SOVIET PHYSICS JETP VOLUME 35(8), NUMBER 5 MAY, 1959

CORRELATION ENERGY OF AN INHOMOGENEOUS ELECTRON GAS

D. A. KIRZHNITS

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor May 21, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) **35**, 1198-1208 (November, 1958)

The influence of a non-uniform distribution of particles on the electron correlation energy is investigated. It is found that this influence is so large that the corresponding expressions obtained on the basis of the uniform distribution model[1,2] are not valid for real systems. The principal part of the correlation energy of the electrons in the crystalline lattice (without consideration of interaction with the vibrations of the latter) has been found for high pressures, low temperatures, and large values of the nuclear charge. Estimates are given for the correlation energy of uncompressed matter.

1. INTRODUCTION

IT is well known that in polyelectronic systems a very important role is assigned to long range (many particle) correlations. In the most systematic form these correlations were studied in the recent work of Gell-Mann and Brueckner[2] (see also reference 3), where the correlation energy of the electron gas was found in the region of high compressions and low temperatures.

It is necessary, however, to emphasize that calculations of electron correlations are usually carried out with the use of a uniform model which greatly simplifies the real situation. In this model the nuclei (or ions) are replaced by a uniformly distributed positive background which guarantees the neutrality of the system as a whole. Such an approach completely ignores the atomistic structure of the positive charge: on the one hand the inhomogeneity of the charge distribution associated, for example, with the crystalline structure of the material is not taken into account, and on the other hand considerations of processes with participation of phonons and also electron-nuclear and nuclear correlations are left out.

The present work is devoted to consideration of the first of the enumerated factors, i.e., it contains the generalization of the results of Gell-Mann and Brueckner in the case of a non-uniform (but specified) distribution of the nuclei. The self-consistent potential $\Phi(\mathbf{x})$ corresponding to this situation, and the limiting Fermi momentum of the electron $p_0(\mathbf{x}) = [2M(E_0 - \Phi(\mathbf{x}))]^{1/2}$ are functions of the coordinates (E_0 is the limiting energy). As will be shown below, the electron correlation energy reveals an extraordinarily strong sensitivity to the presence of non-uniformities. Even in the regions of high compressions, where the distribution of electrons is non-uniform only in small degree, a radical departure takes place from the results contained in reference 2.

Consideration of the rest of the factors mentioned above (in the first place, the lattice vibrations) can also lead to a significant contribution to the correlation energy of the crystalline body. The role of nuclear and electron-nuclear correlations is especially important in the plasma state where the radius and energy of the correlation are determined not by the electronic but by the nuclear mass and charge. These questions, however, require special consideration.

The anomalous sensitivity just mentioned of the correlation toward non-uniformity of the system has a simple physical explanation and is accounted for in the final analysis by the fact that the principal contribution to the correlation energy is made by a narrow strip of phase space adjoining the Fermi surface. It is easy to find the latter from the uniform case: according to references 1 and 2, the principal term of the correlation energy has the form

$$\delta E = -\frac{\Omega e^2}{16\pi^7\hbar^3 a_0}\int\limits_{p_D}^{\infty}\frac{d\mathbf{q}}{q^4}\int\frac{d\mathbf{p}_1 d\mathbf{p}_2}{q^2 + \mathbf{q}(\mathbf{p}_1 + \mathbf{p}_2)}$$

with the conditions $p_{1,2} < p_0$, $|\mathbf{p}_{1,2} + \mathbf{q}| > p_0$. Here Ω is the volume of the system, $p_D = (\hbar p_0/a_0)^{1/2}$ is the Debye momentum, a_0 is the Bohr radius. If the condition

$$\hbar/a_0 p_0 \ll 1, \tag{I}$$

is satisfied then the region of integration over $p_{1,2}$ in the foregoing equation is actually narrow:

$|p_{1,2} - p_0| \sim p_D \ll p_0$.

On the other hand, as was emphasized in reference 4, diffusion of the momentum distribution close to the Fermi surface is inevitably connected with the non-uniformity of the system, even if the system is a step function in the energy representation (the degenerate case). We introduce the characteristic "length of the non-uniformity" l over which p_0 changes by a significant amount, and which is determined by the average value of $p_0/\nabla p_0$. Then, from the indeterminancy principle, we obtain the following expression for the diffusion referred to:

$$\delta p \sim (\hbar / l p_0)^{1/2} p_0.$$

The quantum fluctuations in potential energy in the stationary state must be identical in magnitude; that is, $p_0 \delta p/M \sim p_0^2 \delta x/lM$, whence, with the help of $\delta p \delta x \sim \hbar$, the desired quantity is obtained. At some distance from the Fermi surface, this dispersion of the momentum is shown to be small, since there the distribution did not depend on the momentum; however, in the vicinity of p_0 an intermingling of filled and unfilled regions takes place and the form of the distribution in the vicinity of $|p - p_0| \sim \delta p$ is changed significantly (for details see reference 4). Upon satisfaction of the quasi-classical condition

$$\hbar / l p_0 \ll 1 \qquad \text{(II)}$$

this diffusion occupies the narrow band $\delta p \ll p_0$.

