# Local approximation in the density-functional method

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The applicability of the local-density approximation, on which practical applications of the density-functional method are based, to calculations of the exchange-correlation part of the free energy of a many-electron system is investigated. Locality breakdown mechanisms occurring when the scale of the inhomogeneity becomes equal to the Debye screening radius are determined in density and temperature ranges in which the electron gas is weakly inhomogeneous and is characterized by weak interaction. It is found that the local-density approximation is literally justified only in the high-density limit, is wrong even numerically and in the opposite limit of high temperatures. The situation in the range where the electron gas is strongly inhomgeneous is discussed briefly.

## 1. INTRODUCTION

The density-functional method, widely and successfully employed in the theory of many-electron systems, is a "first principles" approach in the arsenal of modern computational physics.[1] It is based on the expressions for the energy (at temperature $T\neq 0$—the free energy) in the form of a functional $F[n]$ of the particle number density $n(\mathbf{x})$, given near its equilibrium distribution which is described by the equation ($\mu$ is the chemical potential)

$$\delta F/\delta n(\mathbf{x})=\mu. \tag{1.1}$$

The complexity of the formalism of the theory of many interacting particles, which reflects the diversity of objects described by the theory, is manifested in the density-functional method by the fact that it is impossible to write down a closed expression for the exchange-correlation part $F_{XC}$ of the density functional. Thus it would be unthinkable to apply such a method without radical simplifications. The local-density approximation is usually employed for this purpose. This approximation consists of identifying at each point $\mathbf{x}$ the properties of an initial inhomogeneous system having a density $n(\mathbf{x})$ with those of a homogeneous system whose constant density $n$ is equal to $n(\mathbf{x})$. Accordingly, the local-density approximation corresponds to the substitution

$$V\to\int d\mathbf{x},\quad n\to n(\mathbf{x}) \tag{1.2}$$

in the expression $F_{XC}=Vf(n)$ for a homogeneous system of volume $V$.

It is obvious that a sufficient condition for this approximation to be applicable is that the density be continuous in space

$$L\gg l=(d,\lambda,r_D,...), \tag{1.3}$$

where $L$ is the spatial scale of the inhomgeneity and $l$ includes all other system parameters having the dimension of length: the average distance $d$ between particles, the de Broglie wavelength $\lambda$ (exchange-correlation radius), the Debye screening radius $r_D$ (the force correlation radius), and so on. Since the accuracy of the local-density approximation is determined by the smallness of the ratio $l/L$, it would be natural to regard the inequality (1.3) as a necessary condition for this approximation to be applicable.

The real situation, however, has been found to be much more complicated and confused. It has turned out that the local-density approximation is actually applicable in an unexpectedly wide range: calculations based on this approximation agree well with experiment even for a number of strongly inhomogeneous "cold" systems. This is essentially why the density-functional method is so popular. In order to explain it, general arguments based on the satisfaction of special sum rules, on the presence of averaging over angles, etc., have been put forth.[1]

The wide applicability of the local-density approximation is all the more surprising because the conditions (1.3) are satisfied only for densities or temperatures which are so high that the electron-electron and electron-nucleus interactions are insignificant. Under these conditions the electron gas is practically homogeneous and the substitution (1.2) becomes superfluous. In the rest of the $(n,T)$ diagram, which is the region of real interest, the conditions (1.3) break down due to the existence of the relation

$$L\sim r_D, \tag{1.4}$$

which is crucial for our further analysis and indicates that according to the values of the parameters the local-density approximation should not be valid. The relation (1.4), together with doubts about the applicability of this approximation, was discussed by one of us many years ago.[2] These doubts were later confirmed when the problem of the collective oscillations of an electron shell of an atom was solved.[3]

To understand this situation we present below a microscopic analysis of the expressions for $F_{XC}$ in a wide range of values of $n$ and $T$ (Sec. 2). Of course, it would be of greater physical interest to analyze not $F_{XC}$ itself but rather its derivatives. This more complicated problem falls outside the scope of this paper, however, and the solution is unlikely to yield qualitatively new results. The expression for $F_{XC}$ is amenable to such an analysis, since it can be

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represented in explicit form (Sec. 4) in that part of the $(n,T)$ diagram where, together with Eq. (1.4), the weak-coupling condition

$$L \gg d \sim n^{-1/3} \tag{1.5}$$

is also satisfied (Sec. 3). It is to this part of the diagram that the analysis presented below refers.

Microscopic analysis can shed light on the problem of the applicability of the local-density approximation. In particular, it can answer a number of questions associated with the relation (1.4):

1) What are the mechanisms of the breakdown of locality of the quantity $F_{XC}$ which correspond to the ratio $r_D/L$ not being small (Sec. 5)?

2) How does the effectiveness of these mechanisms depend on $n$ and $T$ (Secs. 6 and 7)?

3) Do there exist conditions when $F_{XC}$ no longer depends on the parameter $r_D/L$ and the applicability of the local-density approximation is guaranteed by the values of the parameters (Sec. 6)?

4) Do there exist conditions when, conversely, the local-density approximation is obviously inapplicable (Sec. 7)?

5) Why are the mechanisms under discussion ineffective in the strongly inhomogeneous systems for which the results agree with experiment? Although the restriction (1.5) precludes direct discussion of the last question, a number of considerations concerning this question are presented in the Conclusions.

