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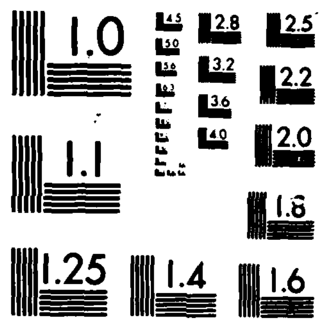

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Density functional theory for excited states in a quasi local density approximation

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Density functional theory has been an important method for studying the ground states for systems involving interacting electrons such as atoms, molecules, and solids. This paper helps to extend this theory to excited states.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) expressions for these quantities, valid for systems of slowly varying density. Even for such systems, however, there are essential non-local effects. Nevertheless both E_{xc}^{M} and v_{xc}^{M} can be calculated in terms of quantities characteristic of appropriate uniform thermal ensembles. This theory is the analog of the ground state local density approximation and allows calculation of excited state energies and densities.

Density Functional Theory for Excited States in a Quasi Local Density Approximation

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ABSTRACT

The starting point of this paper is a recent extension by A.K. Theophilou of the Hohenberg-Kohn-Sham (HKS) density functional theory to ensembles of systems consisting of the M lowest eigenstates, equally weighted. As in the HKS theory the key quantities are the exchange correlation energy, $E_{xc}^{M}[n(r)]$, and potential, $v_{xc}^{M}(r;[n(r')])$. The present paper provides expressions for these quantities, valid for systems of slowly varying density. Even for such systems, however, there are essential non-local effects. Nevertheless both E_{xc}^{M} and v_{xc}^{M} can be calculated in terms of quantities characteristic of appropriate uniform thermal ensembles. This theory is the analog of the ground state local density approximation and allows calculation of excited state energies and densities.

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In its original formulation[1,2] general density functional theory was a ground state theory for non-relativistic interacting electrons in an external potential, $v(r)$. An extension to ensembles at a finite temperature, θ, was soon developed[3,2]. More recently the formal theory was extended to "equi-ensembles" consisting of the lowest M states, equally weighted[4]. Both many-body ensembles are characterized by appropriate exchange correlation functionals, $F_{xc}^{\theta}[n(r)], E_{xc}^{M}[n(r)]$. In terms of these the exchange-correlation potential of the Kohn-Sham (KS) equations can be determined,

$$v_{xc}^{\theta,M}(r) = \begin{cases} \delta F_{xc}^{\theta}[n(r')]/\delta n(r)|_{\theta} & \text{thermal ensemble} \quad (1a) \\ \delta E_{xc}^{M}[n(r')]/\delta n(r)|_{M} & \text{equi-ensemble} \quad (1b) \end{cases}$$

and the ensemble average densities, $n(r)$, free energies, Φ^{θ}, and average energies, E^{M}, respectively, can be calculated.

The local density approximation (LDA) of F_{xc}^{θ} has been previously discussed[5]. In the present note we develop a quasi-local approximation for E_{xc}^{M}, closely related to the LDA for thermal ensembles.

As shown by Theophilou[4], the average density $n(r)$ of the lowest M excited states[6] uniquely determines the external potential $v(r)$ and hence, implicitly, by means of the Schroedinger equation, all eigenstates ψ_m. For every $n(r)$ and M one can then define the functional

$$F^{M}[n(r)] \equiv Av(\psi_m,(T+U)\psi_m) \ , \tag{2}$$

where the symbol Av has the meaning

$$Av\{O_{mm}\} \equiv M^{-1}\ Tr\ O_{mn} = M^{-1}\sum_{1}^{M} O_{mm} \ ; \tag{3}$$

T and U are the kinetic and interaction energy operators; and the ψ_m ($m = 1,\ldots M$) are the M lowest eigenstates corresponding to the potential v(r) which reproduces the average density n(r)[7],

$$n(r) \equiv \mathrm{Av}\, n_m(r) \ . \tag{4}$$

Using the functional F^M one can define the energy functional

$$E^M_{v(r)}[n'(r)] \equiv \int v(r)n'(r)dr + F^M[n'(r)] \ , \tag{5}$$

whose unique minimum is attained when n'(r) is the correct n(r) and has the value $E^M \equiv \mathrm{Av}\, E_m$.

