The uniform quantized electron gas revisited

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Abstract

In this article we continue and extend our recent work on the correlation energy of the quantized electron gas of uniform density at temperature $T = 0$. As before, we utilize the methods, properties, and results obtained by means of classical statistical mechanics. These were extended to quantized systems via the Feynman path integral formalism. The latter translates the quantum problem into a classical polymer problem in four dimensions. Again, the well known RPA (random phase approximation) is recovered as a basic result which we then modify and improve upon. Here we analyze the condition of thermodynamic self-consistency. Our numerical calculations exhibit a remarkable agreement with well known results of a standard parameterization of Monte Carlo correlation energies.

Keywords: electron gas, correlation energy, path integral, liquid state theory

(Some figures may appear in colour only in the online journal)

1. Introduction

In a recent work we considered the problem of the correlation energy of the quantized electron gas based upon methods, results, and reasonings of classical statistical mechanics [1]. With this development the well known RPA of quantized systems was recovered as a basic result for the correlation energy. As already known, RPA results deviate clearly from available Monte Carlo data [2]. Since the RPA is a basic result also from the viewpoint and methods of liquid state theory for classical fluids, the problem will be how to utilize these methods to improve the RPA in the quantum case. In our previous work we focused upon conditions on the pair correlation function. These must reflect the fact that fermions with equal spins are not allowed to be at the same position. For classical systems the repulsive Coulomb interaction will also prevent particles to be at the same position. These conditions can be applied to the equal time correlation functions to improve results. The first condition is exact (Pauli exclusion) while the second turns out not to be so in the quantum mechanical case, especially for increasing energy. For this reason, in [1] the second condition had to be abandoned, which deteriorated somewhat the performance of the approximation.

Our method to improve upon the RPA rests on the introduction of an effective interaction. In the correlation function of the RPA the pair interaction plays a role similar to the direct correlation function for classical systems. It is then known that for a pair of particles at large separation $r$, the direct correlation function approaches the interaction times inverse temperature with minus sign. For smaller separations there will be deviations. But they should change smoothly for interactions that vary likewise. One then expects the effective interaction to behave in a similar way. With this the fermion condition was used to determine a free parameter in the function describing these deviations. This function may be a Yukawa term (shielded Coulomb) or something related whose range can be determined from the given condition.

In the present work, our approximations will be constructed bearing in mind thermodynamic self-consistency. Therefore, the core condition with its uncertainty for unequal spins mentioned above, will not be imposed. The condition of self-consistency is an essential new feature compared to [1]. It is an exact condition and can be used to determine a free parameter in the effective interaction. In this way a higher order correction to the exchange correlation energy is obtained. Although the adjustment of the interaction may look like a classical
interaction, whose tail for large $r$ should be multiplied by an adjustable constant. This, however, is not suitable for an interaction of finite range, the SCOZA and HRT effective interactions simply correspond to the original one multiplied by $\kappa$ as a cut-off parameter $\kappa$ in the resulting effective interaction. This simplifies somewhat the situation. In the case of the ALDA this parameter, $\kappa$, is also evaluated from compressibility-based known results. In order to improve this approach, we will use $\kappa$ as a cut-off parameter in smooth effective interactions and then study possible alternatives, assessing the accuracy of the results.

In section 3 the compressibility with exchange energy only, is considered, and its influence upon the correlation function is written down. It is then found that the exchange energy included alone gives the very simple result $\kappa = \text{const} = 1$.

Then in section 4 the influence of the correlation energy is taken into account. Here we note that by scaling the Coulomb interaction with a parameter $\lambda$, the free energy expression reflects this through a scaling function $G$ with a scaling variable $z = \lambda r_s (r_s \sim \rho^{-1/3})$ where $\rho$ is the particle density. The compressibility and thus the $\kappa$ can be expressed in terms of $G$ and its first and second derivatives. Since the correlation energy is a correction to the exchange energy, it turns out that the former has small influence upon the parameter $\kappa$; it decreases a small amount.

In section 5 the charging principle is considered. Then the interaction is multiplied with the parameter $\lambda$, and the free energy is given by integration of an internal energy type expression where $\lambda$ varies from 0 to 1. The latter expression and the independent one of the compressibility, both based upon the same correlation function, are required to fulfill self-consistency, i.e. give the same result.

In section 6 thermodynamic self-consistency between adiabatic charging and compressibility is considered in more detail. The intention is to use it to improve upon the RPA by determining a free parameter in an effective interaction. Similar to SCOZA and HRT this will give rise to a non-linear partial differential equation. This equation can be demanding to solve numerically, especially in connection with phase transitions and their critical regions. However, in the present case with the scaling variable $z$ the self-consistency problem simplifies to an ordinary differential equation. Furthermore as a result of our investigations we in sections 3–5 realized that the free parameter $\kappa$ would vary little. Thus the resulting self-consistency problem can be solved by a straightforward direct substitution method.