The following units and notation are employed below: Boltzmann's constant is set equal to unity, brackets indicate quantum-mechanical and statistical averaging, and the symbol $d^3p$ denotes the quantity $d\mathbf{p}/(2\pi\hbar)^3$. The matrix and operator notation for two-point functions is often employed to simplify the formulas:

$$A(\mathbf{x},\mathbf{x}') = A_{\mathbf{xx}'} = \mathscr{A} = \hat{A}\delta(\mathbf{x}-\mathbf{x}'),$$

$$\int d\mathbf{x}' A(\mathbf{x},\mathbf{x}') f(\mathbf{x}') = \mathscr{A} f(\mathbf{x}) = \hat{A} f(\mathbf{x}),$$

the trace of the matrix $\mathscr{A}$ (operator $\hat{A}$) being defined by the expressions

$$\mathrm{tr}\,\mathscr{A} = \int d\mathbf{x} A(\mathbf{x},\mathbf{x}) = \mathrm{tr}\,\hat{A} = \int d\mathbf{x} \int d^3p [\hat{A}]_{\mathbf{p}}, \tag{1.6}$$

where

$$[A]_{\mathbf{p}} = \exp(-i\mathbf{px}/\hbar)\hat{A}\exp(i\mathbf{px}/\hbar).$$

Similar formulas with $\mathbf{p}$ replaced by the wave vector $\mathbf{k} = \mathbf{p}/\hbar$ are also employed.

## 2. GENERAL RELATIONS

The exchange-correlation free energy is, by definition,

$$F_{XC} = F - F_0 - F', \tag{2.1}$$

where $F_0$ is the free energy of an inhomogeneous ideal gas and

$$F' = \frac{e^2}{2}\int \frac{d\mathbf{x}d\mathbf{x}' n(\mathbf{x}) n(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} + \int d\mathbf{x} n(\mathbf{x}) U_e(\mathbf{x}) \tag{2.2}$$

is the sum of the self-consistent interaction energy and the energy $U_e$ in an external field. The expression for the total (self-consistent + external) Hartree potential

$$U(\mathbf{x}) = \frac{\delta F'}{\delta n(\mathbf{x})} = e^2 \int \frac{d\mathbf{x}' n(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} + U_e(\mathbf{x}),$$

which determines the quantity $n_t = -\Delta u/4\pi e^2$, which is the total charge density divided by the electron charge $e$, and the expression for the exchange-correlation potential appearing together with $u$ in the Kohn–Sham equation[1]

$$U_{XC}(\mathbf{x}) = \delta F_{XC}/\delta n(\mathbf{x})$$

follow directly from Eq. (2.1). The equation (1.1), which can be set in the form

$$\mu - U(\mathbf{x}) - U_{XC}(\mathbf{x}) = \delta F_0/\delta n(\mathbf{x}), \tag{2.3}$$

is used to switch to the functional argument $n(\mathbf{x})$ by eliminating the combination $\mu - U$ arising in the microscopic calculations. The nonequilibrium value of this argument in a fixed field $U_e$ can be assumed to be an equilibrium value in an appropriately altered field; this makes it possible to use Eq. (1.1).

We employ below less formal approaches instead of the standard Green's functions method. Generalizing the corresponding low-temperature procedure,[1] it is convenient to employ the well-known formula[4]

$$dF/de^2 = \langle d\hat{H}/de^2 \rangle. \tag{2.4}$$

The $e^2$-dependent part of the Hamiltonian $\hat{H}$ differs from Eq. (2.2) in that $n$ is replaced by the operator $\hat{n} = \hat{\psi}_\alpha^+ \hat{\psi}_\alpha$, where $\langle \hat{n} \rangle = n$, and that the self-action

$$\frac{e^2}{2}\int \frac{d\mathbf{x}d\mathbf{x}' n(\mathbf{x})\delta(\mathbf{x}-\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|},$$

is subtracted out, which reduces to eliminating an infinity of the type 1/0 (this regularization is designated below by the index $R$). Equations (2.1) and (2.2) yield the expression

$$F_{XC} = \frac{1}{2}\int_0^{e^2} de^2 \int_R \frac{d\mathbf{x}d\mathbf{x}' K(\mathbf{x},\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}, \tag{2.5}$$

where the correlation function

$$K(\mathbf{x},\mathbf{x}') = \langle \delta\hat{n}(\mathbf{x}) \delta\hat{n}(\mathbf{x}') \rangle, \quad \delta\hat{n} = \hat{n} - n$$

clearly reflects the exchange-correlation character of the quantity (2.1).

We note that the differentiation in Eq. (2.4) and the integration over $e^2$ in the subsequent formulas are performed at constant volume and at constant total particle-number density $N = \int d\mathbf{x} n(\mathbf{x})$. In the homogeneous case this corresponds to a fixed density $n$. It is significant that in the indicated operations the $e^2$-dependence of $n(\mathbf{x})$ can be neglected even in the inhomogeneous case (see also Ref. 1). This result follows from relation (1.1) and from the condition that $N$ must be constant:

$$\frac{dF}{de^2}=\frac{\partial F}{\partial e^2}+\int d\mathbf{x}\,\frac{\delta F}{\delta n(\mathbf{x})}\,\frac{\partial n(\mathbf{x})}{\partial e^2}=\frac{\partial F}{\partial e^2}.$$