It is important that fulfillment of the condition (II) is not at all sufficient that the non-uniformity have only a slight effect on the result. More stringent conditions must be satisfied: the magnitude of the quantum diffusion δp must be much less than the width of the effective region of integration, i.e., in our case, p_D.

For clarification of the possibility of satisfying this condition, let us consider the case of strongly compressed matter where (see Sec. 4)

$$p_0(x) \sim (\hbar Z^{1/3} / R)(1 + (RZ^{1/3} / a_0) f(x/R) + \ldots),$$

and the case of uncompressed matter with a large nuclear charge Z, where[5]

$$p_0(x) \sim (\hbar Z^{2/3} / a_0)\, \varphi(xZ^{1/3} / a_0).$$

Here R is the radius of the neutral cell, x is the distance from its center (this distribution is repeated periodically throughout the other cells), f and φ are slowly varying functions. In both cases, the conditions (I) and (II) are satisfied and the "length of non-uniformity" l has the form*

$$l \sim a_0 Z^{-1/3}.$$

It then follows that the condition $\delta p/p_D \ll 1$ is not only not satisfied, but for heavy nuclei the opposite condition

$$\delta p/p_D \sim (a_0/l)^{1/2} \sim Z^{1/6} > 1,$$

is satisfied; this also testifies to the inapplicability of the uniform model. In what follows we shall for simplicity limit ourselves to ascertaining the asymptotic form of the energy correlation for $Z \to \infty$, i.e., in addition to conditions (I) and (II), we shall consider the condition

$$\delta p/p_D \sim (\hbar p_0/l p_D^2)^{1/2} \gg 1 \qquad \text{(III)}$$

to be satisfied. In the case of compressed matter in addition to (II) a more stringent condition $\hbar/lp_D \ll 1$ is satisfied; however, for uncompressed matter, $\hbar/lp_D \sim 1$.

Finally, we note that the correlation energy is highly sensitive with respect to the temperature inasmuch as the latter, as also the non-uniformity, leads to a diffusion of the Fermi distribution. The limit below which we can use the relations for a degenerate gas is determined not by the temperature of the degeneracy $kT_0 \sim p_0^2/2M$ but by the quantity $p_0 p_D/M \ll kT_0$. In this case it follows from condition (III) that in all regions of degeneracy δp exceeds the width of the temperature diffusion and the effect of non-uniformity considered above takes the place.

We used atomic units: $e = \hbar = M = 1$.

2. PRELIMINARY REMARKS

We proceed to a consideration of other complications associated with the transition to the non-uniform case. In the non-uniform case it is necessary to define more clearly the actual meaning of the correlation interaction. We shall consider as a correlation† that part of the interaction which

---

*We note that in the case of strongly compressed matter ($RZ^{1/2}/a_0 < 1$, the pressure $P \gtrsim 10^8 \times Z^{10/3}$ atmos), in addition to the expression for l written here, there are other parameters of the dimensions of length (the radius of the cell R and also various combinations of R and l). However, these parameters are connected with derivatives (or, what amounts to the same thing, with commutators[4]) of higher order than the first and upon satisfaction of condition (II) they play a relatively unimportant role. An estimate shows that their role is significant only in the region $RZ^{2/3}/a_0 < 1$, $P \lesssim 10^8 Z^5$ atmos, which is relativistic for heavy atoms and is considered neither in reference 4 or in the present research.

†Strictly speaking, we are talking about the so called strong correlation which appears in addition to the exchange correlation.

is not taken into account in the Hartree-Fock approximation (HFA) and appears apart from the mean (self-consistent) interaction. The total energy of the system in the HFA has the form (ρ is the density of electrons, ρ_n is the density of nuclei)

$$E = {}^3/_{10}(3\pi^2)^{2/3}\int \rho^{5/3}\,d\mathbf{x} - {}^3/_4(3/\pi)^{1/3}\int \rho^{4/3}\,d\mathbf{x} + \frac{1}{2}\int\frac{d\mathbf{x}\,d\mathbf{x}'}{|\mathbf{x}-\mathbf{x}'|} \tag{2.1}$$
$$\times(\rho(\mathbf{x})\rho(\mathbf{x}') - 2Z\rho(\mathbf{x})\rho_n(\mathbf{x}') + Z^2\rho_n(\mathbf{x})\rho_n(\mathbf{x}')) + \Delta E.$$

Here we have, respectively, the kinetic energy of the electrons, their exchange energy, the potential energy of interactions of the electrons with each other and with nuclei, and the energy of interaction of the nuclei. The last term, ΔE, corresponds to the specific quantum corrections[6] associated with a non-uniform system,* and upon satisfaction of the condition (II) reduces to the small quantity

$$({}^1/_{72})\int[(\nabla\rho)^2/\rho]\,d\mathbf{x}.$$

In the uniform case, Eq. (2.1) reduces to the first two terms wherein, upon satisfaction of the condition (I), the exchange term plays a small role. In view of this fact we can consider the electrons to be free in the case considered in the HFA. Therefore, we can compute the energy of the electron correlation with the help of perturbation theory, expanding in a series of the Coulomb interaction and throwing away the first correction, which was already considered in the HFA. This was precisely the treatment of the problem given in reference 2.

