4

THE CHEMICAL POTENTIAL

4.1 Chemical potential in the grand canonical ensemble at zero temperature

In the last chapter were obtained the principal equations of the density-functional theory of electronic systems, the equations for the determination of the electron density and the energy for a ground state or equilibrium state of a system of interest. For the ground state, $E[\rho]$ reaches its minimum among densities ρ that integrate to the number of electrons N for the system of interest, where $E[\rho]$ is given by (3.2.3) or (3.4.9). For an equilibrium state at temperature θ in a canonical ensemble, $A[\rho]$ reaches its minimum among densities ρ that integrate to N, where $A[\rho]$ is given by (3.5.15). And for an equlibrium state at temperature θ and chemical potential μ in a grand canonical ensemble, $\Omega[\rho]$ reaches its minimum among all ρ, where $\Omega[\rho]$ is defined by (3.6.12).

We are particularly interested in the zero-temperature limit, for at $\theta = 0$ ($\beta = \infty$), the equilibrium state and ground state become one and the same—the state of primary interest to us. As θ goes to zero, the term $\theta S[\rho]$ disappears from $A[\rho]$ of (3.5.15) and $\Omega[\rho]$ of (3.6.12). At this limit, do the corresponding variational principles remain valid? The answer does not follow from the arguments of §3.5 and §3.6, for in the proofs of the theorems of those sections the concavity of the entropy $S[\hat{\Gamma}]$, as a functional of the density operator, plays a vital role. Detailed analysis for each case is needed. In this section and the next two, we consider the grand canonical ensemble. We take up the canonical ensemble in §4.4.

In the limit as β tends to infinity, the universal functional $F[\rho]$ defined in (3.6.10) becomes

$$F_{\mathrm{GC}}[\rho(\mathbf{r})] = \underset{\Gamma \to \rho}{\mathrm{Min}}\ \mathrm{Tr}\,[\hat{\Gamma}(\hat{T} + \hat{V}_{ee})] \tag{4.1.1}$$

This is the universal ground-state functional proposed by Perdew, Parr, Levy, and Balduz (1982). It extends Levy's constrained search to general density operators $\hat{\Gamma}$ in Fock space (grand canonical ensemble). In (4.1.1), $\hat{V}_{ee}$ is written in place of the general particle–particle interaction potential

$\hat{U}$ because we specialize henceforth to electronic systems. The grand potential at $\beta \to \infty$ correspondingly reduces to

$$\begin{aligned}\Omega[\rho] &= F_{GC}[\rho] + \int \rho(\mathbf{r})(v(\mathbf{r}) - \mu)\, d\mathbf{r} \\ &= E_{GC}[\rho] - \mu N \end{aligned} \tag{4.1.2}$$

into which enters the grand-canonical-ensemble energy functional

$$E_{GC}[\rho] = F_{GC}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} \tag{4.1.3}$$

Note that both $\Omega[\rho]$ and $E_{GC}[\rho]$ are defined for densities integrating to any finite positive number, in contrast with $E[\rho]$ of (3.4.9), which is defined only for densities integrating to positive integers.

Assume now the $\beta \to \infty$ limit of the $\Omega[\hat{\Gamma}]$ variational principle of (3.6.9),

$$\Omega^0 = E^0(N) - \mu N \leqslant \operatorname{Tr} \hat{\Gamma}(\hat{H} - \mu \hat{N}) \tag{4.1.4}$$

where $E^0(N)$ and μ are the energy and the chemical potential of the ground state with N electrons. Following the prescription of (3.6.9), the corresponding density-functional variational principle is then

$$E^0(N) - \mu N \leqslant E_{GC}[\rho(\mathbf{r})] - \mu \int \rho(\mathbf{r})\, d\mathbf{r} \tag{4.1.5}$$

from which follows the variational equation for the ground-state electron density and energy

$$\delta\left\{E_{GC}[\rho] - \mu \int \rho(\mathbf{r})\, d\mathbf{r}\right\} = 0 \tag{4.1.6}$$

and the Euler–Lagrange equation

$$\frac{\delta E_{GC}[\rho]}{\delta \rho(\mathbf{r})} - \mu = 0 \tag{4.1.7}$$

Equivalently,

$$\frac{\delta F_{GC}[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) - \mu = 0 \tag{4.1.8}$$

In the last equation, it has been assumed that $F_{GC}[\rho]$ is differentiable [see Englisch and Englisch (1984a, b) for discussion of the validity of this assumption].

We now show that (4.1.4) is not true in general [see Blaizot and Ripka 1986, p. 410)]; nevertheless, it is valid for atomic and molecular systems. Consider a trial $\hat{\Gamma}$ that describes a ground state with the average number

of electrons $N + \Delta N = \mathrm{Tr}\,\hat{\Gamma}\hat{N}$. Then we have from (4.1.4),

$$E^0(N) - \mu N \leqslant E^0(N + \Delta N) - \mu \cdot (N + \Delta N) \tag{4.1.9}$$

Similarly, from another $\hat{\Gamma}$ with $\mathrm{Tr}\,\hat{\Gamma}\hat{N} = N - \Delta N$,

$$E^0(N) - \mu N \leqslant E^0(N - \Delta N) - \mu \cdot (N - \Delta N) \tag{4.1.10}$$

It follows from (4.1.9) that if $E^0(N)$ is a differentiable function,

$$\mu = \frac{\partial E^0(N)}{\partial N} \tag{4.1.11}$$

Adding (4.1.9) and (4.1.10), we obtain

$$E^0(N + \Delta N) + E^0(N - \Delta N) - 2E^0(N) \geqslant 0 \tag{4.1.12}$$

which demands that the function $E^0(N)$ be convex (see Appendix B). If $E^0(N)$ is twice differentiable, then (4.1.12) implies

$$\frac{\partial^2 E^0(N)}{\partial N^2} \geqslant 0 \tag{4.1.13}$$

Conditions (4.1.11) and (4.1.12) or (4.1.13) are also sufficient to guarantee the validity of (4.1.9). See the theorem before Equation (B.13) in Appendix B.