Returning to expression (2.5), we apply to it the fluctuation-dissipation theorem[4] that expresses the correlation function in terms of the susceptibility $R$—the function characterizing the "charge to external charge" response $\delta n=\mathscr{R}(\delta \mathrm{n}_t-\delta \mathrm{n})$ (in matrix form; see the Introduction). The corresponding relation

$$\mathscr{K}=\frac{i\hbar}{8\pi e^2}\int_0^\infty d\omega\,\mathrm{cth}\left(\frac{\hbar\omega}{2T}\right)[(\Delta\mathscr{R})^+-\Delta\mathscr{R}]$$

gives an expression for $F_{XC}$ in terms of the susceptibility

$$F_{XC}=-\frac{\hbar}{2\pi}\int_0^{e^2}\frac{de^2}{e^2}\int_0^\infty d\omega\,\mathrm{cth}\left(\frac{\hbar\omega}{2T}\right)\mathrm{Im}\,\mathrm{tr}_R\mathscr{R}(\omega). \tag{2.6}$$

The relation

$$\mathscr{R}(\omega)=\Pi(\omega)\mathscr{V}(\omega) \tag{2.7}$$

expresses the susceptibility in terms of the polarization operator $\Pi$—the "charge to a potential $U$" response function

$$\delta n=\Pi\delta U \tag{2.8}$$

and in terms of the effective interaction

$$\mathscr{V}=-4\pi e^2[\Delta+4\pi e^2\Pi]^{-1}, \tag{2.9}$$

which describes the screening. Transforming to the time-dependent representation, and taking into account the delay of the response $\Pi(t)=0$ at $t<0$ and the formula

$$\int_0^\infty d\omega\,\sin(\omega x)\mathrm{cth}(\omega y)=\frac{\pi}{2y}\,\mathrm{cth}\left(\frac{\pi x}{2y}\right),$$

we find

$$F_{XC}=-\frac{T}{2}\int_0^{e^2}\frac{de^2}{e^2}\int_0^\infty dt dt'\times\mathrm{cth}\left[\frac{\pi T}{\hbar}(t+t')\right]\mathrm{tr}_R\Pi(t)\mathscr{V}(t'), \tag{2.10}$$

## 3. CHOICE OF THE PHYSICAL CONDITIONS

When the electron-electron interaction is weak (average distance $d$ between the interacting particles) the response functions in the formula for $F_{XC}$ (Sec. 2) can be expresssed in closed form. On the other hand, the appreciable inhomogeneity of the system is a consequence of the quite strong interaction of the electrons with the nuclei and with the average distribution of the other electrons (the average distance between the particles participating in such an interaction is $Z^{1/3}d$, where $Z\gg 1$ is the charge of a nucleus). It is known that the condition for the interparticle interaction to be weak is that the average interparticle distance must be small compared with the Debye screening radius.[4] For this reason, the $(n,T)$ diagram region considered below, where the microscopic analysis can be performed and the local-density approximation is nontrivial, is determined by the conditions

$$d\ll r_D\lesssim Z^{1/3}d, \tag{3.1}$$

corresponding to a wide range of density and temperature. We confine our attention below to two important limiting cases: A) the degenerate case

$$T\ll\hbar^2n^{2/3}/m, \tag{3.2a}$$

and B) the Boltzmann case

$$T\gg\hbar^2n^{2/3}/m, \tag{3.2b}$$

where $m$ is the electron mass.

The electron de Broglie wavelength $\lambda$ is of the order of $d$ in case A and must less than $d$ in case B. Thus substituting Eq. (1.4) (see Eq. (3.8) below) into the left-hand inequality in the relation (3.1) gives $\lambda\ll L$, which indicates that the electron motion is quasiclassical. Introducing the quasiclassical distribution function[3]

$$f(\mathbf{x},\mathbf{p})=\left\{\exp\left[\frac{p^2-p_0^2(\mathbf{x})}{2mT}\right]+1\right\}^{-1}, \tag{3.3}$$

where the characteristic momentum is

$$p_0(\mathbf{x})=\{2m[\mu-U(\mathbf{x})]\}^{1/2},$$

we obtain the well-known expressions for the density in the case A

$$n=p_0^3/(3\pi^2\hbar^3), \tag{3.4a}$$

in the case B

$$n=\frac{1}{\sqrt{2}}\left(\frac{mT}{\pi\hbar^2}\right)^{3/2}\exp\left(\frac{p_0^2}{2mT}\right), \tag{3.4b}$$

as well as for the Debye electron radius in the case A

$$r_D=\frac{1}{2}\left(\frac{\pi}{3n}\right)^{1/6}a_0^{1/2}, \tag{3.5a}$$

and in the case B

$$r_D=[T/(4\pi e^2n)]^{1/2}. \tag{3.5b}$$

Here $a_0=\hbar^2/me^2$ is the Bohr radius and we have employed the general function

$$r_D^{-2}=4\pi e^2\partial n/\partial\mu. \tag{3.6}$$

The right-hand side inequality in Eq. (3.1) means that the Debye radius is small compared with the average distance between the nuclei, so that the nuclei do not participate in the screening which is of a purely electronic character (this screening is accomplished by the production of a shortage or excess of electron density with respect to the uniform distribution). This is what enables us to employ Eqs. (3.5). Since we are not interested in phonon effects, we can assume that the mass of the nuclei is quite large and we can regard the nuclei simply as fixed sources of an external field.[1)]