Our numerical results for the correlation energy (including its wave vector dependence) are introduced in section 7 and compared with the well known Perdew–Wang (PW) parameterization [2, 9] of the Ceperley and Alder Monte Carlo
results [10]. As the self-consistency condition can only determine one free parameter, the precise form of the smooth effective interaction is not obvious. Therefore, in this section we also investigate various functional forms for the effective interaction, for which the corresponding wave vector dependence of the free energy is determined. We will see how one of them reproduces the PW vector dependence with good accuracy over the entire range of electron densities. Summary and conclusions are presented in section 8.

Finally in the appendix it is shown that for the Coulomb gas the quantum mechanical virial theorem is fully consistent with the charging principle.

2. Compressibility relation

The compressibility relation is valid for quantized fluids as it is for classical fluids. So, if one considers the free fermion gas, the number of particles is given by equation (I15) as \(T \to 0\)

\[
\rho = \frac{g}{2(2\pi)^3} \int \frac{d^3k}{1 + \zeta^2} \to \frac{g}{2(2\pi)^3} \int_{k < k_f} d^3k = \frac{4\pi g}{3(2\pi)^3} k_f^3. \tag{1}
\]

Here and below the numeral I will be used to designate equations of [1]. In equation (1) the \(g = 2\) is the spin degeneracy of electrons, \(\zeta = e^\mu\) where \(\mu\) is the chemical potential, and \(\beta = 1/(k_BT)\) where \(k_B\) is Boltzmann’s constant and \(T\) is temperature. Further

\[
X = F_\beta(k), \quad F_\lambda(k) = \exp(-\lambda E(k)), \quad \text{and} \quad E(k) = \frac{1}{2m}(\hbar k)^2 \tag{2}
\]

where \(m\) is particle mass and \(k\) is wave vector. For the free fermion gas at \(T = 0\) the \(\mu = \mu_f\) is the Fermi energy given by equation (8) below. By differentiation of equation (1) one finds

\[
\frac{\partial \rho}{\partial (\beta \mu)} = \frac{g}{2(2\pi)^3} \int \frac{d^3k}{1 + \zeta^2} = g\tilde{S}(0,0) = \frac{g}{\beta} \tilde{S}(0,0) \tag{3}
\]

where \(\tilde{S}(\lambda, k)\) and \(\tilde{S}(\lambda, k)\) are given by equations (I11) and (I14).

\[
\tilde{S}(\lambda, k) = \frac{\zeta}{(2\pi)^3} \int \frac{F_k(\lambda')}{(1 + \zeta X)(1 + \zeta Y)} d^{3}k' \tag{4}
\]

where \(\lambda' = k' - k\) and \(\lambda = \mu/\hbar\) (\(t\) is time), \(0 < \lambda < \beta\), and

\[
\tilde{S}(\lambda, k) = \frac{\zeta}{(2\pi)^3} \int \frac{1}{i\lambda' + \Delta} \frac{X - Y}{(1 + \zeta X)(1 + \zeta Y)} d^{3}k' \tag{5}
\]

here with \(X = F_\beta(k), \quad Y = F_\delta(k'), \quad \text{and} \quad \Delta = E(k'') - E(k')\), the plus and minus signs denoting fermions and bosons respectively. The \(S(\lambda, r)\) is the pair correlation function (including self-correlation of a single particle) in space and imaginary time \(\lambda (0 < \lambda < \beta)\). The tilde denotes Fourier transform in space with variable \(k\) while the hat also includes Fourier transform in imaginary time with variable \(K\). The \(K = \pi n/\beta\), with \(n\) integer, are also the same as the well known Matsubara frequencies. With equations (I10)–(I12) one has explicitly [2]

\[
g\tilde{S}(K, k) = \frac{mk_f}{2\pi^2\hbar^2} f(Q, x) \tag{6}
\]

\[
f(Q, x) = -\left[Q^2 - \frac{1}{4Q} \ln \left(\frac{x^2 + (Q + 1)^2}{x^2 + (Q - 1)^2}\right)\right]
\]

\[
-1 + x \arctan \left(\frac{1 + Q}{x}\right) + x \arctan \left(\frac{1 - Q}{x}\right) \tag{7}
\]

with

\[
x = \frac{mK}{\hbar^2 k_f}, \quad \mu_f = \frac{(\hbar k_f)^2}{2m}, \quad Q = \frac{k}{2k_f}. \tag{8}
\]

The \(\beta\) can be removed from equation (3) to obtain for its inverse

\[
\frac{\partial \mu}{\partial \rho} = \frac{1}{g\tilde{S}(0,0)}. \tag{9}
\]

For interacting systems the \(\tilde{S}(K, k)\) is to be replaced by the resulting correlation function \(\tilde{\Gamma}(K, k)\). In our case it has the RPA form (I25)

\[
g\tilde{\Gamma}(K, k) = \frac{g\tilde{S}(K, k)}{1 + \Lambda(K)}, \tag{10}
\]

\[
\Lambda(K) = -g\tilde{S}(K, k)(-\tilde{\psi}(k)) = D f(Q, x) Q^2, \tag{11}
\]

\[
\tilde{\psi}(k) = \frac{e^2}{\varepsilon_0 k_f^2}, \quad 4\pi g a_0, a_0 = \frac{4\pi e_0 h^2}{m e^2}, \tag{12}
\]

as given by equations (I15), (I9), (I13), (I16), and (I17). The \(\tilde{\psi}(k)\) is the Fourier transform of the Coulomb interaction, \(a_0\) is the Bohr radius, \(-e\) is the electron charge, and \(\varepsilon_0\) is the vacuum permittivity.

