

6

THOMAS-FERMI AND RELATED MODELS

6.1 The traditional TF and TFD models

Given an N -electron system of interest with Hamiltonian (1.1.2), ground-state energy E , wave function Ψ , and electron density $\rho(\mathbf{r})$, we have proved in Chapter 3, and developed at some length there and in Chapter 4, the fact that $\rho(\mathbf{r})$ determines $v(\mathbf{r})$, N , and the energy $E[\rho]$, and the fact that $\rho(\mathbf{r})$ is a solution of the stationary principle

$$\delta\{E[\rho] - \mu N[\rho]\} = 0 \quad (6.1.1)$$

where μ is a Lagrange multiplier and $N[\rho] = \int \rho(\mathbf{r}) d\mathbf{r}$. $E[\rho]$ is the functional

$$E[\rho] = T[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + V_{ee}[\rho] \quad (6.1.2)$$

where $T[\rho]$ is the kinetic energy and $V_{ee}[\rho]$ is the electron-electron interaction energy. The classical part of $V_{ee}[\rho]$ is the Coulomb potential energy

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (6.1.3)$$

The problem remains, and this problem is of surpassing difficulty, of how to calculate $T[\rho]$, and how to calculate the nonclassical part of $V_{ee}[\rho]$. We will be dealing with these two questions in this and the next two chapters.

The traditional Thomas-Fermi (TF) model is a first approximation: replace $V_{ee}[\rho]$ by $J[\rho]$ of (6.1.3) and take $T[\rho]$ from the theory of a noninteracting uniform electron gas (Fermi 1927, Thomas 1927). We have already introduced this model in §3.1, but we will rederive it in this section. The traditional Thomas-Fermi-Dirac (TFD) model is a reasonable next guess: accept the $T[\rho]$ of Thomas-Fermi theory and for approximation to $V_{ee}[\rho]$ add to $J[\rho]$ the exchange-energy formula for a uniform electron gas (Dirac 1930). Never mind that an atomic or molecular electron cloud obviously is not a uniform gas; let us see what these assumptions bring. The literature of this subject is vast; for reviews see Gombas (1949), March (1957, 1975), and Lieb (1981b). Our summary in this chapter is far from complete.

We will derive TF and TFD theories together, since TF is obtained straightforwardly from TFD by ignoring the exchange contribution. We take as our starting point the Hartree–Fock model of §1.3 and §2.5. For simplicity, consider a nondegenerate closed-shell ground state described by a single-determinantal wave function of the form (1.3.1), a first-order density matrix of the form (2.5.1), and a spinless first-order density matrix of the form

$$\rho_1(\mathbf{r}_1, \mathbf{r}'_1) = 2 \sum_i^{N/2} \phi_i(\mathbf{r}_1) \phi_i^*(\mathbf{r}'_1) \quad (6.1.4)$$

where the ϕ_i are the doubly occupied spatial orbitals. The energy then is given by (2.5.20),

$$\begin{aligned} E_{\text{HF}}[\rho_1] = & \int \left[-\frac{1}{2} \nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \right]_{\mathbf{r}_2=\mathbf{r}_1} d\mathbf{r}_1 + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \\ & + J[\rho] - \frac{1}{4} \iint \frac{1}{r_{12}} \rho_1(\mathbf{r}_1, \mathbf{r}_2) \rho_1(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (6.1.5)$$

Comparing with (6.1.2), we identify

$$T[\rho] = \int \left[-\frac{1}{2} \nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \right]_{\mathbf{r}_2=\mathbf{r}_1} d\mathbf{r}_1 \quad (6.1.6)$$

and

$$V_{ee}[\rho] = J[\rho] - K[\rho] \quad (6.1.7)$$

where $K[\rho]$ is the HF exchange-energy functional

$$K[\rho] = \frac{1}{4} \iint \frac{1}{r_{12}} |\rho_1(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \quad (6.1.8)$$

As expressed in (6.1.7), our first assumption then is that correlation effects can be ignored in $V_{ee}[\rho]$. We are left with the problem of expressing $T[\rho]$ and $K[\rho]$ in terms of the diagonal element of ρ_1 , the electron density ρ . For an approximate solution to this problem, we turn to the electron gas.

In §3.1 we built the uniform-gas description from particle-in-a-box states for which the boundary conditions had the form $\psi(x=0) = \psi(x=l) = 0$. Equivalently, for a large number of particles (equivalence requires N to be large; see Acharya 1983), one can employ periodic boundary conditions, of the type $\psi(x+l) = \psi(x)$. These lead to the orbitals

$$\begin{aligned} \psi(k_x, k_y, k_z) &= \frac{1}{l^{3/2}} e^{i(k_x x + k_y y + k_z z)} \\ &= \frac{1}{V^{1/2}} e^{i\mathbf{k} \cdot \mathbf{r}} \end{aligned} \quad (6.1.9)$$

where

$$k_x = \frac{2\pi}{l} n_x, \quad k_y = \frac{2\pi}{l} n_y, \quad k_z = \frac{2\pi}{l} n_z,$$

with $n_x, n_y, n_z = 0, \pm 1, \pm 2 \dots$. The energy levels are

$$E(n_x, n_y, n_z) = \frac{\hbar^2}{8ml^2} [(2n_x)^2 + (2n_y)^2 + (2n_z)^2]$$

which for large quantum numbers correspond to just the number per unit energy range given by (3.1.3). With (6.1.9) for the orbitals, the density matrix of (6.1.4) becomes

$$\rho_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{2}{V} \sum_{\text{all occupied } \mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \quad (6.1.10)$$

If there are very many occupied states, the sum can be replaced by an integral, giving

$$\begin{aligned} \rho_1(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{4\pi^3} \int e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} d\mathbf{k} \\ &= \frac{1}{4\pi^3} \int_0^{k_F} k^2 dk \iint e^{i\mathbf{k} \cdot \mathbf{r}_{12}} \sin \theta d\theta d\phi \end{aligned} \quad (6.1.11)$$

In going from (6.1.10) to (6.1.11), we have used $dn = (l/2\pi)^3 d\mathbf{k} = (V/8\pi^3) d\mathbf{k}$. The quantity k_F , which may be a function of position, is still to be determined. Since $\rho_1(\mathbf{r}, \mathbf{r}) = \rho(\mathbf{r})$, (6.1.11) gives

$$\rho(\mathbf{r}) = \frac{k_F^3}{3\pi^2} \quad \text{or} \quad k_F(\mathbf{r}) = [3\pi^2 \rho(\mathbf{r})]^{1/3} \quad (6.1.12)$$

For an inhomogeneous system, the natural choice of the argument of $k_F(\mathbf{r})$ to be used in (6.1.11) is the average of \mathbf{r}_1 and \mathbf{r}_2 . We therefore introduce the coordinates

$$\mathbf{r} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \quad \mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2 \quad (6.1.13)$$

and proceed to carry out the integrations in (6.1.11) and to put the result into (6.1.6) and (6.1.8).

Choose \mathbf{s} to lie along the k_z axis. Then (6.1.11) can be evaluated as follows:

$$\begin{aligned} \rho_1(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{4\pi^3} \int_0^{k_F} k^2 dk \int_{\theta=0}^{\pi} \sin \theta e^{ikr_{12}\cos\theta} d\theta \int_0^{2\pi} d\phi \\ &= 3\rho(\mathbf{r}) \left[\frac{\sin t - t \cos t}{t^3} \right] = \rho_1(\mathbf{r}, \mathbf{s}) \end{aligned} \quad (6.1.14)$$

where

$$t = k_F(\mathbf{r})s \quad (6.1.15)$$

Equation (6.1.14) is the important exact formula for the first-order spinless density matrix for a uniform gas, expressed in the coordinates \mathbf{r} and s . Note that only the magnitude of \mathbf{s} enters.

To evaluate the kinetic energy, we need

$$\nabla_{\mathbf{r}_1}^2 = \frac{1}{4}\nabla_{\mathbf{r}}^2 + \nabla_s^2 + \nabla_{\mathbf{r}}\nabla_s, \quad \nabla_{\mathbf{r}_2}^2 = \frac{1}{4}\nabla_{\mathbf{r}}^2 + \nabla_s^2 - \nabla_{\mathbf{r}}\nabla_s \quad (6.1.16)$$

Thus

$$\begin{aligned} [\nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2)]_{\mathbf{r}_2=\mathbf{r}_1} &= [(\frac{1}{4}\nabla_{\mathbf{r}}^2 + \nabla_s^2 + \nabla_{\mathbf{r}}\nabla_s)\rho_1(\mathbf{r}, s)]_{s=0} \\ &= \frac{1}{4}\nabla_{\mathbf{r}}^2 \rho(\mathbf{r}) - \frac{3}{5}(3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3} \end{aligned} \quad (6.1.17)$$

Now for any well-behaved $\rho(\mathbf{r})$,

$$\int \nabla^2 \rho(\mathbf{r}) d\mathbf{r} = 0 \quad (6.1.18)$$

so that the kinetic energy of (6.1.6) becomes

$$T_{\text{TF}}[\rho] = C_F \int \rho(\mathbf{r})^{5/3} d\mathbf{r}, \quad \text{with} \quad C_F = \frac{3}{10}(3\pi^2)^{2/3} = 2.8712 \quad (6.1.19)$$

This is the Thomas–Fermi kinetic-energy formula, (3.1.9).

The exchange energy may be obtained similarly, by substituting (6.1.14) into (6.1.8):

$$\begin{aligned} K_D[\rho] &= \frac{1}{4} \iint \frac{[\rho_1(\mathbf{r}, s)]^2}{s} d\mathbf{r} ds \\ &= 9\pi \int \rho^2(\mathbf{r}) \frac{1}{k_F^2} d\mathbf{r} \left[\int_0^\infty \frac{(\sin t - t \cos t)^2}{t^5} dt \right] \\ &= C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}, \quad \text{with} \quad C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} = 0.7386 \end{aligned} \quad (6.1.20)$$

This is the famous exchange-energy formula of Dirac (1930). The integral in the second line of this derivation can be evaluated as follows. Let $q = (\sin t/t)$. Then

$$\frac{dq}{dt} = - \left[\frac{\sin t - t \cos t}{t^2} \right] \quad \text{and} \quad \frac{d^2q}{dt^2} = - \frac{2}{t} \frac{dq}{dt} - q$$

Therefore

$$\begin{aligned} \int_0^\infty \frac{(\sin t - t \cos t)^2}{t^5} dt &= \int_0^\infty \left(\frac{dq}{dt} \right) \left(\frac{1}{t} \frac{dq}{dt} \right) dt \\ &= \int_0^\infty \left(\frac{dq}{dt} \right) \left(-\frac{1}{2}q - \frac{1}{2} \frac{d^2q}{dt^2} \right) dt \\ &= -\frac{1}{4} \int_0^\infty \frac{d}{dt} \left[q^2 + \left(\frac{dq}{dt} \right)^2 \right] dt = \frac{1}{4} \end{aligned} \quad (6.1.21)$$

Insertion of (6.1.19) and (6.1.20) into (6.1.2) gives, finally,

$$E_{\text{TFD}}[\rho] = C_F \int \rho(\mathbf{r})^{5/3} d\mathbf{r} + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + J[\rho] - C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r} \quad (6.1.22)$$

This is the Thomas-Fermi-Dirac energy functional, and is labeled TFD accordingly. The Thomas-Fermi energy functional of (3.1.10) is obtained by setting $C_x = 0$. The corresponding Euler-Lagrange equation is, from (6.1.1),

$$\mu_{\text{TFD}} = \frac{5}{3}C_F\rho^{2/3}(\mathbf{r}) - \frac{4}{3}C_x\rho^{1/3}(\mathbf{r}) - \phi(\mathbf{r}) \quad (6.1.23)$$

where $\phi(\mathbf{r})$ is the classical electrostatic potential—see (3.1.14). This equation constitutes a generalization of the Thomas-Fermi formula (3.1.13). In the next section we will discuss solution of the TF and TFD equations.

