

Thermal Properties of the Inhomogeneous Electron Gas*

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A variational property of the ground-state energy of an electron gas in an external potential $v(\mathbf{r})$, derived by Hohenberg and Kohn, is extended to nonzero temperatures. It is first shown that in the grand canonical ensemble at a given temperature and chemical potential, no two $v(\mathbf{r})$ lead to the same equilibrium density. This fact enables one to define a functional of the density $F[n(\mathbf{r})]$ independent of $v(\mathbf{r})$, such that the quantity $\Omega = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ is at a minimum and equal to the grand potential when $n(\mathbf{r})$ is the equilibrium density in the grand ensemble in the presence of $v(\mathbf{r})$.

RECENTLY, Hohenberg and Kohn¹ have proposed a new approach to the ground-state properties of an electron gas in an external potential $v(\mathbf{r})$. Underlying their method is a proof that there exists a functional of the density $F[n(\mathbf{r})]$ independent of $v(\mathbf{r})$, such that

$$E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$$

is minimum and equal to the ground-state energy associated with $v(\mathbf{r})$, when $n(\mathbf{r})$ is the ground-state density in the presence of $v(\mathbf{r})$. In this article we prove an analogous theorem which provides a basis for extending their analysis to the problem of the inhomogeneous electron gas in thermal equilibrium at a temperature $T \neq 0$.

We shall work in the grand canonical ensemble at fixed temperature and chemical potential² and shall prove that there exists a functional $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that

$$\Omega \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$$

is minimum and equal to the grand potential associated with $v(\mathbf{r})$ when $n(\mathbf{r})$ is the equilibrium density in the presence of $v(\mathbf{r})$.

To show this we first record a minimum property of the grand potential analogous to that of the ground-state energy. If

$$\Omega[\rho] = \text{Tr}\rho \left(H - \mu N + \frac{1}{\beta} \ln \rho \right), \quad (1)$$

then the grand potential,

$$\Omega = -\frac{1}{\beta} \ln \text{Tr} e^{-\beta(H - \mu N)}, \quad (2)$$

is given by $\Omega[\rho_0]$ where ρ_0 is the grand canonical density matrix,

$$\rho_0 = e^{-\beta(H - \mu N)} / \text{Tr} e^{-\beta(H - \mu N)}. \quad (3)$$

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¹ P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

² The argument to follow can be adapted to the canonical ensemble with a few minor changes.

The functional (1) satisfies

$$\Omega[\rho] > \Omega[\rho_0], \quad \rho \neq \rho_0, \quad (4)$$

for all density matrices ρ , i.e., for all positive definite ρ with unit trace. The classical version of this inequality was proved by Gibbs,³ and it is easy to show quantum mechanically that ρ_0 is a local minimum of $\Omega[\rho]$. In the Appendix we prove that $\Omega[\rho]$ is in fact bounded below by $\Omega[\rho_0]$ for general quantum systems.

Given this property of $\Omega[\rho]$, the generalization of the argument in Ref. 1 is straightforward. Consider a grand canonical ensemble of electrons in an external potential $v(\mathbf{r})$. The Hamiltonian is

$$H = T + V + U,$$

where

$$T = \frac{\hbar^2}{2m} \int \nabla \psi^\dagger(\mathbf{r}) \nabla \psi(\mathbf{r}) d\mathbf{r},$$

$$V = \int v(\mathbf{r}) \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r},$$

$$U = \frac{1}{2} \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r}') \psi(\mathbf{r}') \psi(\mathbf{r}) d\mathbf{r} d\mathbf{r}'.$$

The equilibrium electronic density,

$$n(\mathbf{r}) = \text{Tr} \rho_0 \psi^\dagger(\mathbf{r}) \psi(\mathbf{r})$$

is evidently a functional of $v(\mathbf{r})$, but we can also show that $v(\mathbf{r})$ is uniquely determined by $n(\mathbf{r})$. For suppose there were another potential $v'(\mathbf{r})$ giving rise to the same density $n(\mathbf{r})$. Denote the Hamiltonian, grand canonical density matrix, and grand potential associated with $v'(\mathbf{r})$ by H' , ρ_0' , and Ω' . Since $v'(\mathbf{r}) \neq v(\mathbf{r})$, $\rho_0' \neq \rho_0$,⁴