Note that throughout this work the \(\psi\) will be used as notation for interaction, as is often the case in the theory of fluids. On the other hand, it is also a standard symbol for the wave function of quantum mechanics, but it will not appear as such in this work. The information needed from the wave functions is already contained in the correlation function (4).

Equations (I1)–(I9) above are exact while equations (I10)–(I12) correspond to the RPA. Now with the intention of improving it we further approximate the interaction with an effective one in the RPA. As already mentioned in section 1, the pair interaction plays a role similar to the direct correlation function of classical systems. And with SCOZA and HRT it was found that the precise form of the direct correlation function is not crucial for the equation of state and the resulting correlation function. Simple approximations with a free parameter can predict very accurate results [4–6].

Now the interaction can be replaced by the effective interaction (I27)

\[
\psi_r(r) = \psi(r) f(r), \quad f(r) \to 1 \quad \text{as} \quad r \to \infty \tag{13}
\]

whose Fourier transform can be written as (I26)

\[
\tilde{\psi}_r(k) = \tilde{\psi}(k) L(Q), \quad L(0) = 1. \tag{14}
\]
In the present case with a Coulomb interaction that varies continuously, the \( f(r) \) should vary smoothly to approach 1 as \( r \to \infty \). Furthermore we will assume \( f(r) \to 0 \) as \( r \to 0 \) to make \( \psi_e(0) \) finite. Anyway, the \( f(r) \) will define a cutoff of the Coulomb interaction for small \( r \). But to make the cut useful it should be possible to determine its magnitude and its dependence with a free parameter. The explicit value of the latter will be determined resorting to thermodynamic self-consistency.

With effective interaction (14), equation (11) is replaced by

\[
\hat{A}(K) = \hat{A}_e(K) = -g\hat{S}(K,k)(-\tilde{\psi}_e(k)),
\]

and relation (9) with \( \hat{S} \) replaced by \( \hat{I} \) turns into

\[
\frac{\partial \mu}{\partial \rho} = \frac{1}{g\hat{I}(0,0)} = \frac{1}{gS(0,0)} + \tilde{\psi}_e(0).
\]

Now the \( \tilde{\psi}_e(k) \) like the \( \tilde{\psi}(k) \) diverges when the \( k \to 0 \). However, the electron gas is neutralized by a neutralizing background that cancels the mean field term \( \tilde{\psi}(0) \) (small charges \( 0 \to 0 \) of high density \( \to \infty \)). Furthermore the small \( Q \) behavior of \( L(Q) \) is needed to compensate the divergence of \( \tilde{\psi}(0) \) to obtain a finite contribution to the compressibility. So we expand

\[
L(Q) = 1 - \frac{Q^2}{\kappa^2} + \cdots
\]

where \( \kappa \) is a coefficient to be determined. Thus with pressure \( p \) we end up with the compressibility relation (\( Q \to 0 \))

\[
\frac{1}{\rho} \frac{\partial p}{\partial \rho} = \frac{1}{\rho} \frac{\partial \mu}{\partial \rho} = \frac{1}{gS(0,0)} + \left( \psi_e(Q) - \tilde{\psi}(Q) \right) = \frac{1}{gS(0,0)} + \left( L(Q) - 1 \right) \tilde{\psi}(Q) = \frac{2\pi^2h^2}{mkf(0,0)} - \frac{e^2}{\kappa^2 \epsilon_0(2\kappa_f)^2}
\]

with \( f(Q,x) \) and \( \tilde{\psi}(k) \) given by equations (7) and (12) respectively. From this the \( \kappa \) is the parameter that can be determined via compressibility in a self-consistent way.

3. Compressibility with exchange energy

The chemical potential of the free electron gas is the well known (\( T = 0 \))

\[
\mu_0 = \mu_f \sim k_f^2 \sim \rho^{2/3}
\]

with \( \rho \) given by (1). Helmholtz free energy per unit volume is then

\[
F_0 = \frac{3}{2} \rho \mu_f \sim \rho^{5/3}
\]

since \( \mu_0 = \partial F_0/\partial \rho \). This gives the inverse compressibility (divided by \( \rho \))

\[
\frac{\partial \mu_0}{\partial \rho} = \frac{\partial^2 F_0}{\partial \rho^2} = \frac{2\mu_f}{3\rho} = \frac{\pi^2h^2}{mk_f}.
\]

This is precisely the first term of relation (18) as should be expected noting that from expression (7) the \( f(0,0) = 2 \).