The form of the energy functional (6.1.22) is not especially surprising, as can be seen from the following quick derivation of it up to the values of the coefficients. Suppose that the kinetic energy had the form of a local functional (see definition in Appendix A) $T[\rho] = \int t(\rho) d\mathbf{r}$, where $t(\rho)$ is a function of $\rho(\mathbf{r})$. Let the wave function be $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$. Then if we scale the wave function as in (1.6.16), the density becomes the scaled density

$$\rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r}) \quad (6.1.24)$$

and the kinetic energy becomes, *naively assuming* the scaling of (1.6.17),

$$\begin{aligned} T[\rho_\lambda] &= \int t(\lambda^3\rho(\lambda\mathbf{r})) d\mathbf{r} = \lambda^{-3} \int t(\lambda^3\rho(\mathbf{r})) d\mathbf{r} \\ &= \lambda^2 \int t(\rho(\mathbf{r})) d\mathbf{r} = \lambda^2 T[\rho] \end{aligned} \quad (6.1.25)$$

Accordingly,

$$t(\lambda^3\rho(\mathbf{r})) = \lambda^5 t(\rho(\mathbf{r})) \quad (6.1.26)$$

or

$$t(\lambda\rho) = \lambda^{5/3} t(\rho) \quad (6.1.27)$$

That is to say, $t(\rho)$ is homogeneous of degree $5/3$ in ρ ; $T[\rho] = A \int \rho^{5/3} d\mathbf{r}$, the Thomas-Fermi form. Similarly, since $K[\rho]$ is an electron-electron repulsion term, using (1.6.18) if we had $K[\rho] = \int k(\rho) d\mathbf{r}$, we would naively expect

$$k(\rho_\lambda) = \lambda k[\rho] \quad (6.1.28)$$

so that

$$k(\lambda\rho) = \lambda^{4/3} k(\rho) \quad (6.1.29)$$

This is to say, $k(\rho)$ is homogeneous of degree $4/3$ in ρ ; $K[\rho] = B \int \rho^{4/3} d\mathbf{r}$, the Dirac form. In summary, an energy functional of the form

$$E[\rho] = A \int \rho(\mathbf{r})^{5/3} d\mathbf{r} + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + J[\rho] - B \int \rho(\mathbf{r})^{4/3} d\mathbf{r} \quad (6.1.30)$$

follows from assumptions of locality (in the sense indicated above) of the kinetic energy and exchange energy kernels and scaling arguments; "statistical" ideas as such need not be invoked. As we shall see in §6.5, the Thomas–Fermi–Dirac values of A and B are not sacrosanct. For a discussion of the naiveté of this scaling procedure, see §11.1.

6.2 Implementation

The Euler equations for Thomas–Fermi and Thomas–Fermi–Dirac theory are (3.1.13) and (6.1.23), respectively. In each case the chemical potential μ is to be determined so that $\rho(\mathbf{r})$ is normalized to N .

Without going into a full mathematical analysis, for which see Lieb (1981b), we note that the existence of solutions of these equations, for a particular atomic or molecular system, should not be taken for granted. Further, if a solution for the density exists it may or may not have all of the qualitative properties the exact Schrödinger density should possess. For example, consider the cusp condition (1.5.3) for an atom. From (3.1.14), $\phi(0) = \infty$ for an atom, and in either TF or TFD theory we will have at the nucleus of an atom (or at any nucleus in a molecule)

$$\rho(0) = \infty \quad (6.2.1)$$

This is a basic defect in TF or TFD theory, to which we shall return in §6.4.

For a neutral atom or molecule,

$$\phi(\mathbf{r}) \rightarrow 0 \quad \text{as } r \rightarrow \infty \quad (6.2.2)$$

Since this must also be the behavior of $\rho(\mathbf{r})$, we obtain from (3.1.13)

$$\mu_{\text{TF}}(N = Z) = 0 \quad (6.2.3)$$

This also holds for TFD theory; from (6.1.23)

$$\mu_{\text{TFD}}(N = Z) = 0 \quad (6.2.4)$$

Note, however, that since $\rho^{2/3}$ decays faster than $\rho^{1/3}$, and at large distances $\phi \geq 0$, (6.1.23) gives an incorrect result at large r for a neutral species unless all the electronic charge is contained within some critical radius $r = r_c$; the Thomas–Fermi–Dirac neutral atom has a finite size. Negative ions exist in neither model.

Explicit solution for ρ for the Thomas–Fermi neutral atom proceeds as

follows. Solve (3.1.13) and (3.1.14) each for ϕ , equate, and use (6.2.3). There results

$$C\rho^{2/3}(\mathbf{r}) = \frac{Z}{r} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' = \phi(\mathbf{r}) \quad (6.2.5)$$

Alternatively, $\rho(\mathbf{r})$ is a function of the electrostatic potential $\phi(\mathbf{r})$,

$$\rho(\mathbf{r}) = \left(\frac{1}{C}\right)^{3/2} [\phi(\mathbf{r})]^{3/2} \quad (6.2.6)$$

Now use the Poisson equation of classical electrostatics as applied to the atom,

$$\nabla^2 \phi(\mathbf{r}) = 4\pi\rho(\mathbf{r}) - 4\pi Z \delta(\mathbf{r}) \quad (6.2.7)$$

to give

$$\nabla^2 \phi(\mathbf{r}) = 4\pi \left(\frac{1}{C}\right)^{3/2} [\phi(\mathbf{r})]^{3/2} - 4\pi Z \delta(\mathbf{r}) \quad (6.2.8)$$

This is a differential equation for $\phi(\mathbf{r})$. It, like $\rho(\mathbf{r})$, depends only on the scalar r , since the atom must be spherically symmetric. Write

$$\phi(\mathbf{r}) = \phi(r) = \frac{Z}{r} \chi(r) \quad (6.2.9)$$

so that

$$\nabla^2 \phi(\mathbf{r}) = \frac{Z}{r} \frac{d^2 \chi(r)}{dr^2} - 4\pi Z \chi(0) \delta(\mathbf{r}) \quad (6.2.10)$$

(6.2.8) then becomes

$$\frac{d^2 \chi(r)}{dr^2} = 4\pi \left(\frac{1}{C}\right)^{3/2} \frac{Z^{1/2}}{r^{1/2}} [\chi(r)]^{3/2} \quad (6.2.11)$$

with the boundary condition $\chi(0) = 1$.

Finally, if we let

$$x = \alpha r, \quad \alpha = Z^{1/3} (4\pi)^{2/3} \left(\frac{1}{C}\right) = (128/9\pi^2)^{1/3} Z^{1/3} = 1.1295 Z^{1/3} \quad (6.2.12)$$

we obtain a universal differential equation for $\chi(x)$,

$$\frac{d^2 \chi(x)}{dx^2} = \frac{1}{x^{1/2}} [\chi(x)]^{3/2} \quad (6.2.13)$$

with the boundary conditions

$$\chi(0) = 1, \quad \chi(\infty) = 0 \quad (6.2.14)$$

This problem can be solved numerically. For a table of values of χ and some good discussion, see Landau and Lifshitz (1958), pp. 235–240. The derivatives of $\chi(x)$ at $x = 0$ and $x = \infty$ are of special interest; for them,

one finds

$$\chi'(0) = -1.5881, \quad \chi'(\infty) = 0 \quad (6.2.15)$$

From (6.2.6) and (6.2.9), the electron density as a function of the variable x is given by

$$\rho(x) = \frac{32}{9\pi^3} \left[\frac{\chi(x)}{x} \right]^{3/2} Z^2 = \frac{32Z^2}{9\pi^3 x} \left[\frac{d^2\chi(x)}{dx^2} \right] \quad (6.2.16)$$

Since $x = \alpha r$, we infer the behavior near the nucleus to be

$$\rho(\text{small } r) \sim \frac{1}{r^{3/2}} \rightarrow \infty \quad \text{as } r \rightarrow 0 \quad (6.2.17)$$

For large r , the simple analytic solution of (6.2.13) is the one we want,

$$\chi(x) = \frac{144}{x^3} \quad \text{for very large } x \quad (6.2.18)$$

From this we infer that

$$\rho(\text{large } r) \sim \frac{1}{r^6} \rightarrow 0 \quad \text{as } r \rightarrow \infty \quad (6.2.19)$$

Neither (6.2.17) nor (6.2.19) reproduces the correct behavior of exact atomic densities. The radial distribution function $r^2\rho(r)$ is zero at the origin, peaks at $x = 0.42$, and falls off to zero without showing any shell structure. Half the charge is within $x = 1.50$ or $r = 1.33Z^{-1/3}$. The agreement with real atomic densities is rough at best.

The total energy of a neutral atom in Thomas–Fermi theory is given by the formula

$$E_{\text{TF}} = -0.7687Z^{7/3} \quad (6.2.20)$$

One can establish this result by substituting (6.2.16) into (6.1.22) and performing the integrations numerically. Somewhat more cleanly, one may make use of

$$\begin{aligned} \left(\frac{\partial E}{\partial N} \right)_{N=Z} &= \left(\frac{\partial E}{\partial N} \right)_Z + \left(\frac{\partial E}{\partial Z} \right)_N \left(\frac{\partial Z}{\partial N} \right)_{N=Z} \\ &= \mu + \left(\frac{\partial E}{\partial Z} \right)_N \end{aligned} \quad (6.2.21)$$

the fact that $\mu = 0$ in Thomas–Fermi theory for neutral atoms, and the fact that (from the Hellman–Feynmann theorem, which was shown by Harris, Jones and Miller (1981) to hold in density-functional theory)

$$\left(\frac{\partial E}{\partial Z} \right)_N = - \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} \quad (6.2.22)$$

Consequently, for a neutral atom in Thomas-Fermi theory,

$$\left(\frac{\partial E}{\partial Z}\right)_{N=Z} = \left(\frac{\partial E}{\partial Z}\right)_N = -\int \frac{\rho(\mathbf{r}, z)}{r} d\mathbf{r} \quad (6.2.23)$$

and

$$E = -\int_0^Z dZ \left[\int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} \right] \quad (6.2.24)$$

which can be evaluated employing (6.2.12), (6.2.15), and the second formula in (6.2.16):

$$\begin{aligned} E &= -4\pi \int_0^Z dZ \int \frac{1}{\alpha^2} x\rho(x) dx \\ &= -3/7(1.1295)[\chi'(\infty) - \chi'(0)]Z^{7/3} = -0.7687Z^{7/3} \end{aligned} \quad (6.2.25)$$

This is the energy of the Thomas-Fermi neutral atom. For real atoms we have, in contrast, the Hartree-Fock values exhibited in Table 6.1. Equation (6.2.25) gives too low an energy by 54% for H, by 35% for He, by 20% for Kr, and by 15% for Rn.