In the non-uniform case the HFA must appear as the zeroth approximation while the perturbation is the difference between the Coulombic and the self-consistent interaction of the electrons. Such an approach to the calculation of correlation effects was assumed in the work of Møller and Plesset.[7] As the perturbation Hamiltonian in this method one must choose the expression

$$\hat{H}' = {}^1/_2\sum_{ij}{}'|\mathbf{x}_i-\mathbf{x}_j|^{-1} - \sum_j\int\bar{\psi}_{0j}(\xi)|\mathbf{x}_i-\xi|^{-1}(1-\hat{P})\psi_{0j}(\xi)\,d\xi$$
$$+ {}^1/_2\sum_{ij}{}'[M(0_i0_j,\ 0_i0_j) - M(0_i0_j,\ 0_j0_i)], \tag{2.2}$$

where ψ_{0j} are single-particle wave functions of the fundamental configuration with energy ϵ_{0j},

$$\hat{P}\psi_\alpha(\xi)\psi_\beta(x) \equiv \psi_\beta(\xi)\psi_\alpha(x),$$
$$M(\alpha\beta,\ \gamma\delta) \equiv \int\bar{\psi}_\alpha(\xi)\bar{\psi}_\beta(\eta)|\xi-\eta|^{-1}\psi_\gamma(\xi)\psi_\delta(\eta)\,d\xi\,d\eta.$$

The unperturbed wave function of the system Ψ_0 for the fundamental configuration is a determinant constructed from the functions ψ_{0j} while for the perturbed configurations the index 0 is replaced by n, n′, etc. The third term is introduced in (2.2) in order that the first-order correction to the energy $\delta_1 E = (\Psi_0 H'\Psi_0)$ vanish, since in HFA the energy is equal to the mean value of the exact Hamiltonian.

For computation of the corrections of higher order, it is necessary to know the matrix elements of H′ and the corresponding perturbation energy. A not very difficult calculation yields

$$(\Psi_n H'\Psi_{n'}) = \frac{1}{4}\sum_{ij}{}'\sum_{kl}{}'[M(n_in_j,\ n_k'n_l')$$
$$- M(n_in_j,\ n_l'n_k')]\,\Delta(n_in_k',\ n_jn_l')\,S(n_in_k',\ n_jn_l'), \tag{2.3}$$

where Δ is a matrix which is diagonal for all states except $n_in_jn_k'n_l'$;

$$S = s^{n_i}_{n_k'}s^{n_j}_{n_l'}s^{n_i}_{n_l'}s^{n_j}_{n_k'},$$
$$s^{n_i}_{n_k'} = 1 - \delta_{n_in_k'}\sum_\alpha\delta_{n_i0_\alpha}\sum_\beta\delta_{n_k'0_\beta}. \tag{2.4}$$

Each term of the sum (2.3) corresponds to the transition of a pair of particles from the states n_in_j to $n_k'n_l'$. The factor S (2.4) forbids such transitions when the initial and final states of the particle are identical while they both belong to the fundamental configuration. In the other cases, S = 1 and (2.3) is identical with the matrix element of only a single Coulomb interaction. To find the chief term of the correlation energy we must sum only "platform" diagrams (see below) for which S = 1. Therefore, in actuality, in the present work the expansion is simply carried out over the Coulomb interaction.

So far as the perturbation energy is concerned, it is equal to

$$E_{n'} - E_n = \sum_i(\varepsilon_{n_i'} - \varepsilon_{n_i}).$$

This is connected with the fact that all the perturbed states correspond to one and the same Hamiltonian (self-consistency is obtained only within the framework of the fundamental configuration).

Corrections to the energy are computed according to the general formulas of perturbation theory. In particular, for the second-order correction we have

$$\delta_2 E = {}^1/_2\sum_{ij}{}'\sum_{nn'}{}''\frac{|M(0_i0_j,\ nn')|^2 - M(0_i0_j,\ n'n)M(nn',\ 0_i0_j)}{\varepsilon_{0i}+\varepsilon_{0j}-\varepsilon_n-\varepsilon_{n'}}. \tag{2.5}$$

Here the double prime on the sum denotes summation only over those states n, n′, no one of which is a part of the fundamental configuration. This

---

*The non-uniformity in Eq. (2.1) also appears in trivial form because of the dependence of ρ on the coordinates in the remaining terms of (2.1).

condition follows from the properties of the matrix S.