The inhomogeneity scale $L$ mentioned in the Introduction is given by the formula

$$L^{-2}\sim\frac{\Delta n}{n}\sim\frac{\partial n}{\partial\mu}\,\frac{\Delta p_0^2}{mn}$$

and by Poisson's equation

$$\Delta p_0^2 = 8\pi m e^2 n_t = 8\pi m e^2 (n - Z n_e), \tag{3.7}$$

where $n_e$ is the number density of the nuclei. In the purely homogeneous case, when the positive charge is uniformly "smeared" over space, the right-hand side of Eq. (3.7) is zero and $L \to \infty$. In the case of fixed point nuclei, however, the external sources in Eq. (3.7) can be altogether dropped, since $L$, together with $r_D$, is less than the distance between the nuclei and the inhomogeneity is formed in the space between them. From Eq. (3.6) we indeed arrive at the relation (1.4)

$$r_D \sim L, \tag{3.8}$$

which reflects the fact that the screening and the formation of the inhomogeneity are both Coulomb effects. We note that the result (3.8) is not related to the weak-coupling approximation and remains in force when the left-hand inequality in Eq. (3.1) breaks down.

Thus we consider below a classical system of electrons with weak coupling in a field of fixed external sources (nuclei) under conditions corresponding to the following band in the $(n,T)$ diagram [see Eqs. (3.1) and (3.5)]:

case A

$$a_0^{-3} \ll n \lesssim Z^2 a_0^{-3}, \tag{3.9a}$$

case B

$$e^2 n^{1/3} \ll T \lesssim Z^{2/3} e^2 n^{1/3}. \tag{3.9b}$$

## 4. POLARIZATION OPERATOR

In the weak-coupling approximation the exchange-correlation terms are small and the polarization operator (see Sec. 2) can be calculated in the Hartree approximation. The corresponding equation for the statistical operator $\hat{\rho}$ has the form[4]

$$i\hbar\partial\hat{\rho}/\partial t = [\hat{H},\hat{\rho}], \quad \hat{H} = \hat{p}^2/2m + U. \tag{4.1}$$

In the unperturbed state (corresponding to the subscript 0) $\hat{\rho}_0$ is a function of the variable $\hat{H}_0 - \mu$ and the distribution function is $f_0(\mathbf{x},\mathbf{p}) = [\hat{\rho}_0]_\mathbf{p}$ (see Eqs. (1.6) and (3.3)).

Introducing into the Hamiltonian the small perturbation $\delta U(\mathbf{x},t)$, we find from Eq. (4.1) the corresponding perturbation of the statistical operator

$$\delta\hat{\rho} = \frac{i}{\hbar} \int_{-\infty}^{t} dt' [\hat{\rho}_0, \delta U(\hat{\mathbf{x}}(t'-t),t')], \tag{4.2}$$

where

$$\hat{\mathbf{x}}(t) = \exp(i\hat{H}_0 t/\hbar)\mathbf{x}\exp(-i\hat{H}_0 t/\hbar)$$

is the Heisenberg operator representation of the coordinate. This expression, together with what was said above about the operator $\hat{\rho}_0$, gives

$$\hat{\rho}_0 \Phi(\hat{\mathbf{x}}(t)) = \Phi(\hat{\mathbf{x}}(t^*))\hat{\rho}_0, \quad t^* = t - i\hbar\partial/\partial\mu.$$

The expression (4.2), together with the last identity, makes it possible to find the density perturbation.

$$\delta n = 2 \int d^3p [\delta\hat{\rho}]_\mathbf{p}.$$

The definition (2.8) of the polarization operator leads to the expression

$$\Pi(\mathbf{x},\mathbf{x}',t) = \frac{2}{i\hbar}\theta(t) \int d^3p [\delta(\hat{\mathbf{x}}(-t) - \mathbf{x}') - \delta(\hat{\mathbf{x}}(-t^*) - \mathbf{x}')] f_0(\mathbf{x},\mathbf{p}), \tag{4.3}$$

where the momentum operator appearing in $\hat{\mathbf{x}}$ must be replaced by $\mathbf{p} - i\hbar\phi\nabla$ (the gradient operates on the distribution function).

In the quasiclassical limit ($\hbar \to 0$) the coordinate operator passes into the classical law of motion $\mathbf{x}(t)$ of an electron in a field $U$, where

$$\mathbf{x}(t) = \mathbf{x} + \frac{\mathbf{p}t}{m} + \int_0^t dt'(t-t') \frac{\nabla p_0^2[\mathbf{x}(t')]}{2m^2}. \tag{4.4}$$

The acceleration term in this Newton's integral equation starts to have an effect at times

$$t \gtrsim mL/p_0, \quad p \sim p_0. \tag{4.5}$$

Passage in Eq. (4.3) to the limit $\hbar \to 0$ gives

$$\Pi(\mathbf{x},\mathbf{x}',t) = 2\theta(t) \frac{\partial}{\partial t} \int d^3p \delta(\mathbf{x}(-t) - \mathbf{x}') \frac{\partial f_0(\mathbf{x},\mathbf{p})}{\partial\mu}. \tag{4.6}$$

We also give an expression for the quantity $\Pi(\mathbf{x},\mathbf{x}',\omega)$ at $\omega = 0$:

$$\Pi(\mathbf{x},\mathbf{x}',\omega=0) = -\delta(\mathbf{x}-\mathbf{x}')/(4\pi e^2 r_D^2(\mathbf{x})). \tag{4.7}$$

The expression (4.6), which depends explicitly on the classical trajectory of the electron, has also been used in the case $T = 0$.[3]

We note that in order for the quasiclassical approximation to be valid, the de Broglie wavelength must be small compared with not only the length $L$ (Sec. 3) but also the quantity $|\mathbf{x} - \mathbf{x}'|$. The last condition does not hold for short times

$$t < \hbar m/p_0^2, \tag{4.8}$$

when this quantity, equal to, according to Eqs. (4.4) and (4.6), the path $p_0 t/m$ traversed by a particle over the time $t$, is too small. When the condition (4.8) is satisfied $\hat{\mathbf{x}}(t)$ in Eq. (4.3) must be interpreted as a quantum operator even in the limit $\hbar \to 0$.