Thomas-Fermi-Dirac theory does not constitute an improvement; indeed, it is worse. One can see this without any calculation at all. $K[\rho]$ is positive, so E_{TFD} of (6.1.22) is more negative than E_{TF} of (3.1.10) for a given ρ . Putting the Thomas-Fermi density ρ_{TF} into (6.1.20) gives

$$K_D[\rho_{\text{TF}}] = 0.221Z^{5/3} \quad (6.2.26)$$

This is negligible for large enough Z , but it pulls the energy down. And a full minimization of $E_{\text{TFD}}[\rho]$ with respect to ρ will give a lower energy still.

In both TFD and TF theories, it is readily seen that positive ions have finite size. For the TF theory for molecules, with numerical results for N_2 and C_6H_6 , see Parker (1988).

Table 6.1 Energies of Neutral Atoms ($-E/Z^{7/3}$)

| Atom (Z) | Hartree-Fock Energy ^a | Modified Thomas-Fermi Model ^b |
|--------------|----------------------------------|--|
| He (2) | 0.5678 | 0.4397 |
| Ne (10) | 0.5967 | 0.5763 |
| Ar (18) | 0.6204 | 0.6110 |
| Kr (36) | 0.6431 | 0.6439 |
| Xe (54) | 0.6562 | 0.6599 |
| Rn (86) | 0.6698 | 0.6745 |

^a In conventional Thomas-Fermi theory, the energy is given by (6.2.25) of the text: $-E/Z^{7/3} = 0.7687$.

^b Model of §6.4 of text (Parr and Ghosh 1986).

6.3 Three theorems in Thomas–Fermi theory

Many theorems have been proved in Thomas–Fermi theory (Lieb 1981b). Here we consider just three. The first theorem gives formulas relating the energy quantities T , V_{ne} , V_{ee} , $N\mu$, V_{nn} , E (total electronic energy exclusive of nuclear–nuclear repulsion), and W (total energy including nuclear–nuclear repulsion). For simplicity consider a ground-state Thomas–Fermi atom or molecule at its equilibrium nuclear configuration. Then, by (3.1.13),

$$\rho^{2/3}(\mathbf{r}) = \frac{3}{5C_F} [\phi(\mathbf{r}) + \mu] \quad (6.3.1)$$

The kinetic energy of (6.1.19) therefore becomes, using the definitions of $\phi(\mathbf{r})$, $V_{ne}[\rho]$ and $V_{ee}[\rho]$,

$$T[\rho] = -\frac{3}{5}V_{ne}[\rho] - \frac{6}{5}V_{ee}[\rho] + \frac{3}{5}N\mu \quad (6.3.2)$$

Now the virial theorem of (1.6.10) or (1.6.11) holds for Thomas–Fermi theory, since the scaling proof at the end of §1.6 goes through for any density-functional model with appropriate scaling behavior. Hence

$$\begin{aligned} T[\rho] &= -\frac{1}{2}V_{ne}[\rho] - \frac{1}{2}V_{ee}[\rho] - \frac{1}{2}V_{nn} \\ &= -W[\rho] = -E[\rho] - V_{nn} \end{aligned} \quad (6.3.3)$$

These equations plus (6.3.2) imply the formulas

$$\begin{aligned} V_{ne}[\rho] &\approx \frac{7}{3}E[\rho] + \frac{1}{3}V_{nn} - N\mu \\ V_{ee}[\rho] &\approx -\frac{1}{3}E[\rho] + \frac{2}{3}V_{nn} + N\mu \end{aligned} \quad (6.3.4)$$

These may be called the *Fraga relations* (Fraga, 1964).

The second theorem is the *nonbinding theorem*. Originally asserted by Teller (1962), with a proof faulted and improved by Balazs (1967), and generalized and made rigorous by Lieb and Simon (1973, 1977), this theorem states that in Thomas–Fermi theory no molecular system is stable relative to dissociation into constituent fragments. Indeed, whenever all internuclear distances are dilated uniformly, from any starting nuclear configuration, the *total* energy decreases. (Without the nuclear–nuclear repulsion, the contrary holds: nuclei coming together enhance the electronic component of the binding energy.)

For simplicity, consider a homonuclear neutral diatomic molecule AB, with nuclear charges λZ_A , Z_B , number of electrons $\lambda Z_A + Z_B$, at fixed internuclear distance R . We wish to prove that the binding energy

$$\Delta W(\lambda) = E_{AB}(\lambda) - E_A(\lambda) - E_B + \frac{\lambda Z_A Z_B}{R} \quad (6.3.5)$$

is positive for $\lambda = 1$. To do this we shall use [much as in the derivation of

(6.2.24)] the Hellman-Feynmann theorem to determine $\partial\Delta W(\lambda)/\partial\lambda$, and then calculate $\Delta W(1) = \int_0^1 [\partial W(\lambda)/\partial\lambda] d\lambda$. Thus,

$$\frac{\partial\Delta W(\lambda)}{\partial\lambda} = -Z_A \int \frac{\rho_{AB}(\mathbf{r}, \lambda)}{r_A} d\mathbf{r} + Z_A \int \frac{\rho_A(\mathbf{r}, \lambda)}{r_A} d\mathbf{r} + \frac{Z_A Z_B}{R} \quad (6.3.6)$$

where $\rho_{AB}(\mathbf{r}, \lambda)$ and $\rho_A(\mathbf{r}, \lambda)$ are the (Thomas-Fermi) electron densities for the molecule AB and the atom A, respectively. This can be rewritten as

$$\frac{\partial\Delta W(\lambda)}{\partial\lambda} = Z_A [\phi_{AB}(0, \lambda) - \phi_A(0, \lambda)] \quad (6.3.7)$$

where $\phi_{AB}(0, \lambda)$ is the electrostatic potential at nucleus A in the molecule and $\phi_A(0, \lambda)$ is the corresponding potential in the atom (the terms in ϕ_{AB} and ϕ_A representing the potential due to nucleus A cancel in $\phi_{AB} - \phi_A$.) Now, there is a lemma in Thomas-Fermi theory [Lieb 1981b, Theorem 34 on p. 612], that if the external potential $v(\mathbf{r})$ is increased everywhere (as by the increase of a nuclear charge), with an accompanying electron number change keeping μ constant (at zero in the present case), ϕ increases everywhere. Hence, $\phi_{AB}(0, \lambda) > \phi_A(0, \lambda)$, $\partial\Delta W/\partial\lambda > 0$ for all λ , and since $\Delta W = 0$ for $\lambda = 0$, the theorem follows.

The implications for theoretical chemistry are, of course, devastating. There is no hope of accounting for chemical bonding by Thomas-Fermi theory. It is even worse than that. Balazs (1967) argues that the same will be true for any other model (for example the Thomas-Fermi-Dirac model) for which the electron density turns out to be a function of the total classical electrostatic potential,

$$\rho(\mathbf{r}) = \rho(\phi) \quad (\text{precludes bonding}) \quad (6.3.8)$$

On the other hand, it has been demonstrated (Parr and Berk 1981) that binding is allowed if the electron density is a function of the bare nuclear (external) potential,

$$\rho(\mathbf{r}) = \rho(v) \quad (\text{can sustain binding}) \quad (6.3.9)$$

This last would mean contours of the electron density would be parallel to contours of the bare nuclear potential, which is usually a fair description (Parr and Berk 1981, but see Politzer and Zilles 1984).

The third theorem is rather more constructive. In the limit of high atomic numbers and electron numbers, Thomas-Fermi theory is asymptotically correct in a relative sense. Specifically, let E_Q and E_{TF} be the Schrödinger exact energy and the Thomas-Fermi energy for a system of nuclear charges Z_α , at locations R_α , having N electrons, and let the corresponding electron densities be $\rho_Q(\mathbf{r})$ and $\rho_{TF}(\mathbf{r})$. Then

$$\lim_{\lambda \rightarrow \infty} \lambda^{-7/3} E_Q(\lambda Z_\alpha, \lambda N, \lambda R_\alpha) = \lim_{\lambda \rightarrow \infty} \lambda^{-7/3} E_{TF}(\lambda Z_\alpha, \lambda N, \lambda R_\alpha) \quad (6.3.10)$$

and

$$\lim_{\lambda \rightarrow \infty} \lambda^{-2} \rho_Q(\lambda^{-1/3} r) \approx \lim_{\lambda \rightarrow \infty} \lambda^{-2} \rho_{TF}(\lambda^{-1/3} r) \quad (6.3.11)$$

provided that ρ_{TF} exists. For the neutral-atom case, then, (6.2.20) is the correct formula for the energy at high enough Z . Real atoms are still far from reaching this limit, however, as may be seen from the Hartree–Fock values displayed in Table 6.1. We shall say more about this later.

This theorem was first established by Lieb and Simon (1973, 1977), to whose work one may refer for the formal proof.

6.4 Assessment and modification

The results described in the last section hardly commend the Thomas–Fermi theory as a quantitative theory for atoms and molecules. And the Thomas–Fermi–Dirac theory in most respects is worse.

There are ways to improve these functionals by adding terms involving $\nabla\rho$, $\nabla^2\rho$, $(\nabla\rho)^2$, etc. These will be considered in §§6.7–6.9 below, but more needs to be said before we turn to detailed descriptions of them. We begin by reviewing certain evidence that indicates that (6.1.22) and (3.1.10) are not so poor as they at first seem.

First, as was initially pointed out and documented by Fraga (1964), equations like (6.3.2) and (6.3.4) are surprisingly accurate for atoms and molecules. For simplicity, take neutral atoms and let $\mu = 0$ in (6.3.2) (the Thomas–Fermi neutral-atom result), and consider the implication if we apply the result to the Hartree–Fock formula (1.3.15). It will give

$$\sum \varepsilon_i = E + V_{ee} = \frac{2}{3}E, \quad E = \frac{3}{2} \sum \varepsilon_i \quad (6.4.1)$$

and it is formulas of this general type that appear to have semiquantitative general validity. The extension to molecules entails complications due to V_{nm} , but even for molecules a rough proportionality of E to $\sum \varepsilon_i$ holds (Ruedenberg 1977, Cioslowski 1988b). This is related to a rough homogeneity property of the energy with respect to atomic numbers, which the Thomas–Fermi formula of (6.2.25) exemplifies (Parr and Gadre 1980). For a recent study, see Chen and Spruch (1987).

Second, considerable evidence has accumulated that the TF and TFD energy functionals (and their gradient-expansion extensions of §§6.7 and 6.8) give good energies if one restricts the admissible densities in the minimization procedure to reasonable forms. One may mention the early work of Csavinsky (1968) in this connection, or that of Gázquez and Parr (1978), where exponential forms or their extensions were used. Or there are the studies of Wang and Parr, wherein it is shown that if one requires an atomic density to be piecewise exponential, with as many pieces as

principal quantum shells, one obtains both good energies and densities that exhibit shell structure (Wang and Parr 1977, Wang 1982). And probably most important of all, if one inserts into these energy functionals Hartree-Fock densities themselves, both the total energies and individual energy components come out far better than the 15% and greater errors associated with (6.2.25) (Gordon and Kim 1972, Shih, Murphy, and Wang 1980; and see numerical examples in §§6.8 and 10.2).