Out of all of the diagrams of higher order in reference 2 there were considered only the diagrams of the "platform" type in which in the interaction each particle either becomes excited, i.e., transfers from a region inside the Fermi sphere to a region outside of it, or conversely, gives up its excitation i.e., executes the opposite transition. An example of such a diagram of third order is pictured in Fig. 1, where the solid lines indicate the normal, and dotted lines the perturbed states of the particle; q is the momentum transferred. In diagrams of such type to each act of the interaction there corresponds the denominator q^2. In the diagrams not yet considered there are nodes with momentum transfers with the order of p_0, as a consequence of which the contribution of these diagrams is small. For the same reason we can omit the exchange parts of the platform diagrams (the corresponding arrangement of particles in the final state).

In the non-uniform case we must also consider only platform diagrams since the divergences at the lower limit become stronger, being linear instead of logarithmic (Sec. 3). Therefore, the decisive role of these diagrams becomes still clearer.

In the uniform case there is a logarithmic situation in which one of the two terms of the same type dominates over the other because of the large logarithmic factor. Therefore, the principal term of the energy was slightly sensitive relative to a choice of cumulative diagrams. In the non-uniform case, because of the linear character of the divergence, a correct choice of the diagrams is necessary even for calculation of the principal term.

We note further that the contribution of the exchange effects to the wave functions and the energy of the electrons is unimportant upon fulfillment of conditions (I) and (II). Thus, we can use these quantities in the Hartree approximation.

From what was said above, it follows that the only complication connected with consideration of non-uniformity in essence consists of the replacement of the wave functions and the energy of the free electrons by the corresponding quantities computed with account of non-uniformity.

3. QUALITATIVE CONSIDERATION

For a clarification of the aforementioned effects associated with consideration of non-uniformity, let us first consider the simplified expression for the correlation energy in which the summation of the diagrams of higher order is replaced by cutting off the integral over the momentum transfer in the diagram of second order by a quantity of the order of the Debye momentum p_D. In other words, a screened Coulomb interaction is introduced from the very beginning. A rigorous analysis (Sec. 4) confirms the possibility of such an approach and shows that the non-uniformity has practically no effect on the cut-off momentum.

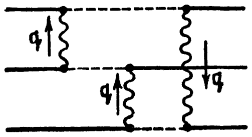

FIG. 1

The expression for the correlation energy of the second order has the form (C (2.5); the exchange diagrams are neglected):

$$\delta_2 E = {}^1/_2 \sum_{ij}{}' \sum_{nn'}{}'' \left| M(0_i 0_j, nn') \right|^2 / (\varepsilon_{0i} + \varepsilon_{0j} - \varepsilon_n - \varepsilon_{n'}). \quad (3.1)$$

It is appropriate to show the transition to the operator representation (3.1). With this aim let us express the matrix element in (3.1) in explicit form. We group the wave functions with the same indices and introduce into consideration the density matrix[6]

$$\rho(x, x') = \Sigma \bar{\psi}(x') \psi(x) = \theta_-(\hat{H}_x - E_0)\, \delta(x - x'),$$

which arises from summation over i, j in (3.1). Here the sum runs over the occupied states, the sum over the unoccupied states (summation over n, n′) is equal to

$$\delta(x - x') - \rho(x, x') = \theta_+(\hat{H}_x - E_0)\, \delta(x - x').$$

Here

$$\theta_\pm(a) = {}^1/_2 (1 \pm a/|a|),$$

$\hat{H}_x$ is the Hamiltonian of the Hartree approximation which acts on the variables x.

We can represent the energy denominator in the form

$$-{}^1/_2 \int_{-\infty}^{\infty} \exp\{-|t|(\varepsilon_n + \varepsilon_{n'} - \varepsilon_{0i} - \varepsilon_{0j})\}\, dt$$

and replace each ϵ in this equation by the Hamiltonian acting on the corresponding wave function in the density matrix. Introducing the notation

$$N_\pm(\mathrm{x}, \mathrm{y}) = \exp(\pm |t| \hat{H}_x)\, \theta_\mp(\hat{H}_x - E_0)\, \delta(x - y),$$

we get for (3.1)

$$\delta_2 E = -\int_{-\infty}^{\infty} dt \int \frac{d\mathrm{x}_1 d\mathrm{x}_2 d\mathrm{x}_3 d\mathrm{x}_4}{|\mathrm{x}_1 - \mathrm{x}_2|\,|\mathrm{x}_3 - \mathrm{x}_4|}$$

$$\times N_+(\mathrm{x}_1\mathrm{x}_3)\, N_+(\mathrm{x}_2\mathrm{x}_4)\, N_-(\mathrm{x}_3\mathrm{x}_1)\, N_-(\mathrm{x}_4\mathrm{x}_2).$$

It is expedient to transform to the momentum representation

$$N_{\pm}(\mathbf{x}, \mathbf{y}) = \int d\mathbf{p} \exp(i\mathbf{p}(\mathbf{x}-\mathbf{y}))\, \mu_{\pm}(\mathbf{x}, \mathbf{p}),$$

hence

$$\mu_{\pm}(\mathbf{x}, \mathbf{p}) = \langle \exp(\pm |t| \hat{H})\, \theta_{\mp}(\hat{H} - E_0) \rangle_{\mathbf{p}}. \tag{3.2}$$