The exchange energy per unit volume \( F_{ex} \) is given by equations (9.5) and (9.9) of [11] as

\[
F_{ex} = \frac{g}{2(2\pi)^3} \int S(0,k)\tilde{\psi}(k)\,dk = -\frac{3\pi^2e^2k_f}{2(2\pi)^3}\epsilon_0 \rho^{4/3}.
\]

The contribution to the inverse compressibility thus becomes

\[
\frac{\partial^2 F_{ex}}{\partial \rho^2} = \frac{1}{3} \cdot \frac{4}{3} \cdot \frac{F_{ex}}{\rho^2} = -\frac{e^2}{\epsilon_0(2k_f)^2}.
\]

When comparing with the last term of equation (18) one finds that the exchange energy alone means that \( \kappa = 1 \) for all densities. Thus \( \kappa = 1 \) is the high density value while for finite densities there will be higher order corrections to this value. Altogether we will find that \( \kappa \) has small variations consistent with the numerical results obtained in [1].

4. Correlation energy and its relation to compressibility

As mentioned earlier, we here want to use thermodynamic self-consistency to obtain more accurate results. For general use it is then preferable to express the correlation free energy per electron as (\( T = 0 \))

\[
f_c = \mu_f G(r_f).
\]

Inserting numerical values of physical constants and using equations (1), (12), and (19) one finds equation (120) for the Fermi energy

\[
\mu_f = \frac{50.1 \text{ eV}}{r_f^2}.
\]

Now we note that if the Coulomb interaction is scaled with a parameter \( \lambda (0 \leq \lambda \leq 1) \), i.e. \( \epsilon^2 \to \lambda \epsilon^2 \); the function \( G(r_f) \) will scale to become \( \tilde{G}(z) \) with \( z = \lambda r_f \) while expression (25) for \( \mu_f \) is unchanged. This use of a parameter \( \lambda \) is the charging principle which we will utilize [2]. (Note, here the parameter \( \lambda \) is not the imaginary time of equations (2) and (4).) The scaling property, consistent with one free parameter for the electron gas, can be seen by considering the Schrödinger equation for a particle in the Coulomb potential or its extension to more particles with Coulomb interactions.

With correlation energy per unit volume, \( F_c = \rho f_c \), and using expressions (24) and (25) we now find for the corresponding contributions to the chemical potential and inverse compressibility (\( r_s \sim 1/\rho^{1/3} \))

\[
\mu_c = \frac{\partial F_c}{\partial \rho} = \frac{\mu_f}{3}(5G - zG')
\]

\[
\frac{\partial^2 F_c}{\partial \rho^2} = \frac{\mu_f}{3}\left(10G - 6zG' + z^2G''\right)
\]

where \( G = G(z) \) and \( G' \) and \( G'' \) are its derivatives with respect to \( z = \lambda r_f \). Here the charging parameter \( \lambda \) (not present in \( \mu_f \)) has been included.

Expression (27) can be directly related to expression (18) in order to determine the parameter \( \kappa \). With use of equations (1), (8), (12) and (21) expression (18) can be rewritten in the convenient form (\( f(0,0) = 2 \))
\[ \frac{\partial^2 F}{\partial \rho^2} - \frac{\partial F}{\partial \rho} = -\frac{\mu_f}{\rho} \left( \frac{2}{3} - \frac{1}{\kappa^2} \frac{4Dz}{3r_s} \right) \]  

(28)

where the parameter \( \lambda \) is also included with \( z = \lambda r_s \). Here \( F \) is the total free energy per unit volume. As already concluded, the exchange energy alone results in \( \kappa = 1 \). Thus for the correlation energy one is left with

\[ \frac{\partial^2 F_c}{\partial \rho^2} = -\frac{\mu_f}{\rho} H(z), \quad H(z) = \frac{4}{3} \left( \frac{1}{\kappa^2} - 1 \right) \frac{Dz}{r_s}. \]  

(29)

So we find

\[ \frac{1}{\kappa^2} = 1 + \frac{3r_s H(z)}{4D} \quad \left( \frac{D}{r_s} = 0.082293 \right) \]  

(30)

where with equations (27) and (29)

\[ H(z) = -\frac{1}{9} \left( 10G - 6zG' + z^2G'' \right). \]  

(31)

5. Charging principle

In [1] we used the RPA type free energy with effective interaction. It was inspired by the mean spherical approximation (MSA) free energy for classical hard spheres with perturbing interaction outside the hard core. In [2] its equation (23), the adiabatic approximation, is used along with the compressibility only given by its equation (31), so as to obtain the ALDA. But there the use of the compressibility only adds a constant to the Fourier transform of the interaction \( \hat{\psi}(k) \) leading to an effective interaction, \( \hat{\psi}_e(k) \), with \( L(Q) = 1 - \hat{Q}^2/\kappa^2 \), the leading terms of equation (17). This means that the added piece is merely a \( \delta \)-function in \( r \)-space. Compared with results for classical fluids and the ‘classical polymer problem’ formed by the quantized electron gas, this is clearly inaccurate. As argued in [1], the Coulomb interaction should be cut by a smooth function in order to obtain the effective one, where we will assume \( L(Q) \to 0 \) as \( Q \to \infty \).

Based on the exact free energy the ALDA curve for \( r_s = 4 \) is obtained in figure 2 of [2]. (This figure gives the \( Q \)-dependent contributions \( \varepsilon_r(Q) \) to the correlation energy according to expressions (32) and (61) below.) There accurate results are obtained for \( Q < 0.7 \), but they become rather inaccurate for larger values of \( Q \). Clearly this is related to the inadequate large \( Q \)-behavior of \( L(Q) \). We can now impose thermodynamic self-consistency using a smooth cut-off function with a free parameter to be determined. In this way the equation of state is required to be the same both via the free energy from the charging principle [2] and the compressibility.