³ J. Willard Gibbs, *Elementary Principles in Statistical Mechanics*, Dover Publications, Inc., New York (1960). See Theorem III, p. 131; J. von Neumann [*Mathematical Foundations of Quantum Mechanics*, Princeton University Press, Princeton (1955), Chap. V, Sec. 3] reduces the quantum case to a point where Gibbs' argument can be applied. A short direct proof of the quantum inequality is given below in the Appendix.

⁴ Note that in the canonical ensemble $v(\mathbf{r})$ and $v'(\mathbf{r})$ must differ by more than a constant for ρ_0 to differ from ρ_0' . Since in the grand ensemble the density matrices at fixed temperature and chemical potential differ even when the v 's differ only by a constant, we are in effect proving that any given equilibrium $n(\mathbf{r})$ can be produced by only one $v(\mathbf{r})$ and only for one value of μ . This is a generalization of the familiar property of systems in the absence of external potentials, that the (uniform) density n is a single-valued function of μ .

and we have from the minimal property (4),

$$\begin{aligned}\Omega' &= \text{Tr}\rho_0' \left(H' - \mu N + \frac{1}{\beta} \ln \rho_0' \right) \\ &< \text{Tr}\rho_0 \left(H' - \mu N + \frac{1}{\beta} \ln \rho_0 \right) \\ &= \Omega + \text{Tr}\rho_0 (V' - V),\end{aligned}\quad (5)$$

so that

$$\Omega' < \Omega + \int d\mathbf{r} (v'(\mathbf{r}) - v(\mathbf{r})) n(\mathbf{r}). \quad (6)$$

But the reasoning of Eq. (5) remains valid when primed and unprimed quantities are interchanged, giving

$$\Omega < \Omega' + \int d\mathbf{r} (v(\mathbf{r}) - v'(\mathbf{r})) n(\mathbf{r}). \quad (7)$$

Adding (6) and (7) leads to the contradiction

$$\Omega + \Omega' < \Omega + \Omega',$$

and therefore only one $v(\mathbf{r})$ can result in a given $n(\mathbf{r})$.

Since $n(\mathbf{r})$ uniquely determines $v(\mathbf{r})$ which in turn determines ρ_0 , the entire equilibrium density matrix ρ_0 is a functional of $n(\mathbf{r})$. In particular,

$$F[n(\mathbf{r})] = \text{Tr}\rho_0 \left(T + U + \frac{1}{\beta} \ln \rho_0 \right) \quad (8)$$

can be taken to be a functional of the density alone with a universal form valid for all $v(\mathbf{r})$. For a given potential $v(\mathbf{r})$, we define the functional

$$\Omega_v[n] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + F[n]. \quad (9)$$

When $n(\mathbf{r})$ is the correct equilibrium density in the potential v , then $\Omega_v[n]$ equals the grand potential Ω . If $n'(\mathbf{r})$ is the equilibrium density associated with any other potential $v'(\mathbf{r})$, then

$$\Omega_v[n'] > \Omega_v[n]. \quad (10)$$

This follows from Eqs. (4) and (1), with the Hamiltonian $T + U + \int d\mathbf{r} \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) v(\mathbf{r})$, since the right side of (10) is the grand potential $\Omega[\rho_0]$, while the left side is $\Omega[\rho_0']$. Thus, the correct density minimizes (9) over all density functions that can be associated with some potential $v(\mathbf{r})$.

This completes the generalization of the basic theorems of Ref. 1 to the case of an electron gas in thermal equilibrium. The corresponding generalizations of the subsequent discussion in that paper can be carried out in a straightforward way. By way of illustration, we mention two typical extensions.