Here and below

$$\langle \hat{a} \rangle_{\mathbf{p}} = \exp(-i\mathbf{p}\cdot\mathbf{x})\, \hat{a} \exp(i\mathbf{p}\cdot\mathbf{x}),$$

where $\hat{a}$ is an arbitrary operator. This yields

$$\delta E = -(4\pi^4)^{-1} \int_{-\infty}^{\infty} dt \int d\mathbf{x} \prod_1^3 d\mathbf{z}_i \int \prod_1^2 (d\mathbf{p}_i d\mathbf{q}_i d\mathbf{k}_i / k_i^2)\, \mu_+ (\mathbf{x}, \mathbf{p}_1)\, \mu_-(\mathbf{x}+\mathbf{z}_1, \mathbf{p}_1+\mathbf{q}_1)$$
$$\times \mu_+(\mathbf{x}+\mathbf{z}_2, \mathbf{p}_2)\, \mu_-(\mathbf{x}+\mathbf{z}_3, \mathbf{p}_2+\mathbf{q}_2) \exp\{i[\mathbf{z}_1(\mathbf{k}_2+\mathbf{q}_1) + \mathbf{z}_2(\mathbf{q}_2-\mathbf{k}_2) - \mathbf{z}_3(\mathbf{q}_2+\mathbf{k}_1)]\}. \tag{3.3}$$

In this case, q_i must vary from p_D to ∞.

Limiting ourselves in this section to the case $lp_D \gg 1$, we can neglect the contributions of z_i to the arguments $\mu_{\pm}$. Actually, because of the presence of the exponent in (3.3), $z_i < p_D^{-1} \ll l$. This permits us to carry out a series of integrations and we obtain the formula*

$$\delta E = -(32\pi^7)^{-1} \int_{-\infty}^{\infty} dt \int d\mathbf{x} \int d\mathbf{p}_1 d\mathbf{p}_2 \int_{p_D}^{\infty} \frac{d\mathbf{q}}{q^4}$$
$$\times \mu_+(\mathbf{x}, \mathbf{p}_1)\, \mu_-(\mathbf{x}, \mathbf{p}_1+\mathbf{q})\, \mu_+(\mathbf{x}, \mathbf{p}_2)\, \mu_-(\mathbf{x}, \mathbf{p}_2-\mathbf{q}). \tag{3.4}$$

For the transition to the uniform case it suffices to say that $\hat{H} = \hat{p}^2/2$, which gives

$$\mu_{\pm}(\mathbf{x}, \mathbf{p}) = \exp(\pm |t| p^2/2)\, \theta_{\mp}(p^2/2 - E_0), \tag{3.5}$$

and we return to the equation for δE given in Sec. 1.

We note that the condition $lp_D \gg 1$ permits us to make use of the law of conservation of momentum (Fig. 2). Actually, the momentum acquired by the particle from the external field consists, as is easy to verify, of a quantity of the order of $1/l$ which is small in comparison with the momentum of transfer p_D.

In this section, we limit ourselves to a qualitative estimate of δE based on the results set forth in the introduction.

We designate by Δp the width of the effective region of momentum space close to the Fermi surface which makes a significant contribution to (3.4). According to (3.2) and (3.4), this quantity is determined by the fact that the particle with momentum $\mathbf{p}_i$ and energy $E < E_0$, acquiring the momentum $\pm\mathbf{q}$ in the interaction, undergoes a transition to a state with momentum $\mathbf{p}_i \pm \mathbf{q}$ and energy $E > E_0$. Integration over t in (3.4) gives the energy gap $\Delta E \sim \Delta(p^2/2) \sim p_0 \Delta p$. With consideration of $\int d\mathbf{p} \sim p_0^2 \Delta p$, $p_0 \sim \rho^{1/3}$, we obtain

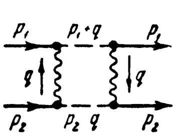

FIG. 2

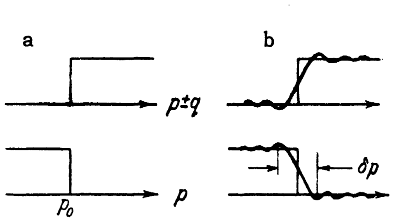

FIG. 3

$$\delta E \sim -\int \rho\, dx \int_{p_D} \frac{dq}{q^4} \Delta p. \tag{3.6}$$

In the uniform case, the width Δp is determined by the conditions $p_i < p_0$, $|\mathbf{p}_i \pm \mathbf{q}| > p_0$, whence $\Delta p \sim q$ and $\delta E \sim -\Omega\rho \ln p_0$.