Setting $\Delta N = 1$ in (4.1.12), we see that

$$E^0(N + 1) - E^0(N) \geqslant E^0(N) - E^0(N - 1) \tag{4.1.14}$$

or

$$I(N + 1) \geqslant I(N) \tag{4.1.15}$$

where $I(N)$ is the ionization potential of the N-electron ground state. Equation (4.1.15) states that successive ionization potentials are not decreasing (for fixed external potential).

For atoms and molecules, no counterexample is known to (4.1.15), although a first-principles proof has never been given. As examples, in Table 4.1 we list all of the successive ionization potentials for the oxygen and carbon atoms; in Figure 4.1 we plot the energy of oxygen as a function of the number of electrons, determined from the formula

$$E(N) = -\sum_{M=1}^{N} I(M) \tag{4.1.16}$$

Phillips and Davidson (1984) give examples of nonconvex $E^0(N)$, though not for electronic systems.

Summarizing the foregoing, we have shown that for systems for which $E^0(N)$ is convex, including atoms and molecules, the zero-temperature limit of grand-canonical-ensemble theory exists, as manifest in (4.1.4),

Table 4.1 Ionization Energies for Carbon and Oxygen

Species	Ionization Potential (eV)	Species	Ionization Potential (eV)
C^-	1.12	O^-	1.47
C	11.26	O	13.61
C^+	24.38	O^+	35.15
C^{2+}	47.86	O^{2+}	54.93
C^{3+}	64.48	O^{3+}	77.39
C^{4+}	391.99	O^{4+}	113.87
C^{5+}	489.84	O^{5+}	138.08
		O^{6+}	739.08
		O^{7+}	871.12

(4.1.5), and (4.1.6). The chemical potential in these equations is the zero-temperature limit of the chemical potential defined for the finite-temperature grand canonical ensemble,

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{\theta,v(\mathbf{r})} = \left(\frac{\partial E}{\partial N}\right)_{\theta,v(\mathbf{r})} - \theta\left(\frac{\partial S}{\partial N}\right)_{\theta,v(\mathbf{r})} \tag{4.1.17}$$

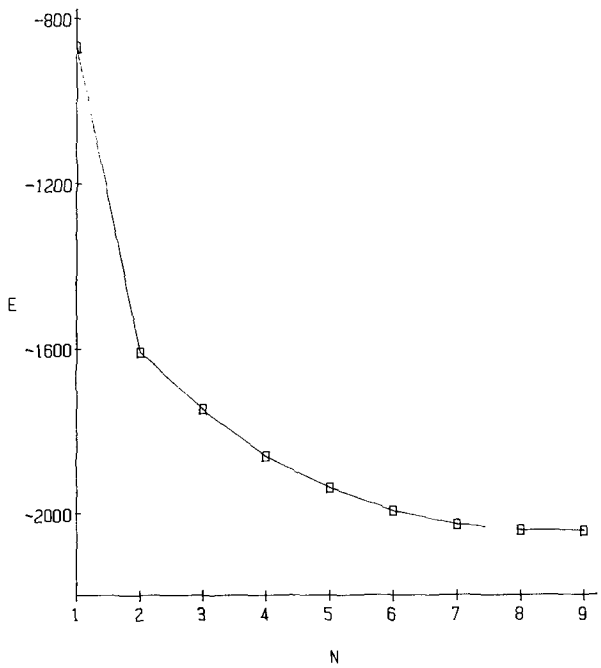

Figure 4.1 Energy (in electron volts) of the oxygen atom and its ions.

where A is the Helmholtz free energy. In this book we generally use the symbol μ to designate this zero-temperature limit, writing

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v = \lim_{\theta \to 0} \left(\frac{\partial A}{\partial N}\right)_{\theta, v(\mathbf{r})} \tag{4.1.18}$$

and we simplify the notation in (4.1.6), (4.1.7), and (4.1.8) to give

$$\delta\{E[\rho] - \mu N[\rho]\} = 0 \tag{4.1.19}$$

and

$$\mu = \left[\frac{\delta E}{\delta \rho}\right]_v = v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \tag{4.1.20}$$

Equations (4.1.19) and (4.1.20) are the basic working equations of the ground-state density-functional theory for atoms, molecules, and solids.

4.2 Physical meaning of the chemical potential

The chemical potential of density-functional theory measures the escaping tendency of an electronic cloud. It is a constant, through all space, for the ground state of an atom, molecule, or solid, and equals the slope of the E versus N curve at constant $v(\mathbf{r})$. The analogy with the chemical potential of ordinary macroscopic thermodynamics is clear and useful.