The adiabatic charging principle, equation (23) of [2], gives the change to the Helmholtz free energy by a small change in the perturbing potential. We first consider the RPA with correlation energy (I18) and (I19) modified by the charging parameter \( \lambda \) where

\[ f_c = \frac{\Delta F_c}{\rho} = 12 \int_0^\infty f_c(k)Q^2 dQ \]  

(32)

\[ f_c(k) = \frac{1}{\pi \mu_f Q} \int \ln(1 + \lambda \hat{A}(K)) - \lambda \hat{A}(K) \]  

dx

(33)

with \( \hat{A}(K) \) given by equation (11). From this we find

\[ u_c(k) = \lambda \frac{\partial f_c(k)}{\partial \lambda} = \frac{1}{\pi \mu_f} \int \left[ \lambda \frac{\hat{A}(K)}{1 + \lambda \hat{A}(K)} - \lambda \hat{A}(K) \right] \]  

dx.

(34)

In terms of the correlation function this can be written as

\[ u_c(k) = \frac{1}{\pi \mu_f} \int g(\hat{\Gamma}(K,k) - \hat{S}(K,k))|\lambda \psi(k)| \]  

dx.

(35)

Now this equation is not tied to the RPA, but is valid more generally. So the problem left is to have a best possible approximation to the resulting correlation function. Then again we keep the MSA form (I38) (with \( \hat{\Gamma} \to \hat{\gamma}, \hat{A}_+ \to \hat{A}_r \)) or equation (10) with \( \hat{A} \to \lambda \hat{A}_r \).

From the results of [1] it was found that exact results were well approximated with \( \kappa \) constant. With such an approximation expression (35) is easily integrated to obtain

\[ \hat{\Gamma}(K,k) = \frac{\hat{S}(K,k)}{1 + \lambda \hat{A}_r(K)} \]  

(36)

\[ \hat{A}_r(K) = \hat{A}(K) L(Q) \]  

(37)

with \( \hat{A}(K) \) given by equation (11). It can be noted that with expression (35) only the \( \hat{\Gamma}_+ \to \hat{\gamma} \) part contributes since \( \hat{\psi}(k) \) at the end of equation (35) is the un-cut interaction. In [1] a \( \hat{\Gamma}_- \) part was also present, but now it will not contribute in (35) as the corresponding un-cut interaction is zero, given that pairs of equal and unequal spins have the same Coulomb interaction.

From the results of [1] it was found that exact results were well approximated with \( \kappa \) constant. With such an approximation expression (35) is easily integrated to obtain

\[ f_c(k) = \frac{\mu_f Q}{\pi L(Q)} \int \ln(1 + \lambda \hat{A}_r(K)) - \lambda \hat{A}_r(K) \]  

dx.

(38)

Our numerical evaluations confirmed that the free energy from the charging principle is well approximated by expression (38). However, here we want to use the exact expression along with thermodynamic self-consistency.

Integral (35) computes the change in free energy due to a change in the interaction. This change is forced to be consistent with compressibility. This gives rise to a non-linear partial differential equation. In the present case, however, the situation simplifies much due to the scaling form (24) by which derivatives with respect to \( \lambda \) and \( \rho \) are essentially the same as they join in the scaling variable \( z = \lambda r_s \). The detailed differential equation of thermodynamic self-consistency is then obtained by equating the \( \partial^2 (\lambda \partial F_c/\partial \lambda) / \partial \rho^2 \) that follows from equations (32)–(35) with the \( \lambda \partial (\partial^2 F_c / \partial \rho^2) / \partial \lambda \) that follows from (29).

6. Thermodynamic self-consistency

To have exact thermodynamic self-consistency with the charging principle we need \( (z = \lambda r_s) \)

\[ U_c = \lambda \frac{\partial}{\partial \lambda} F_c = \frac{\partial}{\partial z} F_c. \]  

(39)
With scaling on \( F_c \) that follows from equation (24) one finds

\[
U_c = \rho \mu g(z) \quad \text{with} \quad g = g(z) = zG'.
\]

(40)

The \( U_c \) is obtained from the \( u_c(k) \) which follows from equations (35)–(37)

\[
u_c(k) = \frac{\mu Q}{\pi L(Q)} \int \left[ \frac{\lambda \tilde{A}_c(K)}{1 + \lambda \tilde{A}_c(K)} - \lambda \tilde{A}_c(K) \right] \, dx,
\]

(41)

and like equation (32)

\[
U_c = 12 \rho \int_0^\infty u_c(k)Q^2 \, dQ.
\]

(42)

So with equation (40)

\[
g(z) = 12 \int_0^\infty \frac{u_c(k)}{\mu} Q^2 \, dQ.
\]

(43)