However, in the non-uniform case, when a scattering of the momentum $\delta p \sim (p_0/l)^{1/2}$ takes place in the state with given energy (Sec. 1), the effective width Δp can depend materially on δp. Upon satisfying the condition (III) ($\delta p \gg p_D$) the width Δp becomes identical with δp. In this case, (3.6) yields

$$\delta E \sim -\int dx \rho \delta p / p_D \sim -\Omega\rho / l^{1/2}. \tag{3.7}$$

Thus, upon consideration of the non-uniformity, the divergence is strengthened, becoming linear instead of logarithmic. This is associated with the fact that the effective range of integration over the momentum in the uniform case tends to zero along with q, while in the non-uniform case it remains finite.

The estimates obtained for the quantity Δp are illustrated in Fig. 3, where the distribution functions over the momentum are plotted for energies less than E_0 (lower curve) and above E_0 (upper curve). Curves a and b correspond to the uniform and non-uniform cases, respectively.

4. CONSIDERATION OF DIAGRAMS OF HIGHER ORDER

In this section we calculate exactly the principal term of the correlation energy by means of summation of the platform diagrams of higher orders. The method used is a direct generalization of the non-uniform case, the method of Gell-Mann and Brueckner,[2] and operates under conditions (I) to (III) (Sec. 1). We note that in reference 2 a condition was obtained which directly contradicts (III); correspondingly, the results obtained below and the results of reference 2 refer to different limiting cases.

---

*The apparent locality of the expression (3.4) in the coordinates is connected with the uniformity of the system at distances of the order of correlation radius $1/p_D$. Actually, as is seen from (3.3), the region $|\mathbf{x}-\mathbf{x}_0| \sim 1/p_D$ makes a contribution to the density of the correlation of the energy at the point $\mathbf{x}_0$.

Let us first consider the case $lp_D \gg 1$ (at the correlation radius the distribution is uniform). For the "propagator function" $F_q(t)$ introduced in reference 2 we must choose in this case the expression:*

$$F_q(t) = (2\pi)^3 \sum_{n,m} \exp[\,|t|(E_n - E_m)]\,\theta_-(E_n - E_0)\,\theta_+(E_m - E_0)$$
$$\times \int d\xi \bar{\psi}_n(x+\xi)\,\psi_n(x)\,\psi_m(x-\xi)\,\bar{\psi}_m(x) \exp(i\mathbf{q}\cdot\xi),$$

where ψ and E are the wave function and the energy in the external field. Making use of (3.2) we can put this expression in operator form:

$$F_q(t) = \int d\mathbf{p}\,\mu_+(\mathbf{x}, \mathbf{p})\,\mu_-(\mathbf{x}, \mathbf{p}+\mathbf{q}). \tag{4.1}$$

In the uniform case, (4.1) undergoes a transition, in accord with (3.5), to the corresponding expression of Gell-Mann and Brueckner:[2]

$$F_q(t) = \int d\mathbf{p} \exp(-|t|(q^2/2 + \mathbf{p}\cdot\mathbf{q})) \tag{4.2}$$

with the conditions $p < p_0$, $|\mathbf{p} + \mathbf{q}| > p_0$. The difference between (4.1) and (4.2) thus consists only in the substitution of the Hamiltonian of the free particles $\hat{p}^2/2$ by the complete Hamiltonian† $\hat{H} = \frac{1}{2}(\hat{p}^2 - p_0^2(\mathbf{x})) + E_0$.

In complete correspondence with reference 2, the sum of the platform diagrams has the form

$$\delta E = -(32\,\pi^4)^{-1} \int d\mathbf{x} \int d\mathbf{q} \int_{-\infty}^{\infty} du \sum_{n=2}^{\infty} A^n/n, \tag{4.3}$$

where $A = 4p_0\varphi_q(u)/\pi q^2$ and

$$\varphi_q(u) = (1/4\,\pi p_0) \int_{-\infty}^{\infty} e^{itu} F_q(t)\,dt. \tag{4.4}$$

The sum in Eq. (4.3) is expressed in finite form and is equal to $A - \ln(1 - A)$. In this case, the integral (4.3) no longer diverges at the lower limit and is cut off at $q \sim (\varphi p_0)^{1/2}$.

In the calculation of $\varphi_q(u)$ the chief difficulty consists in finding the quantity μ which is a function of the Hamiltonian, which itself represents the sum of two non-commuting operators — the kinetic and the potential energy. As was shown in reference 4, to obtain an expression which is valid close to the Fermi surface, we must limit ourselves to a consideration of the first commutator of the operators shown and to all its powers. This gives for the arbitrary function f

$$\langle f(\hat{p}^2 - p_0^2)\rangle_p = \frac{1 - is}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\tau^2 s} f(p^2 - p_0^2 + 2\tau(|\mathbf{p}\nabla p_0^2|)^{1/2})\,d\tau, \tag{4.5}$$

where $s = \mathbf{p}\nabla p_0^2/|\mathbf{p}\nabla p_0^2|$. This expression is valid everywhere except for the extremely narrow (and therefore unimportant) region close to the Fermi surface $|p - p_0| \sim 1/l$.