The chemical potential is the negative of the electronegativity of Pauling and Mulliken (Parr, Donnelly, Levy, and Palke 1978). For, the three-point finite-difference approximation to $\partial E/\partial N$ for a species S is

$$\mu \approx -\frac{I + A}{2} \tag{4.2.1}$$

where $I = E_S^+ - E_S$ and $A = E_S - E_S^-$ are respectively the ionization potential and electron affinity for the species. And Mulliken's formula for electronegativity (Mulliken 1934) is

$$\chi_M = \frac{I + A}{2} \tag{4.2.2}$$

Therefore

$$\mu \approx -\chi_M \tag{4.2.3}$$

and the chemical potential concept is the same as the electronegativity concept.

Mulliken's beautiful argument for (4.2.2) is as follows. Given two species, S and T, which is the more electronegative? The energy required for S to take an electron from T is $I_T - A_S$, while the energy requirement for T to take an electron from S is $I_S - A_T$. If the two requirements were

the same, we would have equal electronegativities:

$$I_T - A_S = I_S - A_T, \qquad I_S + A_S = I_T + A_T$$

The factor $\frac{1}{2}$ is arbitrary.

Density-functional theory is, then, a theory of ground (equilibrium) electronic states in which the electronegativity of chemistry plays in the basic variational principle (4.1.6) just the role that the energy plays in the basic variational principle (1.2.8) of wave-function theory. This result demands attention to the density-functional theory as a description of chemistry. In this description, the chemical potential is the key concept; we shall find in the next chapter that the derivatives of the chemical potential are of comparable importance.

4.3 Detailed consideration of the grand canonical ensemble near zero temperature

In order to have the variational equation (4.1.20), we have seen in §4.1 that we should take the $\theta \to 0$ limit of the grand canonical theory described in §§3.6 and 4.1. We now carefully examine this limiting process. Then we determine the ground-state energy for nonintegral N. The argument derives from Gyftopoulos and Hatsopoulos (1965) and Perdew, Parr, Levy, and Balduz (1982); see also Linderberg (1977).

To see how the analysis goes, it is most helpful first to consider a particular model system, a species that can exist in only three states: the neutral ground state with energy E_0 and number of electrons N_0, a positive-ion ground state with energy $E_0 + I$ and number of electrons $N_0 - 1$, and a negative-ion ground state with energy $E_0 - A$ and number of electrons $N_0 + 1$. All states are assumed nondegenerate. At inverse temperature β and chemical potential μ, the grand canonical partition function will be

$$Z(\beta, \mu) = e^{-\beta(E_0 - \mu N_0)}[1 + e^{-\beta(-A-\mu)} + e^{-\beta(I+\mu)}] \tag{4.3.1}$$

Consequently we have, from standard formulas for ensemble averages,

$$\bar{N} = \frac{1}{\beta}\left[\frac{\partial \ln Z}{\partial \mu}\right]_\beta = N_0 + \left[\frac{e^{\beta(A+\mu)} - e^{-\beta(I+\mu)}}{1 + e^{\beta(A+\mu)} + e^{-\beta(I+\mu)}}\right]. \tag{4.3.2}$$

Also

$$\bar{E} = \left[\frac{\partial \ln Z}{\partial \beta}\right]_\mu = E_0 - \left[\frac{Ae^{\beta(A+\mu)} - Ie^{-\beta(I+\mu)}}{1 + e^{\beta(A+\mu)} + e^{-\beta(I+\mu)}}\right] \tag{4.3.3}$$

and

$$\begin{aligned}\bar{S} &= k[\ln Z + \beta\bar{E} - \beta\bar{N}\mu] \\ &= k\left\{\ln(1 + e^{\beta(A+\mu)} + e^{-\beta(I+\mu)}) - \left[\frac{\beta(A+\mu)e^{\beta(A+\mu)} - \beta(I+\mu)e^{-\beta(I+\mu)}}{1 + e^{\beta(A+\mu)} + e^{-\beta(I+\mu)}}\right]\right\}\end{aligned} \tag{4.3.4}$$

These formulas provide the various average properties for any β and μ. To obtain them for any β and $\bar{N}$, one may eliminate μ using (4.3.2).

Suppose first that $\bar{N} = N_0$—the system has an integral number of electrons. Then from (4.3.2) it immediately follows that $e^{\beta(A+\mu)} = e^{-\beta(I+\mu)}$, or $I + A + 2\mu = 0$, or

$$\mu_0 = -\frac{I+A}{2} \quad [\bar{N} = N_0] \tag{4.3.5}$$

This is just the Mulliken formula of (4.2.2), and it is valid for any temperature.