Fortunately, this operator has, in this case, the form of the free-motion operator

$$\hat{\mathbf{x}}(t) = \mathbf{x} + \hat{\mathbf{p}}t/m.$$

Indeed, thanks to the conditions (4.8) and $\lambda \sim \hbar/p_0 \ll L$ the time $t$ is shorter than the time (4.5), when acceleration starts to have an effect. With allowance for the known Hausdorf formula[2]

$$\exp(\hat{a} + \hat{b}) = \exp(\hat{a})\exp(\hat{b})\exp(\tfrac{1}{2}[\hat{b},\hat{a}])$$

the relation (4.3) gives the expression

$$\Pi(\mathbf{x},\mathbf{x}',t)=-\frac{2}{\hbar}\theta(t)\int d^3p\,d^3k\,f_0(\mathbf{x},\mathbf{p})$$
$$\times\exp[i\mathbf{k}(\mathbf{x}-\mathbf{x}'-\mathbf{p}t/m)]\sin\left(\frac{\hbar tk^2}{2m}\right), \qquad (4.9)$$

which differs from the standard formula of the homogeneous case only by the coordinate dependence of the distribution function and which, for this reason, is local and can be found in accordance with the local-density approximation.

We note that the formulas presented for $\Pi$ express this quantity in terms of $p_0^2$ [see Eq. (3.3)]. The relation (2.3), which assumes the form

$$p_0^2(\mathbf{x})=2m[\delta F_0/\delta n(\mathbf{x})+U_{XC}(\mathbf{x})]$$

is used to switch here and below to the argument $n$. In the case of weak coupling this relation takes the form (3.4).

## 5. SOURCES OF NONLOCALITY

The expressions presented in Sec. 2 for $F_{XC}$ depend, in the general case, on $n$ in a nonlocal manner. Our microscopic approach makes it possible to determine the sources of nonlocality and assess their effectiveness. There are two types of nonlocality: "weak" nonlocality, corresponding to the parameter $\lambda/L\lesssim d/L$ which is small in the region (3.9) studied in this paper (but is appreciable in the strongly inhomogeneous case) and "strong" nonlocality, corresponding to the parameter $r_D/L$ which is comparable with unity even in the region (3.9) (see Sec. 3).

The source of weak nonlocality is the nonzero value of the de Broglie wavelength, which results in quantum gradient corrections to the quasiclassical expressions for any characteristic of the system.$^2$ In particular, corrections to $F_0$ [see Eq. (2.1)], for which the local-density approximation leads to the Thomas–Fermi model,$^3$ have been studied in detail. This quantity contains the characteristic lengths $d$, $\lambda$, and $L$ and the applicability of the local-density approximation to it is limited only by weak nonlocality.

The situation is different for the quantity $F_{XC}$ of interest to us. Here an additional parameter comes into play—the Debye radius $r_D$, which engenders strong nonlocality. Two mechanisms lead to such nonlocality: (a) the polarization operator $\Pi$ and (b) the effective interaction $V$ [see Eqs. (2.6) and (2.7)]. The first mechanism corresponds to dependence of $\Pi$ on the law of motion $\mathbf{x}(t)$, which, owing to the presence of an acceleration term in Eq. (4.4), depends in a nonlocal fashion on $p_0^2$ and on the density [gradients of all possible orders of such quantities arise in iterations of Eq. (4.4)]. According to the condition (4.5) the mechanism (a) is ineffective when$^{2)}$

$$t\ll mL/p_0\sim mr_D/p_0\sim\omega_p^{-1}, \qquad (5.1)$$

where $\omega_p^2=4\pi e^2n/m$ is the squared plasma frequency. This mechanism is inoperative for free motion [in particular, when the condition (4.8) is satisfied]. It is also inoperative in the special case $\omega=0$, owing to the factor $\theta(t)\partial/\partial t$ in the expression for $\Pi$, which singles out the value $t=0$ [see Eqs. (4.6) and (4.7)].

The second mechanism operates also when the polarization operator itself is local but varies in space (nonuniform screening). In this case $V$ is nonlocal owing to the action of the operator (matrix) $\Delta^{-1}$ in Eq. (2.9) on $\Pi$. This can be seen, for example, from the expansion of $V$ in terms of $\Pi$:

$$\mathscr{V}=-4\pi e^2\Delta^{-1}+(4\pi e^2)^2\Delta^{-1}\Pi\Delta^{-1}$$
$$-(4\pi e^2)^3\Delta^{-1}\Pi\Delta^{-1}\Pi\Delta^{-1}+\ldots\,. \qquad (5.2)$$

At high frequencies (short times $t$) this expansion reduces to its first local term—the electron does not have enough time to respond to a fast action. It can be shown that the second mechanism is not effective under a condition, coinciding with (5.1)

$$t\ll\omega_p^{-1}. \qquad (5.3)$$

At the same time, for $\omega=0$, when all values of $t$ are important and when the equation for $V$ is especially simple [see Eqs. (2.9) and (4.7)]

$$[\Delta-r_D^{-2}(\mathbf{x})]V(\mathbf{x},\mathbf{x}')=-4\pi e^2\delta(\mathbf{x}-\mathbf{x}'), \qquad (5.4)$$

the second mechanism, in contrast to first one, operates in full force.