With exact self-consistency and equations (29) and (39) one now has

\[
\lambda \frac{\partial}{\partial \lambda} \left( \frac{\partial^2 F_c}{\partial \rho^2} \right) = \frac{\partial^2}{\partial \rho^2} \left( \lambda \frac{\partial F_c}{\partial \lambda} \right)
\]

(44)

\[
\lambda \frac{\partial}{\partial \lambda} \left( - \frac{\mu}{\rho} H(z) \right) = \frac{\partial^2}{\partial \rho^2} U_c.
\]

(45)

With scaling form (40) on \( U_c \) one finds similar to expression (31)

\[
\frac{\partial^2}{\partial \rho^2} U_c = \frac{\mu}{9 \rho} \left( 10g - 6zg' + z^2 g'' \right).
\]

(46)

So with \( \lambda(\partial/\partial \lambda) = z(\partial/\partial z) \) equation (45) for self-consistency becomes

\[
zH'(z) = - \frac{1}{g} \left( 10g - 6zg' + z^2 g'' \right)
\]

(47)

where \( H(z) \) as a function of \( \kappa = \kappa(z) \) is given by (29) while \( g \) is given by (43). Equation (47) is thus the resulting differential equation for \( \kappa \). Basically it is a partial differential equation in the variables \( \lambda \) and \( \rho \). However, due to their replacement by the scaling variable \( z = \lambda \rho \) it simplifies to an ordinary non-linear differential equation in \( z \). Further as an additional simplification equation (47) can be integrated to recover equation (31) which with \( G' \) and \( G'' \) replaced by \( g \) and \( g' \) becomes

\[
H(z) = - \frac{1}{g} \left( 10g - 7g + zg' \right)
\]

(48)

where \( G \) is determined by

\[
G = G(z) = \int_0^z \frac{g(u)}{u} \, du.
\]

(49)

As pointed to earlier the \( \kappa = \kappa(z) \) varies little. Thus equation (48) can be solved in a straightforward way by simple iteration. As initial value one can start with the high density \((z \to 0)\) value \( \kappa = 1 \) for all \( \rho \) of interest (\( z \lesssim 10 \) in our case).

This is used to compute the \( g(z) \) and thus the right hand side of equation (48). With \( H(z) \) as given by (29) on the left hand side, iterated values for \( \kappa(z) \) are obtained. Then the iteration procedure can be repeated to obtain a very rapidly converging result. This is seen in figure 1.

7. Results

Along the same lines of [1], here we utilize a series of cutoff functions \( f(r) \) (see equation (13)). They are a \( \delta \)-function to be subtracted from the Coulomb interaction and the

\[
1 - e^{-x}, \quad 1 - (1 + x/\sqrt{2})e^{-\sqrt{2}x}, \quad \text{erf}(x/2),
\]

(50)

and \( 1 - (1 + x^2)e^{-x^2} \).
The last equality follows as both expressions solve the differential equation \( y' + 2xy = 1 \). Note these expressions are normalized such that the small \( Q \) expansion (17) is fulfilled.

It is worth mentioning that all these functions in \( r \)-space share the proper \( r \to \infty \) behavior (i.e. \( f(r) \to 1 \)), and vanish as \( r \to 0 \) so that they are well behaved for large \( Q \). Additionally, both \( L_{\text{exp}} \) and \( L_{\text{gauss}} \) fulfill \( f'(r) \to 0 \) as \( r \to 0 \), which gives a functional shape reminiscent of the equal spin pair distribution function.

In the high density limit, \( k_f \to \infty \) or \( r_s \to 0 \), the exact correlation energy is known to have the form

\[
f_c \sim \ln r_s + \text{const.}
\]

Inserted in equations (24) and (25) this means

\[ G(x) = ax^2 \ln x + b \quad (57) \]

where \( a \) and \( b \) are constants. Here \( x = \lambda r_s \) (with \( \lambda = 1 \)). For \( r_s \to 0 \) one finds a good fit to the PW parameterization with \( a = 0.01675 \), and \( b = -1.564 \). This is near the exact limiting result \([13]\) \((f_c = -13.6 \text{ eV} \cdot 0.0622 \cdot \ln(a_k f_k) + \text{const.} = -0.846 \text{ eV} \cdot \ln(a_k f_k) + \text{const.})\), which gives \( a = 0.0169 \).

Also, using expression (57) the small \( z \) behavior of the coefficient \( \kappa \) of the cut function (17) is easily obtained. Thus by differentiation and insertion into equations (30) and (31) with \( a = 0.01675 \) one finds

\[
\frac{1}{\kappa^2} = 1 + 3r_c a + 3.04 a z + \ldots = 1 + 0.051 z + O(z^2),
\]

\[ \kappa = 1 - 0.025z + O(z^2). \quad (59) \]

The calculation of \( \kappa \) is done by iterations of equation (30) together with equation (48). In figure 1 the calculation for the Gaussian cut (55) is shown. As can be seen the iterations converge rapidly to end up close to the PW parameterization [9]. To do so the thermodynamic self-consistency for \( \kappa = \kappa(z) \) is solved as described at the end of section 5. Then via equations (41) and (43) one finds the \( G(z) \) from integral (49).