When $\bar{N} \neq N_0$, (4.3.2) can be rewritten as a quadratic equation and solved, as follows. Let

$$\begin{aligned} \mu &= \mu_0 + \Delta\mu, & \bar{N} &= N_0 + \Delta N, \\ y &= e^{-\beta[(I-A)/2]}, & x &= e^{\beta\,\Delta\mu} \end{aligned} \tag{4.3.6}$$

Then (4.3.2) becomes

$$N = \frac{y(x^2-1)}{y(x^2+1)+x} \tag{4.3.7}$$

the solution of which is

$$x = \frac{\Delta N \pm \{(\Delta N)^2 + 4y^2[1-(\Delta N)^2]\}^{1/2}}{2y(1-\Delta N)} = e^{\beta\,\Delta\mu} \tag{4.3.8}$$

This gives $\Delta\mu$ and hence μ for any β and ΔN or $\bar{N}$. For $\Delta N = 0$, for example, we find $x = \pm 1 = +1$, $\Delta\mu = 0$, $\mu = \mu_0$, recovering (4.3.5) for any β. For $\Delta N \neq 0$, the zero-temperature limits are different for ΔN plus and ΔN minus. Noting that $\lim_{\beta\to\infty} y = 0$ assuming convexity of $\bar{E}(N)$, we find, in the zero-temperature limit:

$$\Delta N > 0: \qquad x = \frac{\Delta N + \Delta N\left\{1 + \dfrac{4y^2}{(\Delta N)^2}[1-(\Delta N)^2]\right\}^{1/2}}{2y(1-\Delta N)} \to \frac{\Delta N}{y(1-\Delta N)} \tag{4.3.9}$$

$$\Delta N < 0: \qquad x = \frac{\Delta N - \Delta N\left\{1 + \dfrac{4y^2}{(\Delta N)^2}[1-(\Delta N)^2]\right\}^{1/2}}{2y(1-\Delta N)} \to \frac{y(1+\Delta N)}{\Delta N} \tag{4.3.10}$$

Consequently, we have for very high β or very low θ,

$$1 > \Delta N > 0: \qquad \Delta\mu = +\left(\frac{I-A}{2}\right) + \frac{1}{\beta}\ln\left(\frac{\Delta N}{1-\Delta N}\right) \tag{4.3.11}$$

$$\mu = -A + \frac{1}{\beta}\ln\left(\frac{\Delta N}{1-\Delta N}\right) \tag{4.3.12}$$

$$-1<\Delta N<0: \qquad \Delta\mu = -\left(\frac{I-A}{2}\right) + \frac{1}{\beta}\ln\left[-\frac{(1+\Delta N)}{\Delta N}\right] \tag{4.3.13}$$

$$\mu = -I + \frac{1}{\beta}\ln\left[-\frac{(1+\Delta N)}{\Delta N}\right] \tag{4.3.14}$$

From (4.3.5), (4.3.12) and (4.3.14), we therefore infer the zero-temperature limits

$$\mu_{\theta=0} = \begin{cases} -I, & N_0-1<N<N_0 \\ -\dfrac{I+A}{2}, & N=N_0 \\ -A, & N_0+1>N>N_0 \end{cases} \tag{4.3.15}$$

To obtain the ground-state energy, we insert (4.3.11) and (4.3.13) into (4.3.3), and take the limit $\beta\to\infty$. The result, writing N for $\bar{N}$, is

$$E^0(N) = \begin{cases} E^0(N_0) - I(N-N_0), & N_0-1<N<N_0 \\ E^0(N_0), & N=N_0 \\ E^0(N_0) - A(N-N_0), & N_0+1>N>N_0 \end{cases} \tag{4.3.16}$$

For this three-state model, the energy at zero temperature is a continuous series of straight-line segments, as shown in Fig. 4.1. The energy for a nonintegral number of electrons is given by linear interpolation between the values for integral numbers of electrons (Perdew, Parr, Levy, and Balduz, 1982).

As can be readily verified by calculation, for typical atomic or molecular values of I and A, it requires a quite high temperature to cause much curvature to appear in $E(N)$ curves. We will return to the curvature at the end of this section. Equations (4.3.15) and (4.3.16), although derived from a three-state model, remain true in general, as will be established below. The essence of the zero-temperature grand-canonical-ensemble theory is captured in (4.3.15) and (4.3.16).

In this three-state model system, all states have been assumed to be nondegenerate. But there is little effect if degeneracy is present. If the degeneracies of positive ion, neutral species, and negative ion are g_+, g_0, and g_-, (4.3.2) is replaced by

$$\Delta N = \frac{g_- e^{\beta(A+\mu)} - g_+ e^{-\beta(I+\mu)}}{g_0 + g_- e^{\beta(A+\mu)} + g_+ e^{-\beta(I+\mu)}} \tag{4.3.17}$$

Equation (4.3.5) is replaced by

$$\mu_0 = -\frac{I+A}{2} + \frac{1}{2\beta}\ln\frac{g_+}{g_-} \qquad [\text{large } \beta,\ N=N_0] \tag{4.3.18}$$

This displays a temperature dependence in μ_0, but in the $\beta \to \infty$ limit this disappears and (4.3.5) results. For N nonintegral, (4.3.12) and (4.3.14) are similarly modified by terms vanishing as $\beta \to \infty$ [Perdew 1985], so that (4.3.15) and (4.3.16) remain valid in the presence of degeneracies.

We now describe the zero-temperature limit of the full grand-canonical-ensemble theory, into which enter ground and excited states of all species, and ions of all possible positive and negative charges. The only assumption is the convexity assumption of (4.1.15). For the general case, the partition function becomes

$$Z = \sum_N \sum_j g_{Nj} e^{-\beta(E_{Nj} - \mu N)} \tag{4.3.19}$$

where g_{Nj} are degeneracies, and in place of (4.3.2)

$$\bar{N} = \frac{1}{Z} \sum_N \sum_j g_{Nj} N e^{-\beta(E_{Nj} - \mu N)} \tag{4.3.20}$$

In the $\theta \to 0$ or $\beta \to \infty$ limit, only the ground states of the various species survive. Calling the ground-state energy and degeneracy for N electrons E_N^0 and g_N^0, we get for very large β and integral N

$$\mu_0 = -\frac{E_{N-1}^0 - E_{N+1}^0}{2} + \frac{1}{2\beta} \ln \frac{g_{N-1}^0}{g_{N+1}^0} \qquad [\text{large } \beta,\ N = N_0] \tag{4.3.21}$$

provided only that the convexity condition of (4.1.5) is satisfied.