In the case of a gas of almost constant density,

$$n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r}), \quad \tilde{n}(\mathbf{r})/n_0 \ll 1, \quad \int d\mathbf{r} \tilde{n}(\mathbf{r}) = 0,$$

Hohenberg and Kohn define a functional $G[n]$ by

$$F[n] = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[n],$$

and show that to second order in \tilde{n} G has the expansion

$$G[n] = G[n_0] + \int d\mathbf{r} d\mathbf{r}' \tilde{n}(\mathbf{r}) \tilde{n}(\mathbf{r}') K(\mathbf{r} - \mathbf{r}'), \quad (11)$$

where $K(\mathbf{r})$ is given in terms of α , the electronic polarizability by

$$K(\mathbf{r}) = \frac{1}{\mathcal{V}} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \frac{2\pi e^2}{q^2} \left[\frac{1}{\alpha(q)} - 1 \right] \quad (12)$$

(\mathcal{V} , the volume). It is a routine application of temperature-dependent perturbation theory to reach the same conclusion when $T \neq 0$, except that α is now the temperature-dependent polarizability, so that Eq. (32) of Ref. 1 must be generalized to

$$\begin{aligned}\alpha(q) &= \frac{4\pi e^2}{q^2} \frac{1}{\mathcal{V}} \sum_{n n'} \frac{w_n - w_{n'}}{E_{n'} - E_n} \langle n | \rho_{\mathbf{q}} | n' \rangle \langle n' | \rho_{-\mathbf{q}} | n \rangle, \\ \rho_{\mathbf{q}} &= \sum_{\mathbf{k}} c_{\mathbf{k}-\mathbf{q}}^\dagger c_{\mathbf{k}}, \\ w_n &= e^{-\beta(E_n - \mu N_n)} / \text{Tr} e^{-\beta(H - \mu N)}.\end{aligned}\quad (13)$$

As a second example, if we neglect exchange and correlation effects and approximate the contribution of the Helmholtz free energy to G by a form which is locally the free-particle expression, we find

$$\begin{aligned}G[n] &= \int \frac{d\mathbf{r} d\mathbf{p}}{(2\pi)^3} \left[-\frac{1}{\beta} \ln(1 + e^{-\beta(p^2/2m - \mu(\mathbf{r}))}) \right. \\ &\quad \left. + \frac{\mu(\mathbf{r})}{e^{\beta[p^2/2m - \mu(\mathbf{r})]} + 1} \right] - \mu \int d\mathbf{r} n(\mathbf{r}).\end{aligned}\quad (14)$$

Here $\mu(\mathbf{r})$ is a functional of the density defined implicitly by

$$n(\mathbf{r}) = \int \frac{d\mathbf{p}}{(2\pi)^3} \frac{1}{e^{\beta[p^2/2m - \mu(\mathbf{r})]} + 1}. \quad (15)$$

Under these assumptions,

$$\begin{aligned}\delta\Omega_v[n] &= \int d\mathbf{r} \delta n(\mathbf{r}) \left[\mu(\mathbf{r}) + v(\mathbf{r}) + e^2 \right. \\ &\quad \left. \times \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') - \mu \right],\end{aligned}\quad (16)$$

which leads to the temperature-dependent Thomas-Fermi equation for the equilibrium density:

$$n(\mathbf{r}) = \int \frac{d\mathbf{p}}{(2\pi)^3} \left\{ \exp \left[\beta \left(\frac{p^2}{2m} + v(\mathbf{r}) + e^2 \right) \times \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') - \mu \right] + 1 \right\}^{-1}. \quad (17)$$