Further with the cutoffs (51)–(55) the resulting free energies are found and compared with the PW parameterization [9] in figure 2. Then the \( G(z) \) is inserted in equation (24) to give the free energy. However, for the ALDA cutoff (51) the initial iterations to obtain \( \kappa \) did not converge, so the \( \kappa \) obtained for the Gaussian cut (55), was used instead for this case.

As found in [1], the Gaussian cut (55) performs substantially better than other cuts, clearly outperforming both the RPA (not shown on the figure) and the ALDA approximation. It gives results very close to the PW parameterization.

Finally, in figure 3 we plot the wave vector decomposition of the correlation energy for various values of \( r_s \) and compare it with those of the PW parameterization. Then we need the \( f_c(k) \) of equation (32). Its relation to the \( u_c(k) \) of (41) must be like relation (49) between \( G(z) \) and \( g(z) \). Thus (\( z = \lambda r_s \), integration variable \( z \to u \))

\[ f_c(k) = \int^\infty_0 u_c(k, u) \, du. \quad (60) \]

From this we, as it is customary, plot the function,
\( \varepsilon_c(Q) = 12Q^2f_c(k) \). \hspace{1cm} (61)

We have just plotted the results from the Gaussian cut, equation (55). Only small deviations from the PW parameterization are found. Since the free energies are almost the same as those of the PW parameterization in figure 2, the plus and minus deviations for large and small \( Q \)-values appear to compensate each other.

### 8. Summary and conclusions

We have evaluated the correlation energy for the uniform quantized fermion gas of electrons. This is an extension of a recent work of ours [1]. In the previous work we focused upon the core condition that implies that fermions with equal spins cannot be at the same position. However, within quantum mechanics, particles with opposite spins have the possibility to be at the same position also with Coulomb repulsion. Thus the average core condition became somewhat undetermined. The basis for the computations in our previous work was the RPA, but with a smooth cut of the Coulomb interaction for small distances. For the free energy an expression inspired by the MSA of classical fluids was used. Compared with the PW parameterization, good results were obtained for certain cut effective interactions while others led to divergence problems.

Inspired by the ALDA of [2] we in this work have focused upon the compressibility relation and thermodynamic self-consistency as used in the SCOZA and HRT for classical fluids [3–6]. This determines a parameter \( \kappa \) in the effective interaction. In addition we impose that the effective or cut interaction must behave as a smooth function. The range of the cut is the inverse of \( \kappa \) (with dimensionless units). With reasonable functional forms for the cut effective interaction a large improvement for the approximated correlation energies is observed. In particular, the Gaussian cut (55) leads to very accurate results.

Finally, as a more sensitive test of our theory and method used to obtain the electron gas free energy we have performed its wave vector decomposition for the Gaussian cut in figure 3. Also for this more detailed analysis we find very good agreement with exact results which reflects the proper form of the effective interaction used. This again means that the resulting correlation function (36) for the quantized electron gas must be close to the exact one too.

For the uniform electron gas ‘exact’ results like the PW parameterization are available, and in this way, the quality of approximations such as ours can be assessed. On the other hand, our results may in some way be extended to the non-uniform electron gas of molecules or electrons on crystal lattices. The basis for the correlation energy will still be the RPA extended to this more general situation where translational symmetry is, however, lost. The reference system correlation function is now to be determined by the eigenstates, including the excited ones, that follow from the density functional theory or Hartree–Fock solution of the problem considered, from which the standard RPA can be established.

Interestingly, even if classical fluid theory methods are usually developed for uniform systems, their extension to the non-uniform case has been well established over the years. In fact, some formalisms, such as graph expansions of classical statistical mechanics will in principle remain unchanged. In this respect the RPA will still represent a valid approach. Again, to improve upon the RPA one will need an effective potential that modifies the given Coulomb interaction, at short distances. We expect this modification to be similar to the one for the uniform electron gas studied here. A crucial result of our work that may be extended in this direction, is that the cut function \( L(Q) \)—and hence the \( f(r) \)—is a smooth one that has small or negligible variation with changing electron density, i.e. \( \kappa \) varies little. On the other hand, complications will appear as density dependence sits in the shift of variable \( k = 2k_fQ \) \((k_f \sim \rho^{1/3})\). Furthermore in
the non-uniform case one needs the effective interaction in \( r \) space, \( \psi(r) = \psi(r)f(r)\psi(r) \sim 1/r \). So with cuts (52)–(55) one has \( f(r) = F(x) \) with \( x = 2k FR \) where \( F(x) \) is the corresponding function of those given by equation (50). Since \( r = r_2 - r_1 \) the \( k_j \sim \rho^{1/3} \) to choose to determine \( x \) will not be obvious. A compromise can be to use some average density for positions 1 and 2, or some weighted average in the spirit of the classical DFT for inhomogenous systems [14]. In any case, further investigations will need numerical calculations on non-uniform quantum systems with basis on the RPA, which exceeds the scope of this paper.