Similarly, if $N = N_0 + \Delta N$, where N_0 is some integer and ΔN is positive, the result should be

$$\mu_{\theta=0} = E_{N_0}^0 - E_{N_0+1}^0, \qquad N_0 + 1 > N > N_0 \tag{4.3.22}$$

If ΔN is negative, on the other hand,

$$\mu_{\theta=0} = E_{N_0}^0 - E_{N_0-1}^0, \qquad N_0 - 1 < N < N_0 \tag{4.3.23}$$

Summarizing, we have

$$\mu_{\theta=0} = \begin{cases} -I, & N_0 - 1 < N < N_0 \\ -\dfrac{I+A}{2}, & N = N_0 \\ -A, & N_0 + 1 > N < N_0 \end{cases} \tag{4.3.24}$$

in accordance with (4.3.15). $E(N)$ as a function of N at $\beta = \infty$ is a series of straight-line segments connecting integral-N values.

To prove the foregoing, we depart from the literature by formulating the problem directly at zero temperature. Instead of using a Lagrange multiplier μ as in (4.1.4), we carry out the energy minimization with proper normalization built in at the start. Thus, we write the ground-state

energy for an arbitrary number of electrons N as

$$E^0(N) = \text{Min}\left\{\sum_M p(M) \cdot E^0(M)\right\} \tag{4.3.25}$$

with constraints

$$\sum_M p(M) = 1 \tag{4.3.26}$$

$$\sum_M Mp(M) = N \tag{4.3.27}$$

$$1 \geqslant p(M) \geqslant 0 \qquad \text{for all } M \tag{4.3.28}$$

where $p(M)$ and $E^0(M)$ are the probability and ground-state energy for the system in same external potential $v(\mathbf{r})$ with M electrons. M is an integer and the sum is over all positive integers. The minimization in (4.3.25) is equivalent to the one in (4.1.4), because we now use for the evaluation of $\text{Tr}\,\hat{\Gamma}\hat{H}$ the eigenstates of the Hamiltonian $\hat{H}$ in which $\hat{\Gamma}$ is diagonal with eigenvalues $p(M)$. The excited states all have zero probabilities, since $E^0(M)$ is the minimum for the expectation value of $\hat{H}$ for states with M electrons.

We now solve for $p(M)$ and $E^0(N)$. This problem is a minimization of a linear function of $p(M)$ with linear constraints; it cannot be solved by the usual Lagrange multiplier method. Instead, the minimum is reached at the boundary of the domain of admissible $p(M)$. Suppose N is between the integers $J-1$ and J. Then we can rewrite (4.3.26) and (4.3.27) as

$$p(J-1) + p(J) = 1 - \sum_L{}' p(L) \tag{4.3.29}$$

$$(J-1) \cdot p(J-1) + J \cdot p(J) = N - \sum_L{}' L \cdot p(L) \tag{4.3.30}$$

which can be solved for $p(J-1)$ and $p(J)$,

$$p(J-1) = J - N - \sum_L{}' p(L) \cdot (J-L) \tag{4.3.31}$$

$$p(J) = N - J + 1 - \sum_L{}' p(L) \cdot (L - J + 1) \tag{4.3.32}$$

where, for the primed summations,

$$\sum_L{}' = \sum_{L \neq J,\, J-1} \tag{4.3.33}$$

Inserting (4.3.31) and (4.3.32) into (4.3.25), we have

$$E^0(N) = (N-J+1) \cdot E^0(J) + (J-N)E^0(J-1)$$
$$+ \text{Min}\left\{\sum_L{}' p(L)[-(L-J+1)E^0(J) - (J-L)E^0(J-1) + E^0(L)]\right\} \tag{4.3.34}$$

in which $p(L)$ needs only to satisfy (4.3.28).

For each L, the value of $p(L)$ that minimizes (4.3.34) depends on the sign of the term in square brackets in (4.3.34), the quantity

$$g(L) = -(L-J+1)E^0(J) - (J-L)E^0(J-1) + E^0(L) \quad (4.3.35)$$

Since the boundary values of $p(L)$ are 0 and 1, to attain the minimum of $E^0(N)$ it is necessary that

$$\left.\begin{array}{lll} p(L)=0 & \text{if} & g(L)>0 \\ p(L)=1 & \text{if} & g(L)<0 \\ 1 \leqslant p(L) \leqslant 0 & \text{if} & g(L)=0 \end{array}\right\} \quad (4.3.36)$$