This minimization can be carried out by solving appropriate Kohn-Sham (KS) equations[4]. We first define

$$T^M_s[n(r)] \equiv \mathrm{Av}\, T_{s,m}[n(r)] \ , \tag{6}$$

where T^M_s is the kinetic energy of an equi-ensemble of <u>non-interacting</u> electrons in the appropriate external potential $v_s(r)$ yielding the given average density n(r)[8]; i.e.,

$$T^M_s[n(r)] = \mathrm{Av}(E_{s,m}) - \int v_s(r)\, n(r)dr \tag{7}$$

where $E_{s,m}$ represents total single particle energy. Now we can define the exchange-correlation energy functional as

$$E^M_{xc}[n(r)] \equiv F^M[n(r)] - \{T^M_s[n(r)] + \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}\, dr\, dr'\} \tag{8}$$

and the effective potential by

$$v^M_{eff}(r) \equiv v(r) + \int \frac{n(r')}{|r-r'|} dr' + v^M_{xc}(r) , \tag{9}$$

where $v^M_{xc}(r)$ is given by (1b). The appropriate KS equations are

$$\{- \frac{1}{2} \nabla^2 + v^M_{eff}(r) - \varepsilon_i\} \phi^M_i(r) = 0 . \tag{10}$$

The density of the m'th KS eigenstate is

$$n_m(r) = \sum_i f^m_i |\phi^M_i(r)|^2 , \tag{11}$$

where f^m_i (= 1 or 0) describes the occupation of the i^{th} single particle state in the m'th N-particle state. The average density n(r) is then given by Eq. (4). For example, if there is no degeneracy and M = 2,

$$n(r) = \sum_1^{N-1} |\phi^2_i(r)|^2 + \frac{1}{2}\{|\phi^2_N(r)|^2 + |\phi^2_{N+1}(r)|^2\} . \tag{12}$$

Eqs. (10) and (4) must be solved self-consistently for n(r) and $v^M_{eff}(r)$, using Eqs. (11), (9) and (1b). Here it is assumed that the dependence of E^M_{xc}, occurring in Eq. (1b), on the density n(r) is known.

It remains to find approximations for E^M_{xc} and v^M_{xc}, in the spirit of the LDA, i.e., valid for systems of slowly varying density.

THERMODYNAMIC CONSIDERATIONS

For M = 1, a non-degenerate ground state, a very simple and useful approximation for E^1_{xc} has been the so-called local density approximation (LDA)

$$E^1_{xc}[n(r)] = \int e_{xc}(n(r))dr, \tag{13}$$

where $e_{xc}(n)$ is the exchange correlation energy per unit volume of a uniform electron gas of density n. This approximation is strictly valid only when n(r) is a slowly varying function of r. However, in practice, it was found to yield good results even when this condition was not satisfied. We shall now generalize this approximation for an equi-ensemble with arbitrary $M \geq 1$.

In the spirit of the LDA, we shall consider systems of slowly varying density n(r). Such systems necessarily occupy a large volume and (unless $n(r) \to 0$) contain a large number, N, of particles. We consider both the ground state of such a system (M = 1) and equi-ensembles of the M lowest eigenstates. Formally we may consider families of density distributions

$$n(r;a) \equiv f(r/a) \qquad a = a_1, a_2, \ldots, \tag{14}$$

where f is a given function and a is a length scale parameter which becomes sufficiently large. We denote the average excitation energy of the equi-ensemble by

$$\Delta E^M \equiv Av(E_m) - E^1 \ . \tag{15}$$

As $a \to \infty$, the spacing between excited states approaches zero. If, as $a \to \infty$, the degree of excitation as measured by $\Delta E^M/E^1$, remains fixed, then clearly $M \to \infty$.

In such a limit the systems can be described by the principles of thermodynamics. Accordingly the differences between a canonical, and equi-ensemble[9] with the same n(r) and same mean energy become negligible. We can write

$$M = e^{S/k} , \tag{16}$$

where S is the entropy. We denote by θ the temperature of the canonical ensemble equivalent to the equi-ensemble with M states, both with the same density n(r).

