

Simplified Self-Consistent Field Equations with Correlations

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It is pointed out that the correlation hole has, qualitatively, features analogous to the exchange one; and to the correlation, there corresponds a potential of the conventional electrical character. We can further obtain—in the case of the free-electron gas—the correlation potential averaged over all the electron states, in close correspondence with the averaged exchange potential of Slater. It is further reasonable to use this potential as the averaged correlation potential of the arbitrary many-electron system where the density of the free-electron gas is replaced by the density of actual charge in the system.

Adding the averaged correlation potential as well as the averaged exchange correlation potential to the Hartree-Fock operators, we obtain the self-consistent field equations with correlations.

1. CORRELATION HOLE

THE physical meaning of the correlation effect lies in considering the fact that in the immediate vicinity of a given electric charge, we have clearly a smaller probability of appearance of another charge of the same sign, than in the regions more distant from the charge in question, due to the Coulomb repulsion effect. Thus, in the many-electron system, e.g., free-electron gas, around a given electron, a charge-free space is formed (without regard to the electron spin) called the correlation hole.

The extent of averaged decrease of electron density caused by the Coulomb correlation among the electrons in the free-electron gas (decrease of the probability of finding a second electron in the neighborhood of the first, when the Pauli principle is neglected) was calculated by Macke.¹ This was given in a rather complicated expression, however, which becomes simply transformed into:

$$a(\mathbf{r}, \mathbf{r}') = \frac{9}{2} \int_0^1 u^2 du \left[\int_{1-u}^{1+u} [1 - (w-u)^2] + \int_0^{1-u} 4uw \right] \times \frac{\sin d' |\mathbf{r} - \mathbf{r}'|}{d' |\mathbf{r} - \mathbf{r}'|} \frac{B(u, w)}{4 \cdot 3^{3/2} \pi^{5/3} \rho^{3/2} + B(u, w)}. \quad (1)$$

This assumes that the relation $P/h = (3\rho/8\pi)^{1/2}$ between maximum momentum P and the density of electrons ρ holds. d' is $(3\pi^2)^{1/3} \rho^{1/3} u$ and

$$B = \{2u(1+w) + [1 - (u+w)^2] \ln(1+u+w) - [1 - (w-u)^2] \ln(1-u+w) + 4uw \ln w\} \frac{1}{u^3} \quad (2)$$

[ρ in the denominator of (1) is the number of density calculated in atomic units, as well as in the corresponding position in succeeding formulas].

It is seen that $a(\mathbf{r}, \mathbf{r}')$ depends in a not too complicated way on $|\mathbf{r} - \mathbf{r}'|$ (the distance from the hole's center) and

ρ . Thus, for each given $|\mathbf{r} - \mathbf{r}'|$ we can determine the density $e\rho a$ in the correlation hole only as a function of ρ .

The case of the exchange was discussed in detail by Slater.² He estimated the radius of the main exchange hole (i.e., of the region where the decrease of the density caused by the Pauli principle effect, is large) as a function of ρ only. It was assumed that the density in this hole is constant, equal to $\rho/2$, and the charge enclosed in the volume of the hole is $1e$.

In the correlation case the situation is not so simple. Qualitatively the relations in the averaged correlation hole are the same as in the exchange case: The shape of the hole is determined only by ρ . The difficulty lies in the fact that charge corresponding to the correlation hole calculated with (1) is infinite, when, in order to make the calculations easier, as it was in the exchange case also, the hole dimensions are spread to infinity. Such a treatment, however, contains simplifications: The quantity a does not take into account the perturbations of a given hole by the remaining electrons, which especially for large $|\mathbf{r} - \mathbf{r}'|$ should act, we may anticipate, in the direction of decreasing a . Nevertheless, the calculation of the charge in the correlation hole indicates clearly that the range of the correlation forces is longer than the range of the exchange ones.

It is possible, however, in the correlation case also, to distinguish the main correlation hole and its radius, in analogy to Slater's work.

We may confine, for instance, the contents of the charge in the hole of the free-electron gas corresponding to the first minimum attained by the correlation density $e\rho a$, beginning from the hole center. Next, we may assume, like Slater, that the electron density in the space which we have distinguished is constant. Thus we attain another analogy with Slater's exchange hole: the main correlation hole as a function of ρ only.

We may reasonably expect that the analogy between exchange and correlation hole does not exist in the free-electron case only. The reason for it is that each electron in the arbitrary multielectron system leaves around itself an empty space, corresponding to the diminution

¹ W. Macke, Z. Naturforsch. **5a**, 192 (1950); see Eq. (51) and inferences before it.