Applying this equation to (3.2) and making use of (3.1) and (4.4), we obtain the following expression for $\varphi_q(u)$ (after some simple calculations*):

$$\varphi_q(u) \equiv \varphi(\lambda) = 1 + \pi\lambda^2 - 2\sqrt{\pi}(\cos\lambda^2\cdot S(\lambda) - \sin\lambda^2\cdot C(\lambda))$$
$$- 4\sqrt{2\pi}\lambda^2 \int_0^{\lambda} [\sin x^2\cdot S(x) + \cos x^2\cdot C(x)]\,dx, \tag{4.6}$$
$$\lambda = u/(2p_0|\nabla p_0^2|)^{1/2},$$

where C and S are the Fresnel integrals. The quantity $\varphi(\lambda)$ is a monotonically decreasing function of λ, and for small λ has the form $1 - \sqrt{2\pi}\,\lambda$, while for large values of λ it has the form $4/\lambda^4$.

Substitution of (4.6) in (4.3) gives

$$\delta E = -\frac{2\sqrt{2}}{3\pi^{7/2}} I \int d\mathbf{x} p_0^2 |\nabla p_0^2|^{1/2},$$

where

$$I = \int_0^{\infty} \varphi^{3/2}(\lambda)\,d\lambda = 0.286.$$

The correlation energy δE, as a functional of the density ρ, has the form

$$\delta E = -0.118 \int (\rho|\nabla\rho|)^{1/2} d\mathbf{x}. \tag{4.7}$$

A correspondence of this expression to the qualitative equation (3.7) is evident. We note that the principal contribution to (4.3) is given by the region $\lambda \sim 1$; therefore, the effective cutoff radius $q \sim p_0^{1/2}$ is identical with the Debye radius.

For a strongly compressed lattice we can, in finding $\rho(x)$, make use of the Thomas-Fermi model (see reference 5)

$$(3\pi^2\rho)^{1/3} = 2\left(E_0 + Z/x - \int \rho(\mathbf{x}')|\mathbf{x} - \mathbf{x}'|^{-1} d\mathbf{x}'\right),$$

whence

$$\rho = (3Z/4\pi R^3)\{1 + (16\,Z/3\pi^2)^{1/3} R(\xi^2/2 + \xi^{-1} - 3/2) + \cdots\}, \tag{4.8}$$

---

*Strictly speaking, this quantity is not a propagator function in the ordinary sense and corresponds to the diagram of Fig. 4. In terms of field theory, there corresponds to it the expression $\bar{\psi}\Gamma G\Gamma\psi$ where ψ encompasses the occupied states, Γ is the vertex part with momentum transfer q, G is the Green's function of the electron. Furthermore, in reference 2 and below, a purely expotential dependence of $F_q(t)$ on the time is assumed.

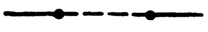

FIG. 4

†The validity of the expression (4.1) also follows from comparison with the formulas of perturbation theory [see for example, (3.4)].

*The condition (III) permits us to replace $\mathbf{p} + \mathbf{q}$ by $\mathbf{p}$ in the argument of the function $\mu_-(4.1)$.

where $\xi = x/R$, R is the radius of the neutral cell. Substitution of this expression in (4.7) gives (N is the total number of particles)*

$$\delta E = -0.106\, NZ^{7/6}.$$

The most important term not considered here is the exchange energy of second order which has a magnitude of the order of 0.02 N (See reference 2). The ratio of (4.9) to the total compressed matter is equal to $2.87\,N\,\rho^{2/3}$ and is a small quantity.

We proceed to find the contribution of the correlation to the equation of state of the material. The corresponding correction to the pressure is determined by the equation

$$\delta P = -\sigma(\delta E)/\partial V = (\rho^2/N)\,\partial(\delta E)/\partial\rho.$$

In view of the fact that the principal term δE does not depend on the ρ, it is necessary to make use of the following terms of an expansion of the type of the second term of (4.8). This gives

$$\delta P \sim Z^{5/6}\rho^{2/3}. \qquad (4.10)$$

The ratio of δP to the principal term in the pressure is equal to $1.92\,\rho^{5/3}$, which is always very small.

We note that the model frequently used in calculations of the equation of state, in which the neutral cell is considered independent of the rest of the material, gives an incorrect value of the correlation contribution to the pressure. The fact is that at high compression, when the dimensions of the lattice R becomes smaller than $1/p_D$ (while the latter quantity, being of the order of $\sqrt{R}$, falls off more slowly than R), distant correlations are not taken into account in this model.

We proceed to the case $lp_D \sim 1$. In this case, we can introduce only symbolic expressions for δE, obtained by replacing the sum in (4.3) by the quantities†

$$\sum_{n=2}^{\infty}\langle(4p_0\varphi(\lambda)/\pi\Delta)^n\rangle_q/n. \qquad (4.11)$$

Here the operator Δ^{-1} acts on all subsequent factors, while in the uniform case and in the case considered above, only the result of the effect of Δ^{-1} on $\exp(i\mathbf{q}\cdot\mathbf{x})$ was important.