It turns out that for the atoms and molecules we always have

$$g(L) \geqslant 0 \quad (4.3.37)$$

which comes from the convexity of $E^0(M)$ in (4.1.15), or equivalently [see Equation (B.1) in Appendix B],

$$\alpha E^0(M_1) + \beta E^0(M_2) - E^0(\alpha M_1 + \beta M_2) \geqslant 0 \quad (4.3.38)$$

for $\alpha \geqslant 0$, $\beta \geqslant 0$, $\alpha + \beta = 1$, and $\alpha M_1 + \beta M_2$ also an integer. For $L > J-1$,

$$\begin{aligned} g(L) &= (L-J+1)\left[\frac{E^0(L)}{L-J+1} + \frac{(L-J)E^0(J-1)}{L-J+1} - E(J)\right] \\ &\geqslant 0 \end{aligned} \quad (4.3.39)$$

using (4.3.38). For $L < J-1$, one finds

$$\begin{aligned} g(L) &= (J-L)\left[\frac{E^0(L)}{J-L} + \frac{(J-L-1)E^0(J)}{J-L} - E(J-1)\right] \\ &\geqslant 0 \end{aligned} \quad (4.3.40)$$

using (4.3.38).

Applying (4.3.39) and (4.3.40), (4.3.36), and (4.3.34), we obtain

$$E^0(N) = (N-J+1)E^0(J) + (J-N)E^0(J-1) \quad (4.3.41)$$

in agreement with (4.3.16). If (4.3.38) is a strict inequality, that is, if $E^0(M)$ is strictly convex, we further have, from (4.3.31) and (4.3.32),

$$\left.\begin{array}{r} p(J-1) = J-N, \\ p(J) = N-J+1, \\ p(L) = 0,\ L \neq J, J-1 \end{array}\right\} \quad (4.3.42)$$

If $E^0(M)$ is only convex, then the set of $p(M)$ that minimizes (4.2.34) is not unique. Equation (4.3.41) still holds, however, as does the chemical

potential expression

$$\mu = \frac{\partial E}{\partial N} = E^0(J) - E^0(J-1) \qquad \text{for } J > N > J-1 \quad (4.3.43)$$

In summary, at the limit of zero temperature the grand-canonical-ensemble theory gives $E^0(N)$ as a continuous linear interpolation among $E^0(M)$ values, where M is integral. This assumes $E^0(M)$ to be convex at all positive integers, which is the case for atoms and molecules.

To end this section, we briefly consider another quantity of interest: the curvature of E as a function of N at 0 K,

$$2\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\theta\to 0} = \lim_{\beta\to\infty}\left[\frac{\dfrac{\partial}{\partial\mu}(\partial E/\partial N)_\beta}{(\partial N/\partial\mu)_\beta}\right] \quad (4.3.44)$$

This is found to be

$$2\eta = \begin{cases} 0, & N < N_0 \\ \lim\limits_{\beta\to\infty}[\eta_0 e^{\beta\eta_0}] = \infty, & N = N_0 \\ 0, & N > N_0 \end{cases} \quad (4.3.45)$$

where

$$\eta_0 = \frac{I - A}{2} \quad (4.3.46)$$

Alternatively, we could define

$$\eta = \left(\frac{I-A}{2}\right)\delta(N - N_0) = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{T=0} \quad (4.3.47)$$

which would accord with the identity

$$\int_{N_0-\Delta}^{N_0+\Delta}\left(\frac{\partial^2 E}{\partial N^2}\right) dN = \left(\frac{\partial E}{\partial N}\right)_{N_0+\Delta} - \left(\frac{\partial E}{\partial N}\right)_{N_0-\Delta} \quad (4.3.48)$$

since $(\partial^2 E/\partial N^2)_{\theta=0}$ is zero for the straight-line segments for $N < N_0$ and $N > N_0$. The quantity $\eta_0 = (I - A)/2$ turns out to be very important; it is the *absolute hardness* of a chemical species (Parr and Pearson 1983). Hardness will be discussed at length in the next chapter.

4.4 The chemical potential for a pure state and in the canonical ensemble

We now consider the concept of chemical potential in the canonical ensemble and for a pure state, both cases in which the number of electrons is integral.

As was described in §3.5, in the canonical ensemble one has a system of interest of N_0 particles and minimizes a functional $A[\rho]$ over densities integrating to N_0. In the $\theta = 0$ limit, which is our present concern, one minimizes $E[\rho]$ subject to proper normalization of ρ; that is,

$$E^0(N) = \underset{\rho(\mathbf{r})}{\mathrm{Min}}\, E_C[\rho] \tag{4.4.1}$$

where

$$E_C[\rho] = F_C[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} \tag{4.4.2}$$

with

$$F_C[\rho] = \underset{\hat{\Gamma}_N \to \rho}{\mathrm{Min}}\, \{\mathrm{tr}\,[\hat{\Gamma}_N(\hat{T} + \hat{V}_{ee})]\} \tag{4.4.3}$$

These are the zero-temperature limits of (3.5.13)–(3.5.15). The variational principle of (4.4.1) follows from (2.3.28), the minimizing density being the ground-state density if the ground state is nondegenerate, or an arbitrary linear combination of the ground-state densities if it is degenerate. The universal functional $F_C[\rho]$ was proposed by Valone (1980a) and Lieb (1982) to extend the Levy constrained search to all mixed states in the N-electron Hilbert space.

In the pure ground-state theory of §3.4, $F[\rho]$ of (3.4.5) is the universal functional instead of (4.4.3). The variational principle (3.4.8) is of the same form as (4.4.1). In the following discussion, these two cases are dealt with at the same time, $E[\rho]$ standing for the energy functional for both canonical ensemble and pure state.