According to the foregoing arguments, it seems that in the TF model energy functional one has a better-quality estimate of the value of energy than of the energy functional derivatives that determine the behavior of the TF electron density via the Euler equation. This idea suggests that one should try to retain the good property of the energy functional for the evaluation of energy but to improve on the density or on the differential equation for the density. Thus, Ashby and Holzman (1970) have proposed to eliminate the divergence of the density near the nucleus by using a cut-off of the TF density in the vicinity of the nucleus and replacing this region by a wave-mechanical density. Recently, Englert, and Schwinger (1984a) have also arrived at a modified TF density that is nondivergent at the nucleus. Their density results from minimization of the energy derived from the TF functional modified by replacing the contribution from the strongly bound electrons by the correct quantum-mechanical energy of these electrons. Attempts have also been made (Englert and Schwinger 1982) to improve the long-range behavior of the TF density. Englert and Schwinger (1984b,c, 1985a,b,c) have achieved substantial improvement in Thomas-Fermi theory.

In a recent study emphasizing this weakness (Parr and Ghosh 1986, Ghosh and Parr 1987b; see also Goldstein and Rieder 1987), it was pointed out that the Thomas-Fermi atomic electron-density behavior, $\rho \sim r^{3/2}$ as $r \rightarrow 0$, implies that $\int \nabla^2 \rho(\mathbf{r}) d\mathbf{r} = \infty$ in Thomas-Fermi theory; the Thomas-Fermi density is discontinuous at the origin. One ought to require continuity at $r = 0$. To do this, one can impose the constraint

$$\int e^{-2kr} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} = \text{finite} \quad (6.4.2)$$

where k is to be determined. Attaching a Lagrange multiplier λ to this gives, in place of (6.1.23), a modified Euler equation for an atom,

$$\mu = \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \frac{Z}{r} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' - \lambda \nabla^2 (e^{-2kr}) \quad (6.4.3)$$

Now the infinity at the origin can be eliminated by requiring $4k\lambda = Z$, which gives

$$\mu = \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \frac{Z}{r} (1 - e^{-2kr}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' - Zk e^{-2kr} \quad (6.4.4)$$

with the parameter k still to be determined. The value of k can be chosen so that the cusp condition (1.5.3) is satisfied. When this is done, remarkably improved values of the energy are obtained, as indicated in Table 6.1. [Note that comparison of Thomas–Fermi energy with Hartree–Fock energy is reasonable in this semiquantitative context because exchange is a small part of the Hartree–Fock energy ($\sim 5\%$).] The electron density at the nucleus, in fact close to proportional to Z^3 but incorrectly predicted to be infinite in Thomas–Fermi theory, turns out well too. It is straightforward to perform the minimization to get these results. Thus a Thomas–Fermi theory in which ρ is required to be continuous and to satisfy the cusp constraint can provide a more reasonable description of atoms than the original Thomas–Fermi theory.

6.5 An alternative derivation and a Gaussian model

In the derivation of Thomas–Fermi–Dirac theory in §6.1, we started from the Hartree–Fock functional of (6.1.5) and arbitrarily substituted into it the first-order density matrix for a uniform gas, (6.1.14). Here we start again with (6.1.5), but this time we avoid making approximations for as long as possible. We will again arrive at TFD theory, but we will also come to a slightly modified version of it, a model that may be called a *Gaussian model* (Lee and Parr 1987; compare Meyer, Bartel, Brack, Quentin, and Aicher 1986).

In addition to (6.1.5), (6.1.6), and (6.1.8), we need one other formula, the normalization condition for the first-order density matrix (for a closed-shell),

$$2N = \iint \rho_1(\mathbf{r}_1, \mathbf{r}_2) \rho_1(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \quad (6.5.1)$$

This follows from (2.5.7) for the closed-shell case. The full idempotency conditions of (2.5.7) constitute an infinity of conditions that we are going to ignore except for their most important single consequence, (6.5.1).

Introducing the interparticle coordinates \mathbf{r} and \mathbf{s} of (6.1.13), we note first that the kinetic energy may be written

$$T = -\frac{1}{2} \iint \left[\nabla_{\mathbf{s}}^2 \left[\rho_1 \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \right]_{\mathbf{s}=0} \right] d\mathbf{r} \quad (6.5.2)$$

Here have been used (6.1.16), symmetry between \mathbf{r}_1 and \mathbf{r}_2 , and the fact that $\nabla^2 \rho(\mathbf{r})$ integrates to zero. In these coordinates we also have

$$K = \frac{1}{4} \iint \frac{\left| \rho_1 \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \right|^2}{s} d\mathbf{r} d\mathbf{s} \quad (6.5.3)$$

$$N = \frac{1}{2} \iint \left| \rho_1 \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \right|^2 d\mathbf{r} ds \quad (6.5.4)$$

Note the similarity between these last two formulas.

Following Berkowitz (1986) and Kemister (1986), we now introduce the expansion of $\rho_1(\mathbf{r} + (\mathbf{s}/2), \mathbf{r} - (\mathbf{s}/2))$ in the Cartesian coordinates of \mathbf{s} and average over the angular coordinates of \mathbf{s} . Define $\beta(\mathbf{r})$ by the formulas

$$\frac{1}{\beta(\mathbf{r})} = \frac{2}{3} \frac{t(\mathbf{r})}{\rho(\mathbf{r})}, \quad \text{with } T = \int t(\mathbf{r}) d\mathbf{r} \quad (6.5.5)$$

and

$$t(\mathbf{r}) = \frac{1}{8} \sum_i^N \nabla \rho_i \cdot \frac{\nabla \rho_i}{\rho_i} - \frac{1}{8} \nabla^2 \rho \quad (6.5.6)$$

where the ρ_i are Hartree-Fock orbital densities. Define also

$$\Gamma(\mathbf{r}, s) = \frac{\overline{\left| \rho_1 \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \right|^2}}{\rho^2(\mathbf{r})} \quad (6.5.7)$$

where the bar denotes the indicated spherical average. Then we find the exact formal expansion

$$\Gamma(\mathbf{r}, s) = 1 - \frac{s^2}{\beta(\mathbf{r})} + \dots \quad (6.5.8)$$

where $\beta(\mathbf{r})$ is the "temperature" parameter of (6.5.5), and the exact formulas

$$T = \frac{3}{2} \int \frac{\rho(\mathbf{r})}{\beta(\mathbf{r})} d\mathbf{r} \quad (6.5.9)$$

$$K = \pi \iiint \rho^2(\mathbf{r}) \Gamma(\mathbf{r}, s) d\mathbf{r} s ds \quad (6.5.10)$$

$$N = 2\pi \iiint \rho^2(\mathbf{r}) \Gamma(\mathbf{r}, s) d\mathbf{r} s^2 ds \quad (6.5.11)$$

It is well known that K involves only a spherical average; the same is seen from (6.5.11) to be true for N . The Taylor series for $\Gamma(\mathbf{r}, s)$ in (6.5.8) must converge in the sense required for the integrals in (6.5.10) and (6.5.11) to exist. The range for s is 0 to ∞ ; $\Gamma(\mathbf{r}, s)$ is everywhere positive. A local "temperature" was introduced first by Ghosh, Berkowitz, and Parr (1984), who even set $\beta(\mathbf{r}) = 1/kT(\mathbf{r})$. See §11.2.

If we can reasonably approximate the higher-order, less important terms in Γ , we will have achieved reasonable approximation to K and N .

We consider two approximations (Lee and Parr 1987). A simple approximation for Γ is a Gaussian,

$$\Gamma(\mathbf{r}, s) \approx \Gamma_G(\mathbf{r}, s) = e^{-s^2\beta(\mathbf{r})} \quad (6.5.12)$$

With this, (6.5.10) and (6.5.11) give

$$K_G = \frac{\pi}{2} \int \rho^2(\mathbf{r})\beta(\mathbf{r}) d\mathbf{r} \quad (6.5.13)$$

and

$$N_G = \frac{\pi^{3/2}}{2} \int \rho^2(\mathbf{r})\beta^{3/2}(\mathbf{r}) d\mathbf{r} \quad (6.5.14)$$

First derived by Ghosh and Parr (1986), (6.5.13) is a useful approximate formula for exchange energy. This is demonstrated in Table 6.2. As indicated in the table, corresponding values of the particle number are reasonably good.

Alternatively, one might try to approximate Γ using spherical Bessel functions, or, in another language, some appropriate combination of sines, cosines, and powers of s . The simplest such approximation that will do involves the square (to guarantee positivity) of the first-order spherical Bessel function $j_1(x) = [\sin x - x \cos x]/x^2$, with x proportional to s . Specifically, if we take

$$\Gamma(\mathbf{r}, s) \approx \Gamma_T(\mathbf{r}, s) = \frac{9(\sin t - t \cos t)^2}{t^6} \quad (6.5.15)$$

with

$$t = \left[\frac{5}{\beta(\mathbf{r})} \right]^{1/2} s \quad (6.5.16)$$

then we again recover (6.5.8). Equations (6.5.10) and (6.5.11) become

$$K_T = \frac{9\pi}{20} \int \rho^2(\mathbf{r})\beta(\mathbf{r}) d\mathbf{r} \quad (6.5.17)$$

Table 6.2 Nonlocal Approximations to the Hartree-Fock Exchange Energy and Particle Number for Neutral Atoms

| Atom | N | N_G^a | N_T^b | K^c | K_G^a | K_T^b |
|------|-----|---------|---------|-------|---------|---------|
| He | 2 | 1.646 | 1.565 | 1.026 | 0.913 | 0.826 |
| Ne | 10 | 9.164 | 8.716 | 12.11 | 11.57 | 10.41 |
| Ar | 18 | 16.24 | 15.45 | 30.18 | 29.24 | 27.16 |
| Kr | 36 | 33.80 | 32.15 | 93.9 | 94.26 | 84.83 |
| Xe | 54 | 50.74 | 48.26 | 179.1 | 181.7 | 163.5 |

^a Gaussian approximation of Equations (6.5.13) and (6.5.14) of the text, calculated using Hartree-Fock wave functions.

^b Trigonometric approximation of Equations (6.5.17) and (6.5.18), calculated using Hartree-Fock wave functions.

^c Accurate Hartree-Fock values.

and

$$N_T = \frac{3\pi^2}{5^{3/2}} \int \rho^2(\mathbf{r})\beta^{3/2}(\mathbf{r}) d\mathbf{r} \quad (6.5.18)$$

Results of calculations with these formulas are included in Table 6.2. They are not bad, but they are inferior to those from (6.5.13) and (6.5.14).

Comparing (6.5.15) with (6.1.14), we recognize that (6.5.15) is just a uniform-gas ansatz for the dependence of the density matrix on the interparticle coordinate s . The numerical comparisons in Table 6.2 demonstrate that for atoms the uniform-gas ansatz is not as good as the Gaussian ansatz. Figure 6.1 bears this conclusion out; in it an accurate $\Gamma(\mathbf{r}, s)$ is compared with Gaussian and uniform-gas approximations to it (Lee and Parr 1987).

At this stage we have obtained interesting approximations to Hartree-Fock theory, but how about density functionals? The preceding formulas can be turned into density functional formulas if $\beta(\mathbf{r})$ can be expressed in terms of $\rho(\mathbf{r})$. The simplest way to do this, and an appealing idea physically, is to assume that $\beta(\mathbf{r})$ is a *function* of $\rho(\mathbf{r})$:

$$\beta(\mathbf{r}) = \beta(\rho(\mathbf{r})) \quad (6.5.19)$$

Scaling arguments then immediately give

$$\beta(\mathbf{r}) = \frac{3}{2C} \rho^{-2/3}(\mathbf{r}) \quad (6.5.20)$$

where C is a constant. Equation (6.5.9) becomes

$$T^{\text{LDA}}[\rho] = C \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \quad (6.5.21)$$

with C yet to be determined, and either (6.5.13) or (6.5.17) gives $K[\rho]$ proportional to the corresponding integral of $\rho^{4/3}(\mathbf{r})$. We use LDA to denote this *local density approximation*.