The case under consideration corresponds to uncompressed material with large Z. The expressions (4.7) to (4.10) obtained above are applicable here only qualitatively. So far as electron correlation in metals is concerned, we must emphasize the impossibility of separate consideration of conduction electrons and ionic electrons, since the correlation radius in a real metal is of the order of the distance between nuclei. Therefore, strong correlation coupling will take place between the conduction electrons and the ionic electrons. In view of the fact that the number of the latter is large in comparison with the number of conduction electrons, we must consider that these correlations play a more important role that the correlations between the conduction electrons. Therefore, although the conduction electrons also form a more uniform distribution than the ionic electrons, the uniform model is inapplicable in this case also.

For an isolated atom we can obtain the dependence of δE on Z; and Eqs. (4.9) ($lp_D \gg 1$) and (4.14) ($lp_D \ll 1$; see below) lead to the same result

$$\delta E \sim Z^{7/6}, . \qquad (4.12)$$

naturally with a small coefficient. Thus, for large Z, the contribution of the correlation to the energy of the atom is small (principal energy term $\sim Z^{7/3}$). It is also actually small for z.

In the case $lp_D \ll 1$, Eq. (4.11) can be materially simplified, since the first term in it will play the fundamental role. Introducing the expression $\psi(u, x) \equiv 4p_0(x)\,\varphi(\lambda(x))/\pi$, we have

$$\delta E = -\frac{1}{128\pi^3}\int_{-\infty}^{\infty} du \int \frac{dxdy}{|\mathbf{x}-\mathbf{y}|^2}\psi(u, x)\,\psi(u, y). \qquad (4.13)$$

Pair correlations in this case play a dominant role and the infrared catastrophe is lacking. The fact is that the momentum acquired by the particles from the external field is so large in this case that it takes the particles out of the small-momentum region that is responsible for the collective motion.

In particular, if the system has such small dimensions L that $Lp_D \ll 1$ (or $LN^{1/3} \ll 1$) then the previous formula reduces to the estimate

$$\delta E \sim N^{7/6}. \qquad (4.14)$$

We note that the independence of δE of the density and the small role of the corrections of higher order follow directly from perturbation theory (Sec. 2). Actually, the matrix element has the order of L^{-1} in this case, while the energy gap is of the order L^{-2}, whereupon the correction of nth order amounts to $\delta_n E \sim L^{n-2}$. These questions were considered in reference 8 in application to two-electron atoms.

In conclusion, we again emphasize the impossibility of using the uniform model to find correlation effects in the range of low temperatures. If

---

*The uniform model reduces to the expression[2] $\delta E = -0.0104\,N\ln\rho + \ldots$, which has nothing in common with (4.9).

†For the derivation of (4.11) it is necessary to make use of the relation $\mu(\mathbf{x} + \mathbf{z}, \mathbf{p}) = \exp(\mathbf{z}\nabla)\mu(\mathbf{x}, \mathbf{p})$ [compare (3.3) and the condition (III)].

the material is in the crystalline state, then, as shown above, accounting for the non-uniformity in the particle distribution, due to the presence of the lattice, is absolutely necessary. If the same material can exist as a plasma, the effects of internuclear and electron-nuclear correlations come to the forefront. The fact is that the nucleus, having a small kinetic energy, is more sensitive to the field acting on it than is the electron. Therefore, the screening parameters are determined primarily by the nuclear mass and charge. In this case the dominant role of the nuclei appears in all temperature ranges where the electron gas is degenerate.

Formulation of the problem on the correlations in an inhomogeneous gas is contained only in the recent work of Hubbard,[9] where the known peculiarities of behavior of electrons in a periodic lattice field are taken into account. In the specific cases considered in the present research, it was possible to avoid the complication connected with this in the application of the approximation close to the quasi-classical.

I express my deep gratitude to V. L. Ginzburg, V. P. Silin, E. L. Fainberg and E. S. Fradkin for numerous discussions and valuable comments. I also thank L. V. Pariiskaia for the numerical computations.

---

[1] W. Macke, Z. Naturforsch, **5a**, 192 (1950); D. Pines, Solid State Physics, N. Y., **1**, 367 (1955).

[2] M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

[3] K. Sawada, Phys. Rev. **106**, 372 (1957).

[4] D. A. Kirzhnits, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 1625 (1958); Soviet Phys. JETP **7**, 1116 (1958).

[5] P. Gombas, Die statistische Theorie des Atoms, Springer, Wien, 1949 (Russian translation, IIL, 1951).

[6] D. A. Kirzhnits, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 115 (1957); Soviet Phys. **5**, 64 (1957).

[7] C. Møller and M. Plesset, Phys. Rev. **46**, 618 (1934).

[8] D. A. Kirzhnitz, Оптика и спектроскопия (Optics and Spectroscopy) **5**, 5 (1958).

[9] J. Hubbard, Proc. Roy. Soc. (London) **A244**, 199 (1958).

Translated by R. T. Beyer
252