We now study the relationships between these two ensembles and their corresponding non-interacting KS ensembles. With the aid of the two appropriate exchange-correlation potentials, v_{xc}^{M} and v_{xc}^{θ}, Eqs. (1a), (1b), we construct the two effective potentials v_{eff}^{M}, Eq. (9), and similarly v_{eff}^{θ}. Next, using these effective potentitals, we solve the appropriate KS equations for ϕ_i^{θ}, ϵ_i^{θ} and ϕ_i^{M}, ϵ_i^{M} , respectively, and form the two non-interacting ensembles corresponding to (M or S, n(r)) and (θ,n(r)) respectively. <u>These two KS ensembles are not identical, even in the thermodynamic limit</u>. The situation is presented in Tableau 1. By construction, the temperatures of the canonical real ensemble and corresponding KS ensemble are equal, θ. Similarly the entropies of the equi-ensemble and corresponding KS ensemble are equal, S. However, the relations between entropy and temperature are different for interacting and non-interacting ensembles of the same density, n(r). This is exemplified by uniform ensembles for which we have

$$S(\theta) \equiv \int_0^{\theta} \frac{C(\theta')}{\theta'} d\theta' \qquad \text{(interacting)} \tag{17}$$

and

$$S_s(\theta) \equiv \int_0^{\theta} \frac{C_s(\theta')}{\theta'} d\theta' \qquad \text{(non-interacting)} \tag{18}$$

with unequal heat capacities C and C_s. In general, referring to the tableau, S and θ are related by

$$S = S(\theta;[n(r)]) , \tag{19}$$

where $S(\theta)$ describes the interacting ensemble. Similarly S_s and θ_s are given by

$$S_s = S_s(\theta;[n(r)]) \tag{20}$$

and

$$S = S_s(\theta_s;[n(r)]) \tag{21}$$

where the function $S_s(\theta')$ refers to the non-interacting ensemble.

Using these relations and Eq. (8), we can write

$$E_{xc}^{M}[n(r)] = \langle T+U\rangle^{\theta}_{n(r)}, - T_s^{\theta_s}[n(r)] - \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}\, dr\, dr' , \tag{22}$$

where θ is given in terms of M by Eq. (19) (with $S = k \log M$), while θ_s is given in terms of M by Eq. (21). Equivalently we can write

$$E_{xc}^{M}[n(r)] = E_{xc}^{\theta}[n(r)] + T_s^{\theta}[n(r)] - T_s^{\theta_s}[n(r)] , \tag{23}$$

where the thermal exchange correlation energy is given by

$$E_{xc}^{\theta}[n(r)] \equiv \langle T+U\rangle^{\theta}_{n(r)}, - T_s^{\theta}[n(r)] - \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}\, dr\, dr' . \tag{24}$$

For systems of slowly varying density, (23) can be rewritten as

$$E_{xc}^{M}[n(r)] = \int e_{xc}^{\theta}(n(r))dr + \int (t_s^{\theta}(n(r)) - t_s^{\theta_s}(n(r))dr , \tag{25}$$

where $e_{xc}^{\theta}(n)$ is the exchange correlation energy per unit volume of a uniform electron gas of density n and temperature θ, and $t_s^{\theta'}(n)$ is the kinetic energy per unit volume of a uniform, non-interacting electron gas of density n and temperature θ'. The relations determining θ and θ_s become, for slowly varying density,

$$k \log M = \int \sigma^{\theta}(n(r)dr = \int \sigma_s^{\theta_s}(n(r))dr, \tag{26}$$

where $\sigma^{\theta}(n)$ and $\sigma_s^{\theta_s}(n)$ are, respectively, the entropy per unit volume of a uniform interacting and non-interacting electron gas.

Note that, since θ and θ_s depend not only on M but, implicitly, on the entire density distributions n(r) through Eqs. (26) the superscripts θ and θ_s appearing in (25) are highly non-local functions of n(r'). This must be remembered when v_{xc}^M is evaluated by taking the functional derivative of E_{xc}^M given by Eq. (25) (cf. Eq. 1b).