² J. C. Slater, Phys. Rev. **81**, 385 (1951).

of electric charge, caused by repulsion. The dimensions of this space depend on the total electron density at the position of the electron, and cannot depend greatly on anything else. Thus, we may here also adopt the idea of the main correlation hole, as dependent only on the total electronic density of the system. Then we have the hole of equal magnitude for any i th of all the one-electron wave functions, depending on coordinates and spin, and building up the given density. The space part of this density is

$$\rho(\mathbf{r}) = \sum_k \psi_k^*(\mathbf{r})\psi_k(\mathbf{r}); \quad (3)$$

$\psi_i(\mathbf{r})$ is the space part of the i th spin-orbital. We may, further, estimate the correlation hole having the same size for all ψ_i , by the corresponding hole of the free electron gas, whose density is the one existing actually in a given point of the many-electron system.

Nevertheless, introduction of the hole of a type as above represents an idealization; indeed, the size of the hole is different for each ψ_i . We may expect, however, as in the exchange case, that these differences are small.

We can obtain some computational insight in these last relations for the free-electron gas. Unfortunately, in the correlation case, we do not have a universal factor (for all ρ), which determines the correlation energy for one electron in terms of the ratio of the magnitude of the momentum p of the electron (in a given state) to the maximum momentum in the system [see Eq. (11), reference 2, for the corresponding factor in the exchange case]. We may see, however, how quickly the magnitude of the total correlation energy increases (for different ρ , corresponding to different fixing of Macke's material constant) when P is replaced by p in the limit of the integral expression for this total energy³ and p is allowed to range from 0 to P . This energy integral (in the case of great ρ) increases roughly in a similar way to the corresponding integral of F , where F is the exchange energy for one electron expressed in terms of p/P . The F was feebly dependent on p , as well as the exchange hole. Thus, we may expect in some way a similar behavior of the correlation hole.

2. CORRELATION POTENTIAL

It does not seem to be possible at present to follow the quantitative discussion of Slater about exchange in the correlation case. From our qualitative considerations, however, we may conclude that the change in the electron density caused by the presence of the correlation hole furnishes a corresponding change in the potential. This new potential, in view of the considerations we made above, has the conventional character of the electrostatic Coulomb potential, as Slater's exchange potential has. For example, we may represent the correlation energy corresponding to the statistical model (where the free-electron approximation of the partial volumes building up the whole volume of the system is

³ See reference 1, Eq. (42).

TABLE I. A comparison between the correlation energy calculated by Nozières and Pines and Hubbard^a (collective description approximation) and that of Macke's scheme; the energies are given in ry.

r_s	1	2	3	4	5
E_{Macke}	-0.109	-0.074	-0.058	-0.050	-0.044
$E_{\text{coll.}}$	-0.115	-0.094	-0.081	-0.072	-0.065

^a See reference 5.

assumed) in the form

$$E_{\text{corr}} = \frac{e^2}{2} \iint \frac{\rho(\mathbf{r})\rho_c(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{v}d\mathbf{v}', \quad (4)$$

which is the potential energy of the interaction of the correlation density ρ_c produced at \mathbf{r}' ,

$$-\epsilon\rho_c(\mathbf{r},\mathbf{r}') = -\epsilon\rho(\mathbf{r}')[-a(\mathbf{r},\mathbf{r}')], \quad (5)$$

with the actual electron density at \mathbf{r} , $\rho(\mathbf{r})$. The density in a is a function of \mathbf{r}' .

It should be still emphasized here, that the correlation energy expressed by a is not equal exactly to the correlation energy of the free-electron gas which may be obtained by summation of the energies of all the orders of approximations (beginning from the second) in the Schrödinger perturbation calculus.

Gell-Mann and Brueckner⁴ pointed out, using the Feynman method, that in Macke's scheme only the whole correlation energy corresponding to the second-order approximation is taken into account. In the third order, only half of the energy is included in Macke's expression. In the next orders, only the corresponding parts of the energy of each approximation are considered. We may assume, however, that most of the correlation energy corresponds to the second- and the third-order approximations; thus, the major part of it is involved in Macke's scheme.

In order to justify the last statement, let us examine in some detail the validity of Macke's approximation in calculating the correlation energy for different gas densities; it seems reasonable to take then, the total correlation energy (exchange terms included) into account. The gas of very high density was discussed already by Gell-Mann and Brueckner in detail. For this case the Macke approximation is almost exact. For less high densities—in the region of about $r_s=1$ and in the region of the metallic densities—let us compare Macke's scheme with the results of the collective description of the correlation energy, which, in the regions in question, should be considered as more correct. In Table I we compare the results of the Bohm-Pines theory, in their refined form of Nozières and Pines,⁵ with results for the total correlation energy of

⁴ M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

⁵ P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958). The results of another collective approach to the correlation energy, that of J. Hubbard [Proc. Roy. Soc. (London) **A243**, 336 (1958)], are very close to those of Nozières and Pines.

the Macke's scheme, as we could estimate them from the graph of his paper. We see that still for $r_s=1$ the agreement of both schemes is very good. For the densities corresponding to $r_s=2$ to $r_s=5$ the results of Macke are from 20 to about 30% lower than those presented by Nozières and Pines, if we take as a base the values of this second scheme. In the low-density limit we may compare the exact correlation energy in its form given by Pines,⁶ as the result of refined Wigner's treatment,⁷ with the low-density limit estimated by Macke. The difference is around 30% of the value of Pines.