How do we implement the variation (4.4.1) within all the densities integrating to integral N? We cannot directly use the Lagrange multiplier technique, because the constraint-free variation $\delta\{E[\rho] - \lambda[\int \rho\, d\mathbf{r} - N]\}$, where λ is the supposed Lagrange multiplier, would require $E[\rho]$ to be defined for nonintegral numbers of electron (see Appendix A), which is not the case in either the canonical ensemble (4.4.2) or the pure state (3.4.9). However, we can explicitly impose the normalization by writing

$$\rho(\mathbf{r}) = \frac{N g(\mathbf{r})}{\int g(\mathbf{r}')\, d\mathbf{r}'} \tag{4.4.4}$$

This allows $g(\mathbf{r})$ to be any nonnegative function, while $\rho(\mathbf{r})$ always still integrates to N, in the same way that normalization of wave functions is taken care of in (1.2.1) and (1.2.3). Thus, we have the ground-state variational principle

$$\frac{\delta E[\rho]}{\delta g(\mathbf{r})} = \int \left(\frac{\delta E}{\delta \rho(\mathbf{r}')}\right)_N \frac{\delta \rho(\mathbf{r}')}{\delta g(\mathbf{r})}\, d\mathbf{r}' = 0 \tag{4.4.5}$$

where we have used the chain rule, (A.24) of Appendix A. The subscript N here indicates that the functional differentiation is performed with N fixed. Using (4.4.4), we get

$$\frac{\delta\rho(\mathbf{r}')}{\delta g(\mathbf{r})} = \frac{N}{\int g(\mathbf{r}'')\,d\mathbf{r}''}\left[\delta(\mathbf{r}'-\mathbf{r}) - \frac{g(\mathbf{r}')}{\int g(\mathbf{r}'')\,d\mathbf{r}''}\right] \tag{4.4.6}$$

so that (4.4.5) gives

$$\left(\frac{\delta E}{\delta\rho(\mathbf{r})}\right)_N = \int \left(\frac{\delta E}{\delta\rho(\mathbf{r}')}\right)_N \frac{g(\mathbf{r}')}{\int g(\mathbf{r}'')\,d\mathbf{r}''}\,d\mathbf{r}' \tag{4.4.7}$$

The right-hand side of (4.4.7) is a constant independent of $\mathbf{r}$. This constant cannot be determined by (4.4.7), because any value makes (4.4.7) an identity. Therefore,

$$\left(\frac{\delta E}{\delta\rho(\mathbf{r})}\right)_N = C \tag{4.4.8}$$

with C an arbitrary constant.

Contained in (4.4.8) is the equivalent of the Schrödinger equation for the ground state. Comparing with (4.1.7), we see that chemical potential μ does not occur in (4.4.8) and its existence in the theory at this stage is solely due to the grand-canonical ensemble extension of the ground-state theory.

The chemical potential concept can also be identified in the canonical ensemble theory, however. The simple way to do this is to follow the procedure that is used for canonical ensemble theory in statistical mechanics, the finite-difference method (see p. 41 of Ashcroft and Mermin 1976). Thus, for the system of N electrons, we take [and note that this accords with (4.3.15)]

$$\mu^- = \frac{E(N-1)-E(N)}{-1} = -I \quad \text{(slope when the system gives up an electron)} \tag{4.4.9}$$

$$\mu^+ = E(N+1)-E(N) = -A \quad \text{(slope when the system adds an electron)} \tag{4.4.10}$$

$$\mu^0 = -\frac{I+A}{2} \quad \text{(slope when an electron is neither given up nor added)} \tag{4.4.11}$$

Also, the curvature of $E(N)$ becomes

$$\eta = \tfrac{1}{2}[E(N+1)-E(N)-(E(N)-E(N-1))] = \tfrac{1}{2}(I-A) \tag{4.4.12}$$

Note the difference between this formula and (4.3.45).

Another way to recover the chemical potential is to extend the minimization (4.4.1) to *all* different *integral* N. In this case the Lagrange multiplier μ becomes fuzzy if one makes no further assumptions (Parr and Bartolotti 1983). Consider at what density the quantity $E[\rho]-\mu N[\rho]$ will in fact be a minimum, if only trial densities normalized to integers are used. If $\int \rho\, d\mathbf{r}=N_0$, the minimum value is $E[\rho_0(N_0)]-\mu N_0$, where $E[\rho_0(N_0)]$ is the ground-state energy for N_0 electrons. Similarly, if $\int \rho\, d\mathbf{r}=N_0+1$, the minimum value will be $E[\rho_0(N_0+1)]-\mu(N_0+1)]$; if $\int \rho\, d\mathbf{r}=N_0-1$, it will be $E[\rho_0(N_0-1)]-\mu(N_0-1)$. Of these three numbers, the smallest depends on the value of μ and on the values of the three energies. The smallest will be the first, $E[\rho_0(N_0)]-\mu N_0$, if μ is in the range

$$A \leqslant -\mu \leqslant I \tag{4.4.13}$$

where I and A respectively are the ionization potential and electron affinity of the species with $N=N_0$. Note that (4.4.9) to (4.4.11) give μ values in this range. With any value of μ satisfying (4.4.13), the minimum of $E[\rho]-\mu N[\rho]$ over all ρ integrating to different integers will give $E[\rho_0(N_0)]-\mu N_0$. Equation (4.4.13) also implies that $E^0(N)$ needs to be convex [see (4.1.15)]. Trial ρ may in fact be limited to those integrating to integers.