The constant C may be determined to force the number of electrons to be correct, as determined from (6.5.14) or (6.5.18). Thus $N_G = N$ gives

$$C_G = \frac{3\pi}{2^{5/3}} = 2.9686 \quad (6.5.22)$$

$$\beta_G^{\text{LDA}}(\mathbf{r}) = \frac{2^{2/3}}{\pi} \rho^{-2/3}(\mathbf{r}) = 0.5053 \rho^{-2/3}(\mathbf{r}) \quad (6.5.23)$$

$$T_G^{\text{LDA}}[\rho] = 2.9686 \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \quad (6.5.24)$$

$$K_G^{\text{LDA}}[\rho] = 0.7937 \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad (6.5.25)$$

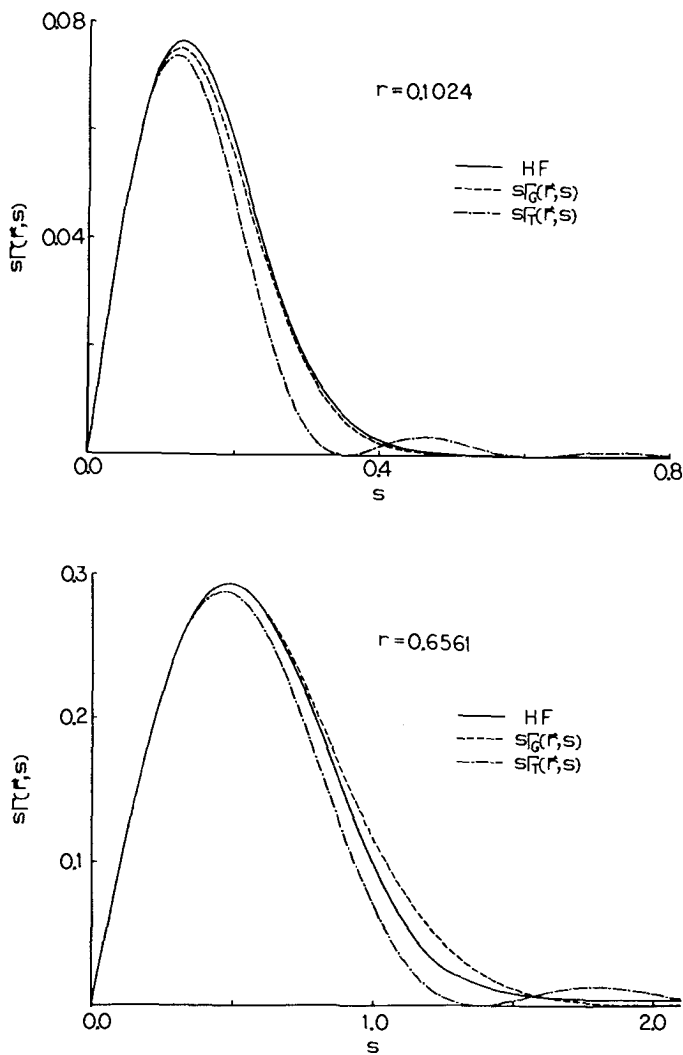


Figure 6.1 The quantity $s\Gamma(r,s)$ for the neon atom. The accurate Hartree-Fock values are compared with the Gaussian approximation of (6.5.12) and the trigonometric approximation of (6.5.15) for two values of r . Above is for the inner radial maximum, $r=0.1024$; below for the outer maximum, $r=0.6561$. Note the artificial, false zeros for the trigonometric approximation. (Reproduced from Lee and Parr (1987).)

Table 6.3 Approximate Kinetic Energy and Exchange Energy Density Functionals for Neutral Atoms, in Various Local-Density Approximations. Hartree-Fock Densities are Used Throughout

| | He | Ne | Ar | Kr | Xe |
|----------------------------|-------|--------|--------|--------|--------|
| Kinetic energy | | | | | |
| Exact ^a | 2.862 | 128.55 | 526.81 | 2752.0 | 7232.1 |
| Gaussian ^b | 2.648 | 121.76 | 506.61 | 2679.3 | 7090.9 |
| Trigonometric ^c | 2.561 | 117.76 | 489.95 | 2591.2 | 6857.7 |
| Exchange energy | | | | | |
| Exact ^a | 1.026 | 12.11 | 30.18 | 93.85 | 179.1 |
| Gaussian ^b | 0.950 | 11.86 | 29.95 | 95.27 | 183.4 |
| Trigonometric ^c | 0.884 | 11.03 | 27.86 | 94.75 | 182.5 |

^a Hartree-Fock values.

^b Equations (6.5.24) and (6.5.25) of text.

^c Equations (6.5.28) and (6.5.29) of the text (traditional Thomas-Fermi-Dirac formulas).

while $N_T = N$ gives

$$C_T = \frac{3}{10}(3\pi^2)^{2/3} = 2.8712 = C_F \quad (6.5.26)$$

$$\beta_T^{\text{LDA}} = 5(3\pi^2)^{-2/3} \rho^{-2/3}(\mathbf{r}) = 0.5224 \rho^{-2/3}(\mathbf{r}) \quad (6.5.27)$$

$$T_T^{\text{LDA}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \quad (6.5.28)$$

$$K_T^{\text{LDA}}[\rho] = 0.7386 \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} = C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad (6.5.29)$$

We have thereby recovered, with the ansatz of (6.5.15), the classical Thomas-Fermi-Dirac theory. From the alternative Gaussian ansatz of (6.5.12), we have obtained a model of precisely the same form but with modified coefficients. For atoms, the Gaussian model is better, as is shown in Table 6.3 (Lee and Parr 1987).

It is striking, to say the least, that the TFD energy functional and an improvement upon it (the Gaussian model) can be derived from two assumptions only, the resummation assumption of (6.5.12) or (6.5.15) and the local approximation of (6.5.19). The only point at which the statistics of the particles [the idempotency condition (2.5.7)] has entered is in the imposition of the gross normalization condition (6.5.1). It will be important to develop improved models by imposition of additional consequences of idempotency.

6.6 The purely local model

We pause now to show how an even simpler but still useful theory results if we make even more sweeping assumptions, not just about $K[\rho]$ but

about the full $V_{ee}[\rho] = J[\rho] - K[\rho]$. After all, it is V_{ee} not K that we are really interested in, and in the Hartree–Fock approximation V_{ee} , like K , is a functional of the first-order density matrix. Furthermore, the self-repulsion (1.3.37) is a large part of both J and K but cancels between them; in modelling K one is modelling this piece that cancels anyway. This section explores how one may approximate the whole V_{ee} using approximations of the type described in the last section (Parr, Gadre, and Bartolotti 1979, Parr 1988).

From (2.4.8), the electron–electron repulsion energy, even beyond the Hartree–Fock approximation, is given by the formula

$$V_{ee} = \iint \frac{1}{r_{12}} \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (6.6.1)$$

where $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ is the diagonal element of the second-order spinless density matrix, (2.4.3). Furthermore, from (2.3.4) or by integration of (2.4.6),

$$\frac{N(N-1)}{2} = \iint \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (6.6.2)$$

We shall obtain the result we want by making an appropriate resummation assumption on $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ after expressing it in the sum and difference coordinates of (6.1.13), making a local assumption, and then imposing (6.6.2).

We write $\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_2(\mathbf{r} + (\mathbf{s}/2), \mathbf{r} - (\mathbf{s}/2))$ and note that ρ_2 is an even function of \mathbf{s} . It therefore has a formal power series expansion in the Cartesian coordinates of \mathbf{s} in which linear terms are missing. Spherically averaging this, we obtain

$$\begin{aligned} \overline{\rho_2\left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2}\right)} &= \frac{1}{4\pi} \int d\Omega_s \rho_2\left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2}\right) \\ &= \rho_2(\mathbf{r}, \mathbf{r}) \left[1 - \frac{s^2 t_2(\mathbf{r})}{3\rho_2(\mathbf{r}, \mathbf{r})} + \dots \right] \end{aligned} \quad (6.6.3)$$

where

$$t_2(\mathbf{r}) = -\frac{1}{2} \nabla_s^2 \rho_2 \left[\left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \right]_{s=0} \quad (6.6.4)$$

The equations (6.6.1) and (6.6.2) become, on performing the integrations over the angular part of \mathbf{s}

$$V_{ee} = 4\pi \iint \rho_2(\mathbf{r}, \mathbf{r}) \Gamma_2(\mathbf{r}, s) d\mathbf{r} s ds \quad (6.6.5)$$

and

$$\frac{N(N-1)}{2} = 4\pi \iint \rho_2(\mathbf{r}, \mathbf{r}) \Gamma_2(\mathbf{r}, s) d\mathbf{r} s^2 ds \quad (6.6.6)$$

where

$$\Gamma_2(\mathbf{r}, s) = 1 - \frac{s^2}{2\beta_2(\mathbf{r})} + \dots \quad (6.6.7)$$

in which $\beta_2(\mathbf{r})$ is defined by

$$t_2(\mathbf{r}) = \frac{3}{2} \frac{\rho_2(\mathbf{r}, \mathbf{r})}{\beta_2(\mathbf{r})} \quad (6.6.8)$$

The analogy of (6.6.5) and (6.6.6) with (6.5.10) and (6.5.11) is clear.

First we make a Gaussian resummation of (6.6.7), à la Berkowitz (1986):

$$\Gamma_2(\mathbf{r}, s) \approx \exp\left(-\frac{1}{2} \frac{s^2}{\beta_2(\mathbf{r})}\right) \quad (6.6.9)$$

We get

$$V_{ee} = 4\pi \int \rho_2(\mathbf{r}, \mathbf{r}) \beta_2(\mathbf{r}) d\mathbf{r} \quad (6.6.10)$$

and

$$\frac{N(N-1)}{2} = (2\pi)^{3/2} \int \rho_2(\mathbf{r}, \mathbf{r}) \beta_2^{3/2}(\mathbf{r}) d\mathbf{r} \quad (6.6.11)$$

Now we make local density assumptions about each of the integrands, and use dimensional arguments, finding

$$\rho_2(\mathbf{r}, \mathbf{r}) \beta_2(\mathbf{r}) = A\rho^{4/3}(\mathbf{r}) \quad (6.6.12)$$

and

$$\rho_2(\mathbf{r}, \mathbf{r}) \beta_2^{3/2}(\mathbf{r}) = B\rho(\mathbf{r}) \quad (6.6.13)$$

Hence the dependence of β_2 on ρ must be (in this approximation)

$$\beta_2(\mathbf{r}) = \left(\frac{B}{A}\right)^2 \rho^{-2/3}(\mathbf{r}) \quad (6.6.14)$$

and the dependence of ρ_2 on ρ must be

$$\rho_2(\mathbf{r}, \mathbf{r}) = \frac{A^3}{B^2} \rho^2(\mathbf{r}) \quad (6.6.15)$$

But in the closed-shell Hartree-Fock case, from (2.5.19) and (2.5.25),

$$\rho_2(\mathbf{r}, \mathbf{r}) = \frac{1}{4}\rho^2(\mathbf{r}) \quad (6.6.16)$$

This will be a very good approximation in general, so we assume it:

$$\frac{A^3}{B^2} = \frac{1}{4} \quad (6.6.17)$$

Equation (6.6.11) then gives

$$\frac{N(N-1)}{2} = (2\pi)^{3/2}(4A^3)^{1/2}N, \quad 4\pi A = 2^{-1/3}(N-1)^{2/3} \quad (6.6.18)$$

so that

$$\begin{aligned} V_{ee} &= 2^{-1/3}(N-1)^{2/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \\ &= 0.7937(N-1)^{2/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (6.6.19)$$

This is a final simplified local formula for the electron-electron repulsion energy.