Let us re-write Eq. (25) as

$$E_{xc}^M[n(r)] = \int e^{\theta}(n(r)dr - \int t_s^{\theta_s}(n(r))dr \tag{27}$$

where

$$e^{\theta}(n) \equiv e_{xc}^{\theta}(n) + t^{\theta}(n), \tag{28}$$

the total energy per unit volume, except for the classical electrostatic energy. Then

$$v_{xc}^M(r;[n(r')]) = \frac{\delta E_{xc}^M[n(r')]}{\delta n(r)}$$

$$= \frac{\partial}{\partial n}\left(e^{\theta}(n) - t_s^{\theta_s}(n)\right)_{n=n(r)} + \frac{\delta\theta}{\delta n(r)} \int e_1^{\theta}(n(r'))dr' - \frac{\delta\theta_s}{\delta n(r)} \int t_{s,1}^{\theta_s}(n(r'))dr' \tag{29}$$

where the subscript 1 denotes diffuentiation with respect to the temperature argument. Thus

$$e_1^{\theta'}(n) \equiv \frac{\partial}{\partial\theta'} e^{\theta'}(n) \quad \text{, etc.} \tag{30}$$

To evaluate $\delta\theta/\delta n(r)$ at constant M (or S) we use eq. (26) which gives

$$\frac{\delta\theta}{\delta n(r)} = -\left(\frac{\partial\sigma^{\theta}(n)}{\partial n}\right)_{n=n(r)} \Bigg/ \int \sigma_1^{\theta}(n(r')dr'; \tag{31}$$

similarly for $\delta\theta_s/\delta n(r)$. Thus (29) becomes

$$v_{xc}^{M}(r;[n(r')] = \frac{\partial}{\partial n}\left(e^{\theta}(n) - t_s^{\theta_s}(n)\right)_{n=n(r)}$$

$$- \left(\frac{\partial\sigma^{\theta}(n)}{\partial n}\right)_{n=n(r)} \frac{\int e_1^{\theta}(n(r'))dr'}{\int \sigma_1^{\theta}(n(r'))dr'} + \left(\frac{\partial\sigma^{\theta_s}(n)}{\partial n}\right)_{n=n(r)} \frac{\int t_{s,1}^{\theta_s}(n(r'))dr'}{\int \sigma_1^{\theta_s}(n(r'))dr'}$$

(32)

PROCEDURE FOR SOLVING THE KS EQUATIONS FOR AN EQUI-ENSEMBLE IN THE QUASI-LDA

For convenience I now describe the entire cycle of solving the KS equations for an equi-ensemble of M states in the quasi-LDA (valid for systems of slowly varying density).

Consider a system of N electrons in a given external potential, $v(r)$. The objective is to calculate the average density, $n(r)$, and average energy, E^M, of the lowest M eigenstates[6].

1. One requires the following thermodynamic functions,[10] for homogeneous interacting and non-interacting electron gases, of the density n and temperature θ'. (The subscript s denotes non-interacting and the subscript 1 differentiation with respect to temperature.)
   a) The entropies per unit volume $\sigma^{\theta'}(n)$ and $\sigma_s^{\theta'}(n)$, (Eqs. (26)) and their temperature derivatives, $\sigma_1^{\theta'}(n)$ and $\sigma_{s,1}^{\theta'}(n)$.
   b) The exchange-correlation plus kinetic energy per unit volume $e^{\theta'}(n)$ (Eq. (28), and its temperature derivative $e_1^{\theta'}(n)$.
   c) The kinetic energy per unit volume of a non-interacting system, $t_s^{\theta'}(n)$ (Eq. (25),ff), and its temperature derivative $t_{s,1}^{\theta'}(n)$.
2. Begin with an initial approximation to $n(r)$. Determine the corresponding interacting temperature θ and non-interacting (KS) temperature θ_s by solving respectively the implicit equations

$$k \log M = \int \sigma^{\theta}(n(r))dr; \; k \log M = \int \sigma_s^{\theta_s}(n(r))dr \qquad (26)$$

3. Construct the effective one particle potential

$$v_{eff}^{M}(r) = v(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{xc}^{M}(r;[n(r')]), \qquad (9)$$

where v_{xc}^{M} is given by Eq. (32).

4. Solve the KS single-particle equations

$$(-\frac{1}{2}\nabla^2 + v_{eff}^{M}(r) - \epsilon_i)\,\phi_i^{M}(r) = 0 \;. \qquad (10)$$

5. Construct the M lowest non-interacting N-particle wave-functions $\psi_{s,m}$(m=1,...M) and calculate their average density n'(r)[6]. (See Eq. (11) ff.)

6. If $n'(r) \equiv n(r)$, then the original n(r) was self-consistent. If not, repeat steps 2-5, starting with a different initial density until self-consistency is achieved.