4.5 Discussion

Although the zero-temperature limit of the grand canonical ensemble provides a natural definition for the ground state of nonintegral-N systems, the *continuous straight-line segments for* $E^0(N)$ *need not be* correct for a species imbedded in some environment, or for an atom or functional group in a molecule. In most actual situations we can reasonably imagine interpolating among values of ground-state energies for integral numbers of electrons, thereby extending the minimum search of (4.4.1) to arbitrary densities. Then we will be able to use Lagrange-multiplier techniques,

$$\delta\left\{E[\rho]-\mu\int \rho\, d\mathbf{r}\right\}=0 \tag{4.5.1}$$

or

$$\mu=\frac{\delta E[\rho]}{\delta\rho(r)} \tag{4.5.2}$$

For example, a parabolic fit of the three points $E^0(N-1)$, $E^0(N)$, and $E^0(N-1)$ for integral N, gives $\mu=-(I+A)/2$, in agreement with (4.4.11), and $\eta=(I-A)/2$ in agreement with (4.4.12).

In fact, (4.5.2) is more convenient to handle than (4.4.8), because

$(\delta E/\delta\rho(\mathbf{r}))_N$ is hard to evaluate. Thus, in many practical applications of density functional theory, instead of (4.4.8), (4.5.2) is used, where some interpolation or other is implicit in the treatment of $E[\rho]$.

The difference between $\delta E/\delta\rho$ and $(\delta E/\delta\rho)_N$ is itself worth some elaboration (Parr and Bartolotti 1983). One has $E = E[\rho, v]$. Writing

$$\rho = N\sigma \tag{4.5.3}$$

where σ is a *shape factor*,

$$\int \sigma(\mathbf{r})\, d\mathbf{r} = 1 \tag{4.5.4}$$

one has $E = E[N, \sigma, v]$ as well. Therefore we may write

$$\begin{aligned}\delta E &= \int \left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_v \delta\rho(\mathbf{r})\, d\mathbf{r} + \int \left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_\rho \delta v(\mathbf{r})\, d\mathbf{r} \\ &= \int \left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_v [\sigma(\mathbf{r})\, \delta N + N\, \delta\sigma(\mathbf{r})]\, d\mathbf{r} + \int \left[\frac{\delta E}{\delta v(\mathbf{r})}\right]_\rho \delta v(\mathbf{r})\, d\mathbf{r}\end{aligned} \tag{4.5.5}$$

and also

$$\delta E = \left(\frac{\partial E}{\partial N}\right)_{\sigma,v} \delta N + \int \left[\frac{\delta E}{\delta\sigma(\mathbf{r})}\right]_{N,v} \delta\sigma(\mathbf{r})\, d\mathbf{r} + \int \left[\frac{\delta E}{\delta v(\mathbf{r})}\right]_\rho \delta v(\mathbf{r})\, d\mathbf{r} \tag{4.5.6}$$

Subtracting these equations we find, since δN and $\delta v(r)$ are independent,

$$\left(\frac{\partial E}{\partial N}\right)_{\sigma,v} = \int \left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_v \sigma(\mathbf{r})\, d\mathbf{r} \tag{4.5.7}$$

and

$$\int \left\{N\left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_v - \left[\frac{\delta E}{\delta\sigma(\mathbf{r})}\right]_{N,v}\right\} \delta\sigma(\mathbf{r})\, d\mathbf{r} = 0 \tag{4.5.8}$$

Equation (4.5.7) will not here concern us further.

Does (4.5.8) mean that the term in curly brackets is identically zero? No, because (4.5.4) implies that

$$\int \delta\sigma(\mathbf{r})\, d\mathbf{r} = 0 \tag{4.5.9}$$

Together, (4.5.8) and (4.5.9) imply that

$$N\left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_v - \left[\frac{\delta E}{\delta\sigma(\mathbf{r})}\right]_{N,v} = \text{constant} \tag{4.5.10}$$

or,

$$\left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_{N,v} = \left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_v + \text{constant} \tag{4.5.11}$$

where the constant cannot be evaluated without more information. The mathematical lemma used here is well known (Courant and Hilbert 1953, p. 201). Note that (4.5.11) is compatible with (4.4.8) and (4.5.2).

In this chapter we have discussed the concept of chemical potential from various angles: the zero-temperature limit of the grand-canonical-ensemble theory, the finite difference in the pure-state theory, the differential in the interpolation theory, and the fuzzy result from consideration of pure states in the Fock space. Equations (4.4.9)–(4.4.12) are clear-cut definitions for most practical purposes. The discontinuity of chemical potential at integral numbers of electrons turns out to be of major importance in calculations of band gaps of solids (Perdew and Levy 1983, Sham and Schlüter 1985. Gunnarsson and Schönhammer 1986, Schönhammer and Gunnarsson 1987, Shen, Bylander, and Kleinman 1988, Sham and Schlüter 1988).

Ensembles other than the ones we have considered are also of interest. For example, see the Tachibana (1989) proposal to incorporate constraints for an apparatus, affording the possibility of turning an excited state into a ground state and thereby making it accessible to ground-state theory.