Given its crude derivation, (6.6.19) is surprisingly accurate, presumably owing to the fact that forcing the normalization condition (6.6.6) on an approximation to Γ_2 makes up for errors in that approximation. Table 6.4 gives some numerical values.

In 1979 there had already been proposed (Parr, Gadre, and Bartolotti 1979) a local energy functional of the form [compare (6.1.30)]

$$E_{\text{PGB}}[\rho] = C \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + BN^{2/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad (6.6.20)$$

where $B = 0.7544$ was derived from the condition that the functional confer zero chemical potentials on neutral atoms. The agreement with (6.6.19) is extraordinary. Of course $(N-1)^{2/3}$ equals $N^{2/3}$ for large N . The former is better for small N ; the atom H is nicely encompassed by (6.6.19); see also Gázquez and Robles (1981) and Pathak, Sharma, and Thakkar (1986).

Table 6.4 Test of Local Formula for V_{ee} for Atoms. Hartree-Fock Densities are Used Throughout

| Atom (Z) | Hartree-Fock V_{ee}^a | $\int \rho^{4/3}(\mathbf{r}) d\mathbf{r}^b$ | V_{ee} From (6.6.19) of Text |
|--------------|----------------------------|---|-----------------------------------|
| He (2) | 1.03 | 1.197 | 0.95 |
| Ne (10) | 54.0 | 14.94 | 51.3 |
| Ar (18) | 201.4 | 37.726 | 198.0 |
| Kr (36) | 1078 | 120.00 | 1019 |
| Xe (54) | 2701 | 230.94 | 2586 |
| Rn (86) | 8244 | 505.01 | 7749 |

^a Values from Clementi and Roetti (1974).

^b Values from Bartolotti (1980).

The big advantage of the energy functional of (6.6.20) is that it causes the corresponding Euler equation to have purely algebraic form. Explicit solution of the whole problem is possible, and with suitable choice of an C value (3.8738 is recommended in Parr, Gadre, and Bartolotti 1979), fairly good energies of atoms are obtained. More work on such functionals is warranted; note that they satisfy the condition (6.3.9).

6.7 Conventional gradient correction

Approximations to the kinetic energy and exchange energy functionals by the Thomas-Fermi and Dirac expressions of §6.1 are examples of the local-density approximation (LDA)—using the corresponding uniform electron gas formulas locally through the local Fermi wave vector $k_F(\mathbf{r})$ of (6.1.12). However, poor accuracy accompanies the oversimplified TF and TFD models. Systematic improvement of the TF kinetic energy functional is the subject of this section. Improvements of the Dirac exchange functional and the correlation-energy functional will be considered in §6.9 and in Chapter 8.

One would expect a better functional to exhibit effects of the inhomogeneity of the electron density, which is large in atoms and molecules but which is ignored in the LDA. This view was first taken by von Weizsacker (1935), who considered modified plane waves of the form $(1 + \mathbf{a} \cdot \mathbf{r})e^{i\mathbf{k} \cdot \mathbf{r}}$, where \mathbf{a} is a constant vector and \mathbf{k} is the local wave vector. There resulted the *Weizsacker correction* to the Thomas-Fermi kinetic energy; namely,

$$T_w[\rho] = \frac{1}{8} \frac{\hbar^2}{m} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \quad (6.7.1)$$

In order to display the dependence on \hbar , atomic units are not used here and throughout this section. The total kinetic energy thus becomes

$$T_{TF\lambda w}[\rho] = T_{TF}[\rho] + \lambda T_w[\rho] \quad (6.7.2)$$

where the parameter λ is 1 in the original work of Weizsacker, but was later shown to be 1/9 from the gradient-expansion approach to be described next. There also exist other empirical values of λ , as will be considered in the next section.

The resulting TFW and TFDW models using (6.7.2) are well-defined corrections to TF and TFD theory. The behavior of the density both near and asymptotically far from the atomic nucleus is improved and the curse of the Teller nonbinding theorem of §6.3 is nullified. Various TFW and TFDW calculations for atoms and molecules will be described in the next two sections.

To generate the correction $T_w[\rho]$ and to make further improvement

from first principles, formal gradient expansion techniques have been developed over the years, through the operator commutator expansion (Kirzhnits 1957, 1967, Hodges 1973, Murphy 1981), the \hbar expansion of Wigner, or the Kirkwood representation of the one-particle Green's function (Jennings and Bhaduri 1975, Jennings, Bhaduri, and Brack 1975, Grammaticos and Voros 1979). We shall not trace the history, but rather simply demonstrate how $T_W[\rho]$ results from the \hbar expansion of the Wigner function. The background is in Appendix D. The basic results are contained in (6.7.21) to (6.7.23).

Consider the ground state of N noninteracting electrons. The spinless first-order reduced density matrix is given by (6.1.4), or equivalently

$$\begin{aligned}\rho_1(\mathbf{r}, \mathbf{r}') &= 2 \sum_i^{\infty} \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') \eta(\epsilon_F - \epsilon_i) \\ &= 2 \langle \mathbf{r} | \eta(\epsilon_F - \hat{H}) | \mathbf{r}' \rangle\end{aligned}\quad (6.7.3)$$

where $\eta(x)$ is the Heaviside step function

$$\eta(x) = \begin{cases} 1, & x > 1 \\ 0, & x < 1 \end{cases}\quad (6.7.4)$$

and \hat{H} is the one-particle Hamiltonian having ϕ_i and ϵ_i as its eigenstates and eigenvalues:

$$\hat{H}\phi_i(\mathbf{r}) = \{-\frac{1}{2}\nabla^2 + w(\mathbf{r})\}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})\quad (6.7.5)$$

with $w(\mathbf{r})$ the *local* potential function, that is, a local operator [see (2.1.24)]; note that this class of Hamiltonian rules out the Fock operator \hat{F} of (2.5.12) in Hartree-Fock theory for more than two electrons] and ϵ_F take any value between the highest occupied and the lowest unoccupied eigenvalue. The last equality in (6.7.3) may be verified by inserting into (6.7.3) an identity operator decomposed in the eigenstates of \hat{H} , namely,

$$I = \sum_i^{\infty} |\phi_i\rangle \langle \phi_i|$$

Our goal is to express the kinetic energy T as a functional of the electron density. The idea is the following: T is determined by $\rho_1(\mathbf{r}, \mathbf{r}')$ as in (6.1.6), $\rho_1(\mathbf{r}, \mathbf{r}')$ in turn by $w(\mathbf{r})$ through (6.7.3); electron density $\rho(\mathbf{r})$ as the diagonal of $\rho_1(\mathbf{r}, \mathbf{r}')$ is also determined by $w(\mathbf{r})$; therefore we can hope to use $w(\mathbf{r})$ as a bridge to connect T to $\rho(\mathbf{r})$.

The key problem is to find $\rho_1(\mathbf{r}, \mathbf{r}')$ in terms of $w(\mathbf{r})$. Note that as expressed in (6.7.3), the N -electron quantity $\rho_1(\mathbf{r}, \mathbf{r}')$ is the matrix representation of a one-particle operator $\hat{\rho}_1 = \eta(\epsilon_F - \hat{H})$. A one-electron problem is much easier to handle than an N -electron one. Many techniques have been developed to manipulate and approximate the

single-electron Green's function (propagator), defined as

$$G(\mathbf{r}, \mathbf{r}'; \beta) = \langle \mathbf{r} | e^{-\beta \hat{H}} | \mathbf{r}' \rangle \\ = \sum_i^{\infty} \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') e^{-\beta \epsilon_i} \quad (6.7.6)$$

where the second equality follows like (6.7.3). $G(\mathbf{r}, \mathbf{r}')$ is in turn related to $\rho_1(\mathbf{r}, \mathbf{r}')$ by an inverse Laplace transform; namely (Golden 1960),

$$\rho_1(\mathbf{r}, \mathbf{r}') = \frac{2}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{d\beta}{\beta} e^{\beta \epsilon_F} G(\mathbf{r}, \mathbf{r}'; \beta) \quad (6.7.7)$$

where γ is any positive constant. To prove (6.7.7), we only need show the same equality in terms of eigenvalues,

$$\eta(\epsilon_F - \epsilon_i) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{d\beta}{\beta} e^{\beta \epsilon_F} e^{-\beta \epsilon_i} \quad (6.7.8)$$

We may use the calculus of residues to verify (6.7.8). For $\epsilon_F > \epsilon_i$, the β -integration contour can be closed on the left-hand side of the complex- β plane and it becomes $C^1 + C^2$, with $R \rightarrow \infty$ (see Figure 6.2). The contribution from C^2 vanishes as $R \rightarrow \infty$. The result of closed-contour integration is given by the residue of $(1/\beta)e^{\beta(\epsilon_F - \epsilon_i)}$ at the pole $\beta = 0$, which is equal to 1. For $\epsilon_F < \epsilon_i$, the β -integration contour can be closed on the right-hand side of the complex- β plane and the result is zero because there is no singularity within the closed contour. Thereby (6.7.8) is proved, and hence (6.7.7) also.

We now invoke $\tilde{G}(\mathbf{r}, \mathbf{p}; \beta)$, the Wigner transformation of $G(\mathbf{r}, \mathbf{r}'; \beta)$ (see Appendix D for details). Following Equation (D.1), define

$$\tilde{G}(\mathbf{r}, \mathbf{p}; \beta) = \frac{1}{(2\pi\hbar)^3} \int ds \left\langle \mathbf{r} - \frac{\mathbf{s}}{2} \left| e^{-\beta \hat{H}} \right| \mathbf{r} + \frac{\mathbf{s}}{2} \right\rangle e^{i\mathbf{p} \cdot \mathbf{s}/\hbar} \\ = \frac{1}{(2\pi\hbar)^3} \int ds G\left(\mathbf{r} - \frac{\mathbf{s}}{2}, \mathbf{r} + \frac{\mathbf{s}}{2}; \beta\right) e^{i\mathbf{p} \cdot \mathbf{s}/\hbar} \quad (6.7.9)$$

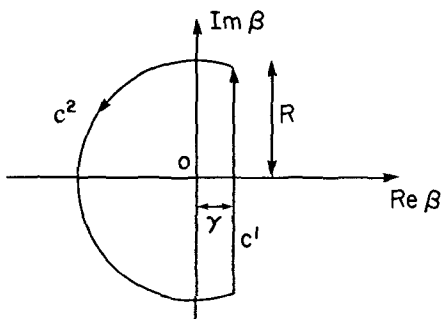


Figure 6.2 Integration contour for Equation (6.7.8) when $\epsilon_F < \epsilon_i$.