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Appendix. Virial theorem

Quantized systems also fulfill the virial theorem. For the quantized electron gas we will show that it is fully consistent with the adiabatic approximation. On the other hand this consistency means that there will be no extra condition to determine some extra parameter. The virial theorem is

\[
p = \frac{2}{3} \rho u_{k} - \frac{1}{6} \int \text{d}r \text{r} \nabla \psi(r) n(r) \quad (A.1)
\]

where \( p \) is pressure, \( u_{k} \) is kinetic energy per particle, and \( n(r) \) is the pair distribution function. This theorem is also valid for quantized systems. (For hard core particles one has to take the proper limit of the integral. This limit is different in the classical and quantum cases.) For an ionic fluid that is neutralized by an oppositely charged background the \( n(r) \) is replaced by \( \rho^2 h(r) \) where \( h(r) \) is the pair correlation function.

With Coulomb interaction \( \psi \sim 1/r \) by which

\[
\text{r} \nabla \psi(r) = r \frac{\partial}{\partial r} \psi(r) = -\psi(r). \quad (A.2)
\]

The integral in equation (A.1) can also be written as a Fourier integral. Then \( \text{r} \nabla \psi(r) \rightarrow -\nabla(\text{k} \psi(k)) \). So with \( \psi(k) \sim 1/k^2 \)

\[
\nabla(\text{k} \psi(k)) = \frac{\partial}{\partial k_i} (k_i \psi(k)) = -\psi(k) \quad (A.3)
\]

which is equivalent to equation (A.2) \( (k_i k_i = k^2, \sum, i = 1, 2, 3) \). So with Fourier transform and use of equation (A.3) for Coulomb interaction the virial theorem becomes

\[
p = \frac{2}{3} \rho u_{k} + \frac{1}{3} \rho u_{p}, \quad (A.4)
\]

\[
\rho u_{p} = \frac{1}{2(2\pi)^3} \int \text{d}k \rho^2 h(k) \psi(k) \quad (A.5)
\]

where \( u_{p} \) is the potential energy per particle for the neutral ionic fluid. Now the total energy per particle is the same as the internal energy \( u = u_{k} + u_{p} \). With this \( u_{k} = u - u_{p} \) by which

\[
p = \frac{2}{3} \rho u - \frac{1}{3} \rho u_{p}. \quad (A.6)
\]

At \( T = 0 \) the free energy per particle \( f \) is the same as the internal energy \( u \) since entropy is zero (or finite) for quantized systems in their ground states. For the quantized reference system the correlation function is (equal time correlations \( \lambda = 0 \))

\[
\rho^2 \tilde{h}_{ex}(k) = gS(0, k) - \rho. \quad (A.7)
\]

This leads to the exchange energy while the remaining part of the correlation function is the one that leads to the correlation energy

\[
\rho^2 \tilde{h}_{c}(k) = g\tilde{S}(0, k) - gS(0, k). \quad (A.8)
\]

With equations (34) and (35) for \( u_{c}(k) \) which along with equation (A.5) leads to \( u_{p} = \lambda(\partial f/\partial \lambda) \), one altogether finds

\[
p = \frac{2}{3} \rho f - \frac{1}{3} \rho \lambda \frac{\partial f}{\partial \lambda}. \quad (A.9)
\]

To see this more clearly the free energy can be split in three contributions

\[
f = f_0 + f_{ex} + f_{c} \quad (A.10)
\]

where for the reference system contribution, \( \partial f_0/\partial \lambda = 0 \). For the exchange and correlation energies one with equations (A.7) and (A.8) has

\[
\rho \lambda \frac{\partial f_{ex}}{\partial \lambda} = \frac{1}{2(2\pi)^3} \int \text{d}k (gS(0, k) - \rho) \lambda \tilde{\psi}(k) \quad (A.11)
\]

\[
\rho \lambda \frac{\partial f_{c}}{\partial \lambda} = \frac{1}{2(2\pi)^3} \frac{1}{2\pi} \int \text{d}K \int \text{d}k g(\tilde{\Gamma}(K, k) - \tilde{S}(K, k)) \lambda \tilde{\psi}(k) \quad (A.12)
\]

\((equation (A.12) with variables of integration \( K \) and \( k \) is the same as equations (32)–(36).) What remains is to show that the pressure (A.9) also follows from the standard free energy route by differentiation with respect to density. One has the thermodynamic relation

\[
p = \rho^2 \frac{\partial f}{\partial \rho}. \quad (A.13)
\]

To show this we utilize the scaling form equations (24) and (25) for \( f_{c} \) which also is valid for the whole free energy at \( T = 0 \). With \( \mu_{f} \sim 1/r^2 \sim \rho^{1/3} \) and \( r_{s} \rightarrow \lambda r_{s} \sim \lambda/\rho^{1/3} \) we can write

\[
f = \rho^{2/3} F(x), \quad x = \frac{\lambda}{\rho^{1/3}}. \quad (A.14)
\]

Thus

\[
\rho \frac{\partial f}{\partial \rho} = \frac{2}{3} \rho^{2/3} F(x) + \rho^{2/3} F'(x) \left( -\frac{1}{3} \right) = \frac{2}{3} \rho - \frac{1}{3} \frac{\partial f}{\partial \lambda} \quad (A.15)
\]

which inserted in equation (A.13) is the same as expression (A.9). Thus result (A.9) from the virial theorem is same as the one from the free energy route.
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