Thus the general condition for the absence of strong-nonlocality effects is that the characteristic times in Eq. (2.10) satisfy the inequality

$$t,t'\ll\omega_p^{-1}. \qquad (5.5)$$

We note, writing the trace in Eq. (2.10) in the form

$$\int_R d\mathbf{x}d\mathbf{x}'\Pi(\mathbf{x},\mathbf{x}',t)V(\mathbf{x}',\mathbf{x},t'),$$

that there is another trivial source of nonlocality of this expression—the fact that the first two arguments of $\Pi$ and $V$, which determine the point in space to which $p_0^2$ and the density refer, are different [see Sec. 4 and Eq. (5.4)]. The condition (5.5) guarantees that this source is also ineffective in view of the relation $|\mathbf{x}-\mathbf{x}'|\sim p_0t/m$ (see Sec. 4).

Thus the solution of the question of strong nonlocality entails an estimate of the times $t$ and $t'$, and it is this estimate that we obtain below for different values of $n$ and $T$.

## 6. DEGENERATE CASE

We start our detailed analysis of the expression for $F_{XC}$ with the low-temperature case (3.2a), when $f_0(\mathbf{x},\mathbf{p})=\theta(p_0^2-p^2)$ [see (3.3)] and

$$\Pi(\mathbf{x},\mathbf{x}',t)=\frac{mp_0(\mathbf{x})\theta(t)}{\pi^2\hbar^3}\frac{\partial}{\partial t}\overline{\delta(\mathbf{x}(-t)-\mathbf{x}')} \qquad (6.1)$$

[see Eq. (4.6)]. Here the substitution $\mathbf{p}\rightarrow p_0(\mathbf{x})\mathbf{n}$ in Eq. (4.4) is implied, and the overbar indicates averaging over the directions of the unit vector $\mathbf{n}$. The expression (2.10) assumes the form

$$F_{XC}=-\frac{\hbar}{2\pi}\int_0^{e^2}\frac{de^2}{e^2}\int_0^\infty\frac{dtdt'}{t+t'}\mathrm{tr}_R\Pi(t)\mathscr{V}(t'). \qquad (6.2)$$

Substitution here of the zeroth term of the expansion (5.2) gives the following expression for the purely exchange free energy

$$F_X=-\frac{\hbar e^2}{2\pi}\int_0^\infty \frac{dt}{t}\int d\mathbf{x}d\mathbf{x}'\,\frac{\Pi(\mathbf{x},\mathbf{x}',t)}{|\mathbf{x}-\mathbf{x}'|}. \qquad (6.3)$$

Here strong nonlocality does not arise—for the mechanism $b$ due to the trivial form of $V$ and for the mechanism $a$ for the following reason. Substituting Eq. (6.1) into Eq. (6.3) and using Eq. (4.4) leads to strong divergence of the integral at $t=0$. This divergence reflects the fact that the quasiclassical description cannot be used to describe exchange effects, which are inherently of a quantum nature. This means that the short times

$$t\sim\frac{\hbar m}{p_0^2}\ll\omega_0^{-1}$$

[see Eq. (4.8), satisfying the criterion (5.1)], play the main role in Eq. (6.3). Using instead of Eq. (6.1) the quantum expression (4.9) and switching to the argument $n$ with the help of Eq. (3.4a) we obtain the well-known formula for the uniform case with the substitution (1.2),[4] corresponding to the local density approximation:

$$F_X=-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}e^2\int d\mathbf{x}n^{4/3}. \qquad (6.4)$$

The correlation effects correspond to the remaining terms in the expansion (5.2), which leads to a series in powers of the small [in the region (3.9)] interelectron interaction constant. However, thanks to the infrared divergences, the contributions of the terms of this series become comparable at long times $t\sim\omega_0^{-1}$. For this reason, it is sufficient to take into account, with logarithmic accuracy, only the second term in the expansion (5.2), introducing a "cutoff" of the integral over $t$ in Eq. (6.2) at the value $\omega_p^{-1}$. The divergence arising in so doing at short times $t$ means, as above, that quasiclassical approximation is not applicable and requires an additional lower cutoff at $t\sim\hbar m/p_0^2$. This gives

$$F_C=-\frac{1}{4\pi^5\hbar a_0^2}\int_0^\infty\frac{dtdt'}{t+t'}\int d\mathbf{x}d\mathbf{x}'A(\mathbf{x},\mathbf{x}',t)A(\mathbf{x}',\mathbf{x},t'), \qquad (6.5)$$

where

$$A(\mathbf{x},\mathbf{x}',t)=\overline{p_0(\mathbf{x})/|\mathbf{x}(-t)-\mathbf{x}'|}.$$

The substitutions $t'\to ts$ and $\mathbf{x}'=\mathbf{x}-t\mathbf{y}$ reduce the expression (6.5) to an integral of the type $\int dtf(t)/t$, which must be cut off in the manner indicated above.