In view of the above, we may consider the general statement, that the greater part of the correlation energy (at least to about 70%) is included in Macke's scheme, as established. A big advantage of Macke's treatment—besides its mathematical convenience for our purposes—is that it gives the correct behavior of the correlation energy as a function of the density for both very large and very small densities. This is not the case of the collective description correlation formula.^{5,6}

To the correlation energy given in (4) there corresponds the potential

$$V_c = -e \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} [-a(\mathbf{r},\mathbf{r}')] dv'. \quad (6)$$

Now, substituting further Eq. (3) for ρ in (6) we might obtain the universal potential corresponding to the correlation, acting upon ψ_i . However (6) still remains complicated. Besides, (6) is strongly dependent on the shape of the hole, the preservation of which, coming from the free-electron gas to arbitrary many-electron system, seems doubtful. Thus, the average correlation potential should be calculated.

It was mentioned above, that the correlation hole should not be subject to strong changes with changes of the electron state; hence it is reasonable to regard also that the correlation potential corresponding to different ψ_i will not depend much on i . We have not, however, even in the free-electron case, the representation of the potential correlation energy as a function of momentum convenient for averaging. Thus we shall refrain from averaging over all momentum space in this case, and choose to calculate the averaged correlation potential by computing the potential energy of an electron in the center of the averaged correlation charge distribution $e\rho_a$.⁸

For this purpose, we have integrated (6) over the whole space of the correlation hole, assuming that the actual electronic density is practically unchanged over this region. With the boundaries of integration going to infinity, we do not obtain, unfortunately, a convergent result in (6) (the long range of the correlation forces is

here of importance). In order, however, to obtain an expression of finite value let us apply a trick taken from Bloch⁹: Instead of $\text{sing}|\mathbf{r}-\mathbf{r}'|/d'|\mathbf{r}-\mathbf{r}'|$ we introduce the mean of this expression,

$$\frac{1}{2\Delta d'} \int_{d'-\Delta d'}^{d'+\Delta d'} \frac{\text{sing}|\mathbf{r}-\mathbf{r}'|}{d'|\mathbf{r}-\mathbf{r}'|} d(d'), \quad (7)$$

where $\Delta d'$ is small. Then we obtain in (6) a convergent result:

$$V_{\bar{c}} = e \cdot \frac{3}{2} \left(\frac{3}{\pi} \right)^{\frac{1}{2}} \rho^{\frac{1}{2}} \times \int_0^1 du \left[\int_{1-u}^{1+u} [1-(w-u)^2] + \int_0^{1-u} 4uw \right] \times dw \frac{B(u,w)}{4\pi^{5/2} 3^{\frac{1}{2}} \rho^{\frac{1}{2}} + B(u,w)}. \quad (8)$$

Next, inserting $V_{\bar{c}}$ into the expression for the potential energy

$$-\frac{1}{2} e \int V_c \rho dv, \quad (9)$$

instead of V_c , we obtain the expression for the correlation energy equal to that given for this energy by Macke.

We see that (8) depends only on ρ —in full analogy with the averaged exchange potential presented by Slater. Based on this, and on the preceding discussion, it is reasonable to consider the averaged correlation potential of the arbitrary many-electron system, similarly to the exchange one, as dependent mainly on the density. Thus, we may approximate this potential by the averaged potential of the free-electron gas of the same density. In this way, it is possible to enlarge the potential acting on the given electron by the simplified correlation potential, in the same sense as the exchange terms were replaced by Slater by the averaged exchange potential approximated by the results for the free-electron gas.

In an analogous manner to $V_{\bar{c}}$ we introduce the average exchange correlation potential corresponding to correlation correction of the exchange effect. Assuming, in view of simplicity, that the number of electrons of both kinds of spin is practically the same, we obtain

$$V_{\bar{c}-\bar{a}} = -e \cdot \frac{3}{2} \left(\frac{3}{\pi} \right)^{\frac{1}{2}} \rho^{\frac{1}{2}} \times \int_0^1 du \left[\int_{1-u}^{1+u} [1-(w-u)^2] + \int_0^{1-u} 4uw \right] \times dw \frac{G(u,w)}{4\pi^{5/2} 3^{\frac{1}{2}} \rho^{\frac{1}{2}} + B(u,w)}, \quad (10)$$

⁶ D. Pines, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1.