Then, by (D.3)

$$G(\mathbf{r}, \mathbf{r}'; \beta) = \int d\mathbf{p} e^{-i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar} \bar{G}(\frac{1}{2}(\mathbf{r} + \mathbf{r}'), \mathbf{p}; \beta) \quad (6.7.10)$$

Inserting (6.7.10) in (6.7.7), we obtain

$$\rho_1(\mathbf{r}, \mathbf{r}') = \int d\mathbf{p} e^{-i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar} \bar{\rho}_1(\frac{1}{2}(\mathbf{r} + \mathbf{r}'), \mathbf{p}) \quad (6.7.11)$$

where

$$\bar{\rho}_1(\mathbf{r}, \mathbf{p}) = \frac{2}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{d\beta}{\beta} e^{\beta\epsilon_F} \bar{G}(\mathbf{r}, \mathbf{p}; \beta) \quad (6.7.12)$$

Via the foregoing equations, the \hbar expansion of \bar{G} developed in Appendix D provides an explicit approximation of $\rho_1(\mathbf{r}, \mathbf{r}')$ in terms of the potential $w(\mathbf{r})$. Thus, from (D.30), to the order \hbar^2 ,

$$\begin{aligned} \bar{G}(\mathbf{r}, \mathbf{p}; \beta) &= \frac{1}{(2\pi\hbar)^3} \exp[-\beta H(\mathbf{r}, \mathbf{p})] \\ &\times \left\{ 1 + \hbar^2 \left[-\frac{\beta^2}{8m} \nabla^2 w(\mathbf{r}) + \frac{\beta^3}{24m} |\nabla w(\mathbf{r})|^2 + \frac{\beta^3}{24m} (\mathbf{p} \cdot \nabla)(\mathbf{p} \cdot \nabla) w(\mathbf{r}) \right] \right\} \end{aligned} \quad (6.7.13)$$

with

$$H(\mathbf{r}, \mathbf{p}) = \frac{p^2}{2m} + w(\mathbf{r}) \quad (6.7.14)$$

Correspondingly, by (6.7.12),

$$\begin{aligned} \bar{\rho}_1(\mathbf{r}, \mathbf{p}) &= \frac{2}{(2\pi\hbar)^3} \eta(\epsilon_F - H(\mathbf{r}, \mathbf{p})) + \frac{2\hbar^2}{(2\pi\hbar)^3} \\ &\times \left\{ -\frac{1}{8m} \eta^{(2)}(\epsilon_F - H(\mathbf{r}, \mathbf{p})) \nabla^2 w(\mathbf{r}) + \eta^{(3)}(\epsilon_F - H(\mathbf{r}, \mathbf{p})) \right. \\ &\times \left. \left[\frac{1}{24m} |\nabla w(\mathbf{r})|^2 + \frac{1}{24m^2} (\mathbf{p} \cdot \nabla)(\mathbf{p} \cdot \nabla) w(\mathbf{r}) \right] \right\} \end{aligned} \quad (6.7.15)$$

where (6.7.8) has been used and

$$\eta^{(n)}(\epsilon_F - H(\mathbf{r}, \mathbf{p})) \equiv \frac{\partial^n}{\partial \epsilon_F^n} \eta(\epsilon_F - H(\mathbf{r}, \mathbf{p})) \quad (6.7.16)$$

In the limit $\hbar \rightarrow 0$, only the first term of (6.7.15)—remains. This is the step-function distribution in phase space—the classical approximation to the step-function operator (6.7.3) in Wigner transformation.

We are now ready to compute the basic quantities with which we are concerned. On inserting (6.7.15) into (6.7.11), we find for the total

electron density,

$$\begin{aligned} \rho(\mathbf{r}) &= \rho_1(\mathbf{r}, \mathbf{r}) = \int \tilde{\rho}_1(\mathbf{r}, \mathbf{p}) d\mathbf{p} \\ &= \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} [\varepsilon_F - w(\mathbf{r})]^{3/2} \eta(\varepsilon_F - w(\mathbf{r})) \\ &\quad \times \left\{ 1 - \frac{1}{8} \frac{\hbar^2}{2m} [\nabla^2 w(\mathbf{r})(\varepsilon_F - w(\mathbf{r}))^{-2} + \frac{1}{4} |\nabla w(\mathbf{r})|^2 (\varepsilon_F - w(\mathbf{r}))^{-3}] \right\} \end{aligned} \quad (6.7.17)$$

where we have used the integral formula

$$\begin{aligned} \int \eta\left(\varepsilon_F - \frac{\mathbf{p}^2}{2m} - w(\mathbf{r})\right) d\mathbf{p} &= \int \eta\left(\varepsilon_F - w(\mathbf{r}) - \frac{\mathbf{p}^2}{2m}\right) 4\pi p^2 dp \\ &= \frac{4\pi}{3} p_F^3(\mathbf{r}) = \frac{4\pi}{3} [2m(\varepsilon_F - w(\mathbf{r}))]^{3/2} \eta(\varepsilon_F - w(\mathbf{r})) \end{aligned} \quad (6.7.18)$$

and its derivatives with respect to ε_F . The total kinetic energy according to (D.8) is given by

$$\begin{aligned} T &= \int \frac{p^2}{2m} \tilde{\rho}_1(\mathbf{r}, \mathbf{p}) d\mathbf{r} d\mathbf{p} \\ &= \int d\mathbf{r} \frac{\hbar^2}{10\pi^2 m} \left(\frac{2m}{\hbar^2} \right)^{5/2} [\varepsilon_F - w(\mathbf{r})]^{5/2} \eta(\varepsilon_F - w(\mathbf{r})) \\ &\quad \times \left\{ 1 - \frac{5}{8} \frac{\hbar^2}{2m} \left[\frac{5}{3} \nabla^2 w(\mathbf{r})(\varepsilon_F - w(\mathbf{r}))^{-2} - \frac{3}{4} |\nabla w(\mathbf{r})|^2 (\varepsilon_F - w(\mathbf{r}))^{-3} \right] \right\} \end{aligned} \quad (6.7.19)$$

where we have employed the integral formula

$$\begin{aligned} \int \eta\left(\varepsilon_F - \frac{\mathbf{p}^2}{2m} - w(\mathbf{r})\right) \mathbf{p}^2 d\mathbf{p} &= \int \eta\left(\varepsilon_F - \frac{p^2}{2m} - w(\mathbf{r})\right) 4\pi p^4 dp \\ &= \frac{4\pi}{5} [2m(\varepsilon_F - w(\mathbf{r}))]^{5/2} \eta(\varepsilon_F - w(\mathbf{r})) \end{aligned} \quad (6.7.20)$$

and its derivatives with respect to ε_F .

It is now elementary to eliminate $\varepsilon_F - w(\mathbf{r})$ from (6.7.19) by use of (6.7.17). We only need to keep the accuracy of this elimination

consistently to the order \hbar^2 . The result found is the TF- $\frac{1}{9}W$ functional:

$$T^{(2)}[\rho] = T_{\text{TF}}[\rho] + \frac{1}{9}T_W[\rho] \\ = \frac{\hbar^2}{m} \left[\frac{3}{10} (3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3} d\mathbf{r} + \frac{1}{9} \cdot \frac{1}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \right] \quad (6.7.21)$$

If we used only the zeroth-order approximation, we would obtain only the TF kinetic energy. For a derivation of this formula from a mean-path approximation to $G(\mathbf{r}, \mathbf{r}'; \beta)$, see Yang (1986).

We can also use the \hbar expansion to higher order in \hbar to get higher-order gradient correction; for details, see Hodges (1973), Murphy (1981), and Grammaticos and Voros (1979). The gradient expansion to fourth order is given by (Hodges 1973)

$$T^{(4)}[\rho] = T_{\text{TF}}[\rho] + \frac{1}{9}T_W[\rho] + T_H[\rho] \quad (6.7.22)$$

$$T_H[\rho] = \frac{\hbar^2}{m} \frac{1}{540(3\pi^2)^{2/3}} \\ \times \int \left[\frac{(\nabla^2\rho)^2}{\rho^{5/3}} - \frac{9}{8} \frac{\nabla^2\rho(\nabla\rho)^2}{\rho^{8/3}} + \frac{1}{3} \frac{(\nabla\rho)^4}{\rho^{11/3}} \right] d\mathbf{r} \quad (6.7.23)$$

The sixth-order formula may be found in Murphy (1981).

It is very satisfying that the TF kinetic energy and its systematic gradient corrections can be derived in this way from the semiclassical \hbar -expansion of the Wigner transform of the one-particle Green's function. Indeed in zeroth order this constitutes a derivation from first principles of the Thomas–Fermi kinetic-energy formula itself that makes no use of an ad hoc assumption of local behavior.

One might naively expect that higher accuracy would be achieved with higher-order gradient corrections. For atoms and molecules this is only true to fourth order, as will be documented in the next two sections. To one's dismay, the sixth-order gradient correction for atoms diverges!

As an approximation to the exact $T[\rho]$, $T^{(4)}[\rho]$ is still poor; only an average behavior of the electrons is described. And the road to better accuracy through gradient corrections ends at fourth order. However, the idea of employing just the electron density as in the TF theory is not dead, for recently there has been developed an integral formulation of density-functional theory that uses it. This will be the subject of §7.5.

6.8 The Thomas–Fermi–Dirac–Weizsacker model

Having developed the gradient correction for the Thomas–Fermi kinetic-energy functional, we now add it to the existing Thomas–Fermi–Dirac

energy functional of (6.1.22). To second order we then obtain the Thomas-Fermi-Dirac-Weizsacker (TFDW or TFD- λ W) model,

$$E_{\text{TFD-}\lambda\text{W}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \lambda \frac{1}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + J[\rho] - C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad (6.8.1)$$

The parameter λ is 1/9 in the conventional gradient expansion of the last section. Other empirical values of λ have also been employed, however: $\lambda = 1/5$ by Yonei and Tomishima (1965), based on a fitting for hydrogenic atoms (noninteracting electrons in the Coulomb potential due to the nucleus); $\lambda = 0.186$ by Lieb (1981) from analysis of the large-atomic-number limit of atoms; and $\lambda = 1.4/9 \sim 1.5/9$ ($\sim 1/6$) by Brack (1985) as a means to effectively include the fourth-order effect in the second-order formula. Justification from a Green's-function approach has been provided for all these λ values (Yang 1986). Compare the discussion in Levy, Perdew, and Sahni (1984), which emphasizes the case $\lambda = 1$.

The Euler equation for TFD- λ W atoms or molecules becomes

$$\mu_{\text{TFD-}\lambda\text{W}} = \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) + \frac{\lambda}{8} \left[\frac{|\nabla\rho(\mathbf{r})|^2}{\rho^2(\mathbf{r})} - 2 \frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})} \right] - \phi(\mathbf{r}) - \frac{4}{3} C_x \rho^{1/3}(\mathbf{r}) \quad (6.8.2)$$

where the rules of Appendix A have been employed to evaluate the functional derivative of the gradient term, and $\phi(\mathbf{r})$ is the classical electrostatic potential. The solution of (6.8.2), with $\mu_{\text{TFD-}\lambda\text{W}}$ determined by proper normalization, is the electron density of the TFD- λ W atom. Although this model has been established for a long time, numerical investigations of it have not been available until recently (Tomishima and Yonei 1966, Gross and Dreizler 1979, Stich, Gross, Malzacher, and Dreizler 1982, Yang 1986).

