Appendix B

TWO THEOREMS IN DENSITY-FUNCTIONAL THEORY

In this appendix we prove two of the key results of density-functional theory, usually called the Hohenberg–Kohn–Mermin theorems. In doing so we use a simplified notation in which

$$\mathrm{Tr}\cdots \equiv \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \iint \cdots \, \mathrm{d}\mathbf{r}^N \, \mathrm{d}\mathbf{p}^N$$

This operation is called the "classical trace", by analogy with the corresponding operation in quantum statistical mechanics. The definition of the grand partition function Ξ and the normalisation of the equilibrium phase-space probability density f_0 can then be expressed in the compact form

$$\Xi = \mathrm{Tr} \exp\left[-\beta(\mathcal{H} - N\mu)\right], \quad \mathrm{Tr}\, f_0 = 1$$

We first prove the following lemma.

Lemma. *Let f be a normalised phase-space probability density and let $\Omega[f]$ be the functional defined as*

$$\Omega[f] = \mathrm{Tr}\, f(\mathcal{H} - N\mu + k_\mathrm{B}T \ln f) \tag{B.1}$$

Then

$$\Omega[f] \geqslant \Omega[f_0] \tag{B.2}$$

where f_0 is the equilibrium phase-space density.

PROOF. From the definition of f_0 in (2.4.5) it follows that

$$\begin{aligned}\Omega[f_0] &= \mathrm{Tr}\, f_0(\mathcal{H} - N\mu - k_\mathrm{B}T \ln \Xi - \mathcal{H} + N\mu) = -k_\mathrm{B}T \ln \Xi \\ &\equiv \Omega\end{aligned} \tag{B.3}$$

where Ω is the grand potential. Thus

$$\Omega[f] - \Omega[f_0] = k_\mathrm{B}T\left[\mathrm{Tr}(f \ln f) - \mathrm{Tr}(f \ln f_0)\right] \tag{B.4}$$

The term inside square brackets can be written as

$$\mathrm{Tr}(f \ln f) - \mathrm{Tr}(f \ln f_0) = \mathrm{Tr}\, f_0\big[(f/f_0)\ln(f/f_0) - (f/f_0) + 1\big] \tag{B.5}$$

The right-hand side is always non-negative, since $x \ln x \geqslant x - 1$ for any $x > 0$. The inequality (B.2) is thereby verified.

This result is an example of the Gibbs–Bogoliubov inequalities, which are essentially a consequence of the convexity of the exponential function.

Theorem 1. *For given choices of V_N, T and μ, the intrinsic free-energy functional*

$$\mathcal{F}\big[\rho^{(1)}\big] = \mathrm{Tr}\, f_0(K_N + V_N + k_\mathrm{B}T \ln f_0) \tag{B.6}$$

is a unique functional of the equilibrium single-particle density $\rho^{(1)}(\mathbf{r})$.

PROOF. The equilibrium phase-space probability density f_0 is a functional of $\phi(\mathbf{r})$. The same is therefore true of the single-particle density $\rho^{(1)}(\mathbf{r}) = \mathrm{Tr}(f_0\rho(\mathbf{r}))$, where $\rho(\mathbf{r})$ is the microscopic density. Let us assume that there exists a different external potential, $\phi'(\mathbf{r}) \neq \phi(\mathbf{r})$, that gives rise to the same $\rho^{(1)}(\mathbf{r})$. With the hamiltonian $\mathcal{H}' = K_N + V_N + \Phi'_N$ we may associate an equilibrium phase-space density f'_0 and grand potential Ω'. The inequality (B.2) implies that

$$\begin{aligned}\Omega' = \mathrm{Tr}\, f'_0(\mathcal{H}' - N\mu + k_\mathrm{B}T \ln f'_0) &\leqslant \mathrm{Tr}\, f_0(\mathcal{H}' - N\mu + k_\mathrm{B}T \ln f_0)\\ &= \Omega + \mathrm{Tr}\big[f_0(\Phi'_N - \Phi_N)\big]\end{aligned} \tag{B.7}$$

or

$$\Omega' < \Omega + \int \rho^{(1)}(\mathbf{r})\big[\phi'(\mathbf{r}) - \phi(\mathbf{r})\big]\,\mathrm{d}\mathbf{r} \tag{B.8}$$

If the same argument is carried through with primed and unprimed quantities interchanged, we find that

$$\Omega < \Omega' + \int \rho^{(1)}(\mathbf{r})\big[\phi(\mathbf{r}) - \phi'(\mathbf{r})\big]\,\mathrm{d}\mathbf{r} \tag{B.9}$$

Addition of the two inequalities term by term leads to a contradiction:

$$\Omega + \Omega' < \Omega' + \Omega \tag{B.10}$$

showing that the assumption concerning $\rho^{(1)}(\mathbf{r})$ must be false. We therefore conclude that there is only one external potential that gives rise to a particular single-particle density. Since f_0 is a functional of $\phi(\mathbf{r})$, it follows that it is also a unique functional of $\rho^{(1)}(\mathbf{r})$. This in turn implies that the intrinsic free energy (B.6) is a unique functional of $\rho^{(1)}(\mathbf{r})$ and that its functional form is the same for all external potentials.

Theorem 2. *Let $n(\mathbf{r})$ be some average of the microscopic density. Then the functional*

$$\Omega_\phi[n] = \mathcal{F}[n] + \int n(\mathbf{r})\phi(\mathbf{r})\,\mathrm{d}\mathbf{r} - \mu \int n(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{B.11}$$

has its minimum value when $n(\mathbf{r})$ coincides with the equilibrium single-particle density $\rho^{(1)}(\mathbf{r})$.

PROOF. Let $n(\mathbf{r})$ be the single-particle density associated with a phase-space probability density f'. The corresponding grand-potential functional is

$$\begin{aligned}\Omega[f'] &= \mathrm{Tr}\, f'(\mathcal{H} - N\mu + k_\mathrm{B}T \ln f') \\ &= \mathcal{F}[n] + \int n(\mathbf{r})\phi(\mathbf{r})\,\mathrm{d}\mathbf{r} - \mu \int n(\mathbf{r})\,\mathrm{d}\mathbf{r} = \Omega_\phi[n]\end{aligned} \tag{B.12}$$

The inequality (B.2) shows that $\Omega[f_0] \leqslant \Omega[f']$. It is also clear that $\Omega_\phi[\rho^{(1)}] = \Omega[f_0] = \Omega$. Thus $\Omega_\phi[\rho^{(1)}] \leqslant \Omega_\phi[n]$: the functional $\Omega_\phi[n]$ is minimised when $n(\mathbf{r}) = \rho^{(1)}(\mathbf{r})$ and its minimum value is equal to the grand potential.