The term that is logarithmically large in the parameter

$$p_0^2/\hbar\omega_p m\sim(a_0n^{1/3})^{1/2}$$

is separated from this integral with the help of the formula

$$\int_{\hbar m/p_0^2}^{\omega_p^{-1}}\frac{dt}{t}f(t)=\frac{1}{2}\ln(a_0n^{1/3})f(0) - \int_0^{\omega_p^{-1}}dt\ln(t\omega_p)f'(t). \qquad (6.6)$$

This term corresponds to $t=0$, and according to Eq. (5.5) it does not have strong nonlocality. Direct calculation of this term indeed gives the well-known Gell-Mann–Brueckner formula[2] for the homogeneous case with the substitution (1.2) in accordance with the local-density approximation:

$$F_C=-\frac{1-\ln 2}{\pi^2}\int d\mathbf{x}n\ln(a_0n^{1/3})\frac{e^2}{a_0}. \qquad (6.7)$$

However, the nonlogarithmic terms [second term in Eq. (6.6) and the contribution of the higher order terms in the series (5.2)] are determined by long times $t\sim\omega_p^{-1}$, which destroys both criteria (5.5) and makes the local-density approximation inapplicable, at least literally. We present without derivation an expression for the gradient correction to the logarithmic term (6.7)

$$\delta F_C=-\frac{1-\ln 2}{324\pi^4}(3\pi^2)^{1/3} \times\int d\mathbf{x}(\nabla n)^2n^{-5/3}\ln(a_0n^{1/3})\frac{e^2}{a_0}, \qquad (6.8)$$

which is characterized by a very small numerical coefficient.

We note in concluding this section that if the inequality $L<r_D$ were realized, the following change would appear in Eq. (6.7)

$$\ln(a_0n^{1/3})=2\ln(n_2n^{1/3})\to 2\ln(Ln^{1/3}). \qquad (6.9)$$

This is the situation in the special case of a homogeneous system with randomly distributed impurities, where the electron mean free path plays the role of $L$ ($L<r_D$, $Ln^{1/3}>1$). For $t<Lm/p_0$ electrons move freely, and over longer times they diffuse with a diffusion coefficient $Lp_0/m$. Using the well-known expression for the probability of displacement of a diffusing particle, and averaging the exprression (6.5) over the corresponding distribution, it is easy arrive at the substitution (6.9).

## 7. BOLTZMANN CASE

In the high-temperature case [see Eq. (3.2b)] there are no exchange effects (the first term of Eq. (5.2) does not contribute after regularization; see below) and the correlation free energy (2.10) assumes the simple form

$$F_C=-\frac{T}{2}\int_0^{e^2}\frac{de^2}{e^2}\mathrm{tr}_R\Pi(\omega=0)\mathscr{V}(\omega=0). \qquad (7.1)$$

In accordance with what was said in Sec. 5 the mechanism $a$ in this case is ineffective [$t=0$ in Eq. (5.5)] and the mechanism $b$ operates in full force ($t'$ runs through all values). With allowance for Eq. (3.5b), the equation (5.4) takes the Debye–Hückel form[4] but with variable coefficients:

$$(\Delta-4\pi e^2n(\mathbf{x})/T)V(\mathbf{x},\mathbf{x}')=-4\pi e^2\delta(\mathbf{x}-\mathbf{x}'). \qquad (7.2)$$

The formula (7.1) has then the form

$$F_C=\frac{1}{2}\int_0^{e^2}de^2\int_R d\mathbf{x}n(\mathbf{x})V(\mathbf{x},\mathbf{x}). \qquad (7.3)$$

Here the regularization (Sec. 2) means substitution of

$$V(\mathbf{x},\mathbf{x}') - e^2/|\mathbf{x}-\mathbf{x}'|$$

for $V(\mathbf{x},\mathbf{x})$ in the limit $\mathbf{x}'\to\mathbf{x}$. This corresponds directly to elimination of the self-action, as done in the elementary Debye–Hückel theory.[4]

The other, operator formulation based on the relations (2.9), (4.7), and (7.1) leads to the expression

$$F_C = \frac{T}{2}\,\mathrm{tr}_R \ln(1-\Delta^{-1}r_D^{-2}), \tag{7.4}$$

or, with allowance for Eq. (1.6),

$$F_C = \frac{T}{2}\int d\mathbf{x}\int d^3k\left\{[\ln(-\Delta + r_D^{-2})]_{\mathbf{k}} - \ln k^2 - \frac{r_D^{-2}}{k^2}\right\}, \tag{7.4$'$}$$

where $r_D^{-2} = 4\pi e^2 n/T$. If the function $n(x)$ were to vary sufficiently smoothly in space, the noncommutation of the operators in the first logarithm in Eq. (7.4′) could be neglected and we would arrive at the well-known Debye–Hückel formula for a homogeneous system with the substitution (1.2):

$$F_C^0 = -\frac{2}{3}e^3\left(\frac{\pi}{T}\right)^{1/2}\int d\mathbf{x} n^{3/2}. \tag{7.5}$$

In reality, however, the variation of $n(\mathbf{x})$ is determined by Poisson's equation (3.7), which assumes, substituting Eq. (3.4b), the form

$$\Delta n - (\nabla n)^2/n = 4\pi e^2 n^2/T. \tag{7.6}$$

It is evident directly from Eq. (7.6) that in accordance with Eq. (1.4) the scale $L$ of the inhomogeneity is identical to the Debye radius. For this reason, the gradient corrections to Eq. (7.5), which are associated with the noncommutation of the operators appearing in Eq. (7.4′), are not literally small compared with the zeroth term, which is in fact how the mechanism $b$ is manifested. Calculation of these corrections by the standard method[2] (see also Ref. 5) shows that it corresponds to introducing into the integrand in Eq. (7.5) the additional factor

$$1 - \frac{T}{128\pi e^2}\left[\frac{4\Delta n}{n^2} - \frac{(\nabla n)^2}{n^3}\right] + \ldots,$$

where a correction only of second order in the gradients is given. A complicated expression for fourth-order corrections is presented in a paper by Kirzhnits[5] and the following inequality is also derived from Eq. (7.6):

$$\frac{F_C}{F_C^0} < 1 - \frac{1}{8} - \frac{3}{640} + \ldots \approx 0.870. \tag{7.7}$$