7. Now determine the average energy, E^M, of the equi-ensemble as follows. Let $E_{s,m}$(m=1,...M) be the energies of the M lowest KS states. Then

$$E^M = \mathrm{Av}\; E_{s,m} - \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|} dr\, dr' - \int v_{xc}^{M}(r)n(r)dr$$

$$+ \int \{e^{\theta}(n(r)) - t_s^{\theta_s}(n(r))\}dr \;, \qquad (33)$$

We now add some remarks about the thermodynamic properties of uniform electron gases, listed in 1) above.

We call a temperature, θ', "low" when $k\theta' \ll \bar{E}_F$ where $\bar{E}_F$ is a mean Fermi energy of the ground state $E_F \equiv \langle k_F^2/2 \rangle \equiv \frac{1}{2} 3\pi^2 \langle n(r)^{2/3} \rangle$, the bracket denoting an appropriate average. In this regime, the temperature dependence of all thermodynamic quantities are determined by the low temperature parameters $\gamma(n)$ and $\gamma_s(n)$ characterizing the linear specific heat per unit volume:

$$C^{\theta'}(n) = \gamma(n)\theta' \; ; \; C_s^{\theta'}(n) = \gamma_s(n)\theta' . \qquad (34)$$

Some calculations of the thermodynamic functions of an interacting uniform electron gas over various ranges of n and θ' have already been reported[11,12]. It is generally believed that $e_{xc}(n)$, for $\theta' = 0$, has been most accurately determined (with a precision of order 0·1%) by Monte Carlo methods[13]. It is hoped that similarly accurate results will soon become available for the finite temperature quantities $\sigma^{\theta'}(n)$, $e_{xc}^{\theta'}(n)$ and $v_{xc}^{\theta'}(n)$. Calculation of the non-interacting quantities $\sigma_s^{\theta'}(n)$ and $t_s^{\theta'}(n)$ is, of course, elementary.

CONCLUDING REMARKS

The reader may be puzzled by the rather intricate interplay, in this paper, between equi- and canonical ensembles of different temperatures and different entropies. Indeed, in principle a knowledge of the physical properties of canonical ensembles alone determines the densities $n_m(r)$ (averaged over any multiplets) and energies, $E_m(r)$ of all eigenstates ψ_m. For example, let us write the partition function as

$$Z(\theta) \equiv \int_{-\infty}^{\infty} n(E)\, e^{-E/k\theta}\, dE , \qquad (35)$$

where

$$n(E) = \sum_m \delta(E-E_m) \quad . \tag{36}$$

Then clearly n(E) is the inverse Laplace transform of $Z(\theta)$ and, by Eq. (36), determines the positions (and multiplicities) of all eigenvalues E_m. Similarly for the densities $n_m(r)$. However such a procedure has two serious drawbacks. Even for M = 2 it requires a knowledge of $Z(\theta)$ for <u>all</u> θ and a calculation of <u>all</u> single particle ϕ_i and ϵ_i. Secondly, to obtain n(E) from $Z(\theta)$ requires an anlytic continuation into the complex θ-plane Since $Z(\theta)$, for real θ, can be only approximately known, such a continuation may give entirely misleading results.

Why then do we not deal exclusively with the equi-ensemble, but express both $E^M_{xc}[n(r)]$ and $v^M_{xc}[n(r)]$ by means of thermal quantities? The reason is that both of these functionals are, even for systems of slowly varying densities, <u>highly non-local</u>. There is no simple LDA for them, i.e.

$$\left.\begin{aligned} E^M_{xc}[n(r)] &= \int e^M_{xc}(n(r))dr \\ v^M_{xc}(r) &= \frac{\partial}{\partial n}\left[e^M_{xc}(n)\right]\Big|_{n=n(r)} \end{aligned}\right\} \quad \underline{\text{not}}\ \text{possible.} \tag{37}$$

For, for a given M, the local contribution to E^M_{xc} at r depends not only on M and n(r) but also on the entire density distribution n(r'), which determines how the total entropy, S = k log M, is apportioned between different volume elements, dr'. On the other hand <u>thermal</u> quantities <u>can</u> be expressed in the form of a simple LDA, e.g.

$$E_{xc}^{\theta}[n(r)] = \int e_{xc}^{\theta}(n(r))\,dr, \qquad (38)$$

since, for a given temperature, the local contribution to E_{xc}^{θ} depend only on the local n(r) and not on the density at other points. We can take advantage of the convenient LDA form (38) by noting that an equi-ensemble is equivalent to a thermal ensemble with the same n(r) and a temperature which depends on both M and the entire density distribution n(r). This is, of course, true of interacting real ensembles and of non-interacting KS ensembles. The non-locality of E_{xc}^{M} and v_{xc}^{M} enters through the temperatures of the appropriate corresponding thermal ensembles.