⁷ E. P. Wigner, *Trans. Faraday Soc.* **34**, 678 (1938).

⁸ It seems of value to mention here that Slater, reference 2, has obtained the same result in both ways, in the exchange case.

⁹ F. Bloch, *Z. Physik* **57**, 545 (1929).

where B is given in (2), and

$$G = -\frac{2}{u} \{ (w+u) \ln(1+w+u) - (w-u) \ln(1+w-u) - 2u(1+\ln w) \}. \quad (11)$$

Replacement of V_c by $V_{\bar{c}-\bar{a}}$ in (9) gives also the expression corresponding to the exchange correlation energy presented by Macke.¹⁰ It should be noticed that in (10) an approximation introduced by Macke is included [reference 1, Eq. (24)].

3. SIMPLIFIED SELF-CONSISTENT FIELD EQUATIONS

If we include (3) and put $V_{\bar{c}}$ and $V_{\bar{c}-\bar{a}}$ into the Schrödinger equation, we obtain the self-consistent field equations developed by the correlation potentials:

$$\left\{ H + U + A - e^2 \cdot \left(\frac{3}{2} \right) \left(\frac{3}{\pi} \right)^{\frac{1}{2}} \left\{ \sum_k \psi_k^* \psi_k \right\}^{\frac{1}{2}} \int_0^1 du \left[\dots \right] \right. \\ \left. \times \frac{dw}{4\pi^{5/2} 3^{\frac{1}{2}} \left\{ \sum_k \psi_k^* \psi_k \right\}^{\frac{1}{2}} + B(u,w)} \right\} \psi_i = E_i \psi_i, \quad (12)$$

¹⁰ There are some printing errors in Macke's paper which are removed by derivation of the formulas (10), as well as (1) and (8).

where H, U, A , respectively, have conventional meaning of the Hamiltonian operator of the one-electron problem and the Coulomb and exchange operators of the given multielectron problem (Hartree-Fock operators), and where the brackets enclose the same integrals as in Eqs. (8) and (10). Three important consequences of (12) which were already a feature of the Hartree-Fock equations and their simplification given by Slater¹¹ hold: 1. The ψ_i functions may be presented in orthogonal form (one-potential problem); 2. When the density of charge is periodic and A has the form of the density function, then the potential in (12) is also periodic; and 3. Eqs. (12) may be applied generally in all cases: atoms, molecules and solids.

It should be noticed here, as was the case in the Slater work, that the functions ψ_i —although they differ from the exact solutions of the correlation problem—may give good results for energies in view of the fact that the calculation of the mean value of the energy over such a function gives values which have errors only of the second order in small quantities.

¹¹ See reference 2.

Temperature Dependence of the Nuclear Quadrupole Spectrum of Nb⁹³ in Ferroelectric KNbO₃†

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The nuclear electric quadrupole interaction of Nb⁹³ in ferroelectric KNbO₃ has been measured as a function of temperature in the tetragonal, orthorhombic and rhombohedral phases. The values of $(1/\nu)(d\nu/dT)$ for these three phases are approximately -10^{-3} , -10^{-3} , and -10^{-4} per degree centigrade, respectively. In the tetragonal phase at 220°C, e^2qQ/h has been measured as 24 Mc/sec and the asymmetry parameter η is zero. An ionic calculation of field gradients in the tetragonal phase has been made including point charge and induced dipole contributions. The results of this calculation give the Sternheimer antishielding factor $(1-\gamma_\infty)$ as 15 in good agreement with its estimated value of +16. The temperature dependence of the electric field gradient at the Nb⁹³ site as calculated from this ionic model is in agreement with the measured temperature dependence in the tetragonal phase.

I. INTRODUCTION

THE most successful model of ferroelectric behavior has been constructed for the perovskite ferroelectrics with the assumption of an electrostatic driving interaction. However, the validity of this model is critically dependent on the existence of an ionic environment for all of the crystal's constituent ions. Since an alternate mechanism for the perovskite ferroelectric behavior has been proposed by Megaw¹ where a covalent bond between the face-centered oxygen ions and the body-centered ions of this structure is to

provide the ferroelectric driving action, it has become important to investigate the environment of the body-centered ion in these perovskite ferroelectrics.

KNbO₃ is a perovskite ferroelectric with four known crystal phases. Above 430°C it has a cubic structure. The oxygen ions in the face-centered position, form an octahedron about the body-centered niobium ions. The potassium ions are in the corners of the unit cell. As the crystal is cooled, its cubic, perovskite structure changes successively to tetragonal, orthorhombic and rhombohedral phases. The phase transitions occur at about 430°C, 220°C, and -50°C respectively. The structure changes occur by elongations along an edge

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¹ H. D. Megaw, *Acta Cryst.* 7, 187 (1954).