It can be shown that the left-hand side of Eq. (7.7) necessarily falls between 0 and 1.[5]

Numerical calculations of the ratio $F_C/F_C^0$ from the relation (7.4) are now being conducted with the help of the special method of Ref. 5 for determining the logarithm of the determinant of an operator, having the form of a nonrelativistic Hamiltonian, by reducing the problem to a scattering problem. Here the problem reduces to determining the values of the wave function (solution of the corresponding Schrödinger equation) for zero energy at the origin of coordinates. Omitting the details, we give the preliminary results:3)

$$F_C/F_C^0 = 0.4 - 0.7. \tag{7.8}$$

It follows from everything said above that the local-density approximation is quantitatively inapplicable for calculating the correlation free energy of a weakly inhomogeneous Boltzmann gas.

## 8. CONCLUSIONS

The above analysis refers to the region of the $(n,T)$ diagram that is most favorable for application of the local-density approximation as a nontrivial approximation. Even in this region there arises a factor (the Debye radius coincides with the inhomogeneity scale) that engenders a series of specific mechanisms of nonlocality which prevent application of the local-density approximation (first question in the Introduction). Their effectiveness depends on the density and temperature, and increases with increasing temperature (question 2). It is only at $T=0$ and high density that these mechanisms are inoperative and the applicability of the local-density approximation is guaranteed by the values of the parameters (question 3). In the opposite limit—the case of high temperatures—this approximation is clearly inapplicable (question 4).

Thus the applicability of the approximation considered here not only is not universal but, in addition, it is more of an exception. The arguments given in the Introduction in support of this approximation, which by virtue of their generality should also hold in the Boltzmann case, are guaranteed by the answer to question 4. More precisely, these arguments are simply qualitative considerations supporting the local-density approximation, which themselves do not solve the problem but must be checked quantitatively in each specific case. Such a confirmation exists, in particular, for the purely exchange energy of a degenerate system (see Ref. 1). This quantity is, however, of little interest, since the mechanisms leading to breakdown of locality do not operate for it (see Sec. 6).

As for the ability to explain the local-density approximation, as applied to a number of strongly inhomogeneous "cold" systems (question 5 of the Introduction) by the arguments advanced above, the contents of this paper are not directly applicable to such systems. Nonetheless the results of the present paper also make it possible to say something about this ability.

First, we underscore that the local-density approximation is successful not because the parameters are small but because the corresponding numerical coefficients are anomalously small: In the region of strong degeneracy at $T=0$ the parameters $d/L$ and $\lambda/L$ also become of the order of unity together with $r_D/L$. The possibility of the appearance of such an anomalous smallness is illustrated at least by the relations (6.7) and (6.8). Another instructive example is the problem, already mentioned above many times, of collective atom oscillations whose damping was found to be anomalously smaller (by 3–4 orders of magnitude) than their energy.[3,6] In this example, just as in the problem studied in the present paper, owing to the smallness of the numerical coefficients the answer (zero damping) obtained within the dynamical theory using the local-density approximation approaches the exact answer. It is not excluded that this coefficient also arises in the nonlogarithmic term of the correlation energy of a weakly inhomogeneous "cold" system (see Sec. 6), and this favors the local-density approximation.

Is this smallness a purely empirical fact or is there a profound theoretical basis for it? This question can hardly be answered at the present time. In any case, such laws cannot be simple and general: This is already indicated by the complicated and nontrivial situation in the above-studied region of applicability of the weak-coupling approximation. For this reason, the success of the local-density approximation in application to strongly inhomogeneous systems, so important for practical applications of the density functional method, must for the time being be considered as a "gift of fate," whose range of applicability is unclear and obviously limited.

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1) We note that, by virtue of the same inequality, the electron-nucleus correlations are not equal to the nucleus-nucleus correlations. This is manifested, in particular, by the existence of intact atomic shells in the region under study. This fact makes it impossible to circumvent the problem of the local density approximation in the case $B$ by considering a two-component plasma (electrons+nuclei) that has a uniform Gibbs average. Such difficulties do not arise when the problem is formulated in the manner adopted above (the "hot" atom model[3]).

2) It is because the condition (5.1) breaks down that the local density approximation is inapplicable in the problem of colletive oscillations of an atom (see above) with frequencies of the order of $\omega_p$ and characteristic times of the order of $\omega_p^{-1}$.

3) The nonconstancy of (7.7) arises as follows. At first glance this relation should be equal to a constant, because the only system parameter appearing in Eqs. (7.4) and (7.6) is $r_D$. However, the boundary conditions to Eq. (7.6) also lead to the appearance of other parameters: At short distances from a nucleus there is a "cold" core (the condition (3.2b) is violated) and at large distances there is the boundary of a neutral cell, where $\partial n/\partial r=0$ (an isolated "hot" atom does not exist, because the coulomb center cannot prevent the gas from expanding). The is why the temperature, pressure, and nuclear-charge dependences arise in Eq. (7.8).

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