quad (A4)$$

where U satisfies the Poisson equation

$$\nabla^2 U = -4\pi\rho_0 \quad (A5)$$

with boundary conditions

$$U \sim -\xi^{-1} \quad \text{as} \quad \xi \to 0$$
$$\sim \ 0 \quad \text{as} \quad \xi \to \infty. \quad (A6)$$

The problem of finding ρ_0 is now solved approximately by adapting a method due to Alfred and March[2,5] which would appear to be quite accurate. Solving (A4) for ρ_0 gives

$$\rho_0 = 1 - \{\tfrac{1}{5} + (16/25 + \lambda U/2E_F)^{1/2}\}^3, \quad (A7)$$

and this equation does not define ρ_0 below some value ξ_c, say, given by

$$16/25 + \lambda U(\xi_c)/2E_F = 0. \quad (A8)$$

This is a well-known characteristic of the T.F. method and is due to a transition to a region into which the electron cloud is not allowed to penetrate. We, thus, solve (A5) for $\xi < \xi_c$ with $\rho_0 = 1$ while for $\xi > \xi_c$ we take the asymptotically exact large ξ solution of (A5) and (A7) obtained by linearization. Explicitly,

$$U = -1/\xi + \beta - \tfrac{2}{3}\pi\xi^2 \quad (\xi < \xi_c)$$
$$= -(\alpha/\xi)\exp(-q\xi) \quad (\xi > \xi_c), \quad (A9)$$

where $q^2 = 15\pi\lambda/(4E_F)$ and α, β and ξ_c are constants determined from (A8) and equations expressing the continuity of U and ∇U across $\xi = \xi_c$. On finding U, the function ρ_0 is calculated from (A4). The discontinuity in ρ_0 across $\xi = \xi_c$ is barely perceptible to graphical accuracy.