Another possibly puzzling issue is the following. It may seem questionable whether the quasi-LDA of the present paper, derived with the aid of thermodynamic arguments pertaining to bulk ensembles with very dense energy spectra, is applicable to the lowest few states of the system, say M = 1, 2 or 3. We shall now explain that this justified question is of the same nature as the question whether the LDA for the ground state is applicable to small systems of 2, 3 or 4 electrons.

The ground state LDA is logically justified only for systems of many electrons, N>>1, with slowly varying density, n(r); for the physical assumption underlying the integral, Eq. (13), for E_{xc}^{1} [n(r)] is that, locally, the electrons can be regarded as a uniform electron gas. Nevertheless, the ground state LDA yields quantitatively useful results for systems with as few as 2, 3 or 4 electrons - even 1!

Similarly, the present quasi-LDA is logically valid only for systems of many electrons whose density varies on a large enough length scale, a (see Eq. (14) and for $M>>1$. For such systems, as already mentioned, the spacing between excited states approaches zero as $a\to\infty$. Therefore, for large enough a, there exists a value M_0 of M which simultaneously satisfies the following two conditions:

$$1. \quad M_0>>1 \qquad 2. \quad (\Delta E^{M_0})/E^1 \leq \delta \tag{39}$$

(See Eq. (15)), where δ is arbitrarily small.

In view of the first condition , (39), thermodynamic considerations such as the equivalence of equi-ensembles and canonical ensembles hold for $M \geq M_0$. On the other hand, because of the second condition, (39) the quasi-LDA yields

$$E^M_{xc}[n(r)] = E^1_{xc}[n(r)]; \; v^M_{xc}[n(r)] = v^1_{xc}[n(r)] \quad \text{for } M \leq M_0 \tag{40}$$

with arbitrarily small error. This is in fact the physically correct result under the second condition (39).

How useful the quasi-LDA is for excited states when the conditions $N>>1$, and $n(r)$ slowyly varying, are not well satisfied, remains to be seen.

By successive calculations for increasing M, starting with $M = 1$, the excited state energies E_m and densities $n_m(r)$ (averaged over multiplets) can be obtained in the quasi-LDA of the present paper.

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2. W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).
3. N. D. Mermin, Phys. Rev. 137, A 1441 (1965).
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5. W. Kohn and P. Vashishta, in Theory of the Inhomogeneous Electron Gas, Eds. S. Lundquist and N. H. March, Plenum Publishing Corporation, New York, 1983, p. 124.
6. When there is a degeneracy all states of a multiplet are to be simultaneously included.
7. We assume here that such a v(r) exists, i.e. that n(r) is "v-representable".
8. The subscript s denotes non-interacting. v-representability of n(r) by an equi-ensemble of M non-interacting N-particle states, $\psi_{s,m}$, is assumed.
9. Of course, also equivalent is a micro-canonical ensemble which will, however, not interest us further.
10. In what follows these functions are regarded as known.
11. A review up to 1975 is in "Ergebnisse der Plasmaphysik und der Gaselektronik", vol. 5, R. Rompa and M. Steenbeck Eds., Akademie Verlag, Berlin 1976, p. 15 ff.
12. U. Gupta and A. I. Rajagapol, Phys. Rev. B 22, 2792 (1980).
13. D. M. Ceperley and R. J. Alder, P. R. L. 45, 566 (1980).

Tableau 1

Temperature, Entropy, Density in Ensembles

	Real(interacting) Ensemble	Corresponding KS(non-interacting) Ensemble
Canonical Ensemble	$\theta, S, n(r)$	$\theta, S_s, n(r)$
Equi-Ensemble	$\theta, S, n(r)$	$\theta_s, S, n(r)$

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