APPENDIX

We wish to show that

$$\Omega[\rho] > \Omega[\rho_0], \quad \rho \neq \rho_0, \quad (A1)$$

for all positive definite ρ with unit trace, where the density matrix functional $\Omega[\rho]$ is given by (1) and ρ_0 is the grand canonical density matrix (3). We define

$$\rho_\lambda = e^{-\beta(H + \lambda\Delta - \mu N)} / \text{Tr} e^{-\beta(H + \lambda\Delta - \mu N)}, \quad (A2)$$

where $\Delta = -(1/\beta) \ln \rho - H + \mu N$. Since ρ is positive definite, Δ is Hermitian. Now

$$\rho_\lambda = \rho_0, \quad \lambda = 0; \quad = \rho, \quad \lambda = 1. \quad (A3)$$

Hence

$$\Omega[\rho] - \Omega[\rho_0] = \int_0^1 \frac{\partial}{\partial \lambda} \Omega[\rho_\lambda] d\lambda. \quad (A4)$$

To evaluate the derivative write

$$\Omega[\rho_\lambda] = \text{Tr} \rho_\lambda \left(H + \lambda\Delta - \mu N + \frac{1}{\beta} \ln \rho_\lambda \right) - \lambda \text{Tr} \Delta \rho_\lambda. \quad (A5)$$

The first trace is just the grand potential for a Hamiltonian $H + \lambda\Delta$, and is therefore stationary for variations of ρ_λ about the corresponding grand canonical density matrix (A2). We need therefore differentiate only with respect to the explicit occurrence of λ in this term, so

(A5) yields simply

$$\frac{\partial}{\partial \lambda} \Omega[\rho_\lambda] = -\lambda \text{Tr} \Delta \frac{\partial}{\partial \lambda} \rho_\lambda. \quad (A6)$$

We can find $\partial \rho_\lambda / \partial \lambda$ by using the operator identity

$$\frac{\partial}{\partial \lambda} e^{-\beta(H - \mu N + \lambda\Delta)} = -e^{-\beta(H - \mu N + \lambda\Delta)} \int_0^\beta d\beta' \Delta_\lambda(\beta'), \quad (A7)$$

$$\Delta_\lambda(\beta') = e^{\beta'(H - \mu N + \lambda\Delta)} \Delta e^{-\beta'(H - \mu N + \lambda\Delta)}. \quad (A8)$$

[To prove (A7), note that both sides satisfy the same first order differential equation in β , and both vanish when $\beta = 0$.] From (A7) and (A2)

$$\frac{\partial}{\partial \lambda} \rho_\lambda = - \int_0^\beta d\beta' \rho_\lambda [\Delta_\lambda(\beta') - \langle \Delta \rangle_\lambda], \quad (A9)$$

where

$$\langle X \rangle_\lambda = \text{Tr} \rho_\lambda X.$$

Therefore,

$$\frac{\partial}{\partial \lambda} \Omega[\rho_\lambda] = \lambda \int_0^\beta d\beta' (\langle \Delta \Delta_\lambda(\beta') \rangle_\lambda - \langle \Delta \rangle_\lambda^2). \quad (A10)$$

By cyclically permuting operators within the trace, one can verify that

$$\begin{aligned} \langle \Delta_\lambda(\beta') \rangle_\lambda &= \langle \Delta \rangle_\lambda \quad \text{for any } \beta', \\ \langle \Delta \Delta_\lambda(\beta') \rangle_\lambda &= \langle \Delta_\lambda(\frac{1}{2}\beta')^\dagger \Delta_\lambda(\frac{1}{2}\beta') \rangle. \end{aligned} \quad (A11)$$

With these identities, we can rewrite (A10):

$$\begin{aligned} \frac{\partial}{\partial \lambda} \Omega[\rho_\lambda] &= \lambda \int_0^\beta d\beta' \langle (\Delta_\lambda(\frac{1}{2}\beta') - \langle \Delta \rangle_\lambda)^\dagger \\ &\quad \times (\Delta_\lambda(\frac{1}{2}\beta') - \langle \Delta \rangle_\lambda) \rangle_\lambda. \end{aligned} \quad (A12)$$

The right side of (A12) is non-negative and can be zero only if Δ is a multiple of the unit operator, i.e., if $\rho_0 = \rho$. Thus, (A12) and (A4) establish (A1).