The TFDW model provides considerable improvement over the TF or TFD model (Gross and Dreizler 1979). The electron density is finite at the nucleus instead of diverging as it does in the TF or TFD model—Equation (6.2.17). The electron density decreases exponentially far from the nucleus,

$$\rho_{\text{TFD-}\lambda\text{W}} \sim \left(\frac{1}{r^2}\right) \exp \left[- \left(- \frac{8\mu_{\text{TFDW}}}{\lambda} \right)^{1/2} r \right], \quad \text{for } r \rightarrow \infty \quad (6.8.3)$$

in contrast with the improper inverse power decay of (6.2.19). Also, inclusion of the gradient term in the energy functional invalidates Teller's nonbinding theorem (see §6.3) and makes molecular binding possible in

Table 6.5 Atomic Energies from Various TFD- λ W Models (a.u.)^{a,b,c}

| | TF | TFD | TFD $\frac{1}{9}$ W | TFD $\frac{1}{6}$ W | TFD(0.186)W | TFD $\frac{1}{5}$ W | TFD $\frac{1}{3}$ W | TFDW | HF |
|----|----------|---------|---------------------|---------------------|-------------|---------------------|---------------------|----------|----------|
| Ne | -165.61 | -176.3 | -139.91 | -132.53 | -130.33 | -128.83 | -117.09 | -86.43 | -128.55 |
| Ar | -652.72 | -680.7 | -561.98 | -537.34 | -529.94 | -524.91 | -485.00 | -378.51 | -526.82 |
| Kr | -3289.50 | -3377.9 | -2898.54 | -2796.95 | -2766.29 | -2745.60 | -2578.10 | -2132.19 | -2752.05 |
| Xe | -8472.46 | -8646.1 | -7563.13 | -7330.95 | -7260.72 | -7213.92 | -6827.59 | -5828.96 | -7232.13 |

^a Values for TFD, TFD $\frac{1}{5}$ W, and TFDW from Tomishima and Yonei (1966); HF results from Clementi and Roetti (1974).

^b TF results from (6.2.23) of the text.

^c TFD $\frac{1}{9}$ W, TFD $\frac{1}{6}$ W, TFD(0.186)W, TFD $\frac{1}{3}$ W results. From Yang (1986).

the TFD- λ W model. However, because of numerical difficulties, even for diatomic molecules, the strength of binding in the TFD- λ W model is still uncertain (Yonei 1971, Gross and Dreizler 1979, Berk 1983).

There are two main ways to solve (6.8.2): the finite-difference method (Tomishima and Yonei 1966, Yang 1986) and the spline-representation method (Stich, Gross, Malzacher, and Dreizler 1982). The procedure in the first case is the following. (1) Make an initial guess of the density $\rho_0(\mathbf{r})$. (2) Compute the electrostatic potential $\phi_0(\mathbf{r})$ from this guessed $\rho_0(\mathbf{r})$. (3) Use this $\rho_0(\mathbf{r})$ in (6.8.2) to solve for a new density $\rho(\mathbf{r})$ whose normalization determines the value of $\mu_{\text{TFD-}\lambda\text{W}}$. (4) Insert $\rho(\mathbf{r})$ back in step (1) and repeat until self-consistency is reached. Total atomic energies for the inert gas atoms Ne, Ar, Kr, and Xe in the TFD- λ W model are listed in Table 6.5, for various λ values. The behavior of the resulting electron density is shown in Figure 6.3. The paper of Stich, Gross, Malzacher, and Dreizler (1982) contains more atomic calculations with $\lambda = 1/5$ and also some results for positive ions.

From Table 6.5, it is evident that the TFD- λ W models (except for $\lambda = 1$) all considerably improve the total energies of the TF or TFD model, and that indeed $\lambda = 1/5$ is an optimal choice for approximation of total energy, in agreement with the argument of Yonei and Tomishima (1965). However, analysis of the various energy components shows no strong preference for the value $\lambda = 1/5$ (Yang 1986). As shown in Figure 6.3, the TFD- λ W atomic density is a beautiful average of the HF density, smoothing out the atomic shell structure.

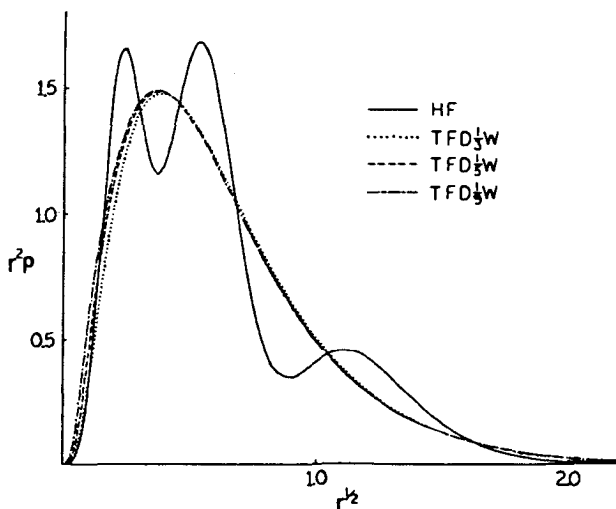


Figure 6.3 Electron density for argon from various models (after Yang 1986.)

The TFD- λW model, very recently extended by Engel and Dreizler (1989) to include fourth-order gradient correction, is the most sophisticated of the TF-type models for many-electron systems that has been solved self-consistently. Note that inclusion of higher-order gradient correction in the energy functional (6.8.1) tremendously complicates the resulting Euler equation. The TFD- λW model is still very unsatisfactory and cannot be regarded as a rigorous approach. Atomic shell structure is absent and molecular binding is in doubt. Also, negative ions are not stable (Stich, Gross, Malzacher, and Dreizler 1982).

6.9 Various related considerations

The gradient expansion to fourth order of §6.7 reproduces well the electronic kinetic energies of atoms and molecules if one inputs into it Hartree-Fock electron densities (Wang, Parr, Murphy, and Henderson 1976, Shih 1976, Murphy and Parr 1979, Murphy and Wang 1980, Wang and Rasolt 1976, Allan, West, Cooper, Grout, and March 1985, Lee and Ghosh 1986). From (6.7.23) the gradient expansion of $T[\rho]$ to fourth order may be written

$$T^{(4)}[\rho] = T_0[\rho] + T_2[\rho] + T_4[\rho] \quad (6.9.1)$$

where

$$T_0[\rho] = T_{TF}[\rho], \quad T_2[\rho] = \frac{1}{9}T_W[\rho], \quad T_4[\rho] = T_H[\rho] \quad (6.9.2)$$

Tables 6.6 and 6.7 present some numerical results for atoms (Murphy and Wang 1980) and molecules (Lee and Ghosh 1986). The results are remarkably good, although hardly quantitative. Extending this approach is neither feasible nor promising, however. $T_6[\rho]$ diverges for atoms.

Closer to what one wants, of course, is accuracy in the *local kinetic energy density* $t[\rho(\mathbf{r})] = t(\mathbf{r})$. This is defined up to an additive contribution $C\nabla^2\rho$, where C is an arbitrary constant, by the formula $T[\rho] = \int t(\mathbf{r}) d\mathbf{r}$. To complete the definition, one may take [cf. (6.5.6), where for another purpose a different amount of $\nabla^2\rho$ was included]

$$\begin{aligned} t(\mathbf{r}) &= \frac{1}{2}[\nabla_1\nabla_2\rho_1(\mathbf{r}_1, \mathbf{r}_2)]_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}} \\ &= \frac{1}{8} \sum_i n_i \left[\frac{\nabla\rho_i(\mathbf{r}) \cdot \nabla\rho_i(\mathbf{r})}{\rho_i(\mathbf{r})} \right] \end{aligned} \quad (6.9.3)$$

Here the sum is over natural spin-orbital components; in Hartree-Fock approximation it is over the N Hartree-Fock orbital components with $n_i = 1$. With this definition,

$$t(\mathbf{r}) \geq 0 \quad (6.9.4)$$

which is a strong and useful requirement on any approximation. Equation (6.9.3) has been shown to nicely exhibit shell structure for atoms, and

Table 6.6 Kinetic Energy Gradient-Expansion Components for Hartree-Fock Noble-gas Atoms. Percentage Errors in Parentheses

| Atom (Z) | T_{HF}^a | T_0 | T_2 | T_4 | $T_0 + T_2$ | $T_0 + T_2 + T_4$ |
|--------------|-------------------|----------------|--------|--------|----------------|-------------------|
| He (2) | 2.8617 | 2.5605 (-10.5) | 0.3180 | 0.0846 | 2.8785 (0.59) | 2.9631 (3.54) |
| Ne (10) | 128.55 | 117.77 (-8.39) | 10.07 | 1.94 | 127.84 (-0.55) | 129.78 (0.96) |
| Ar (18) | 526.82 | 489.95 (-7.00) | 34.27 | 6.21 | 524.22 (-0.49) | 530.43 (0.69) |
| Kr (36) | 2752.1 | 2591.2 (-5.85) | 141.9 | 24.1 | 2733.0 (-0.69) | 2575.1 (0.18) |
| Xe (54) | 7232.1 | 6857.7 (-5.18) | 325.8 | 53.8 | 7183.5 (-0.67) | 7237.3 (0.07) |

^a $T_{\text{HF}} = -E_{\text{HF}}$, E_{HF} from Clementi and Roetti (1974).

Table 6.7 Kinetic Energies for Molecules. Quantities in Parentheses Indicate Relative Errors, in Percent, With Respect to Hartree-Fock Values

| Molecule | T_{HF} | T_0 | $T_0 + T_2$ | $T_0 + T_2 + T_4$ |
|-------------------------------|-----------------|---------------|----------------|-------------------|
| H ₂ | 1.128 | 0.981 (-13.0) | 1.107 (-1.88) | 1.178 (4.44) |
| BH ₃ | 26.34 | 23.83 (-9.5) | 26.38 (0.17) | 26.94 (2.29) |
| CH ₄ | 40.17 | 36.45 (-9.3) | 40.10 (-0.19) | 40.91 (1.85) |
| HF | 100.0 | 91.30 (-8.7) | 99.42 (-0.59) | 101.0 (1.00) |
| NH ₃ | 56.16 | 50.97 (-9.2) | 55.88 (-0.49) | 56.90 (1.32) |
| H ₂ O | 76.08 | 69.19 (-9.1) | 75.61 (-0.62) | 76.92 (1.11) |
| BF | 124.2 | 113.2 (-8.9) | 123.7 (-0.41) | 125.8 (1.30) |
| CO | 112.7 | 102.2 (-9.3) | 112.1 (-0.52) | 114.1 (1.28) |
| C ₂ H ₂ | 76.70 | 69.52 (-9.4) | 76.52 (-0.25) | 77.93 (1.60) |
| N ₂ | 108.7 | 98.53 (-9.4) | 108.1 (-0.54) | 110.1 (1.25) |
| H ₂ CO | 113.8 | 103.3 (-9.2) | 113.2 (-0.54) | 115.3 (1.30) |
| F ₂ | 198.5 | 180.6 (-9.0) | 196.8 (-0.85) | 199.9 (0.66) |
| CO ₂ | 187.5 | 170.3 (-9.2) | 186.42 (-0.60) | 189.5 (1.05) |
| N ₂ O | 183.6 | 166.7 (-9.2) | 182.5 (-0.59) | 186.2 (1.38) |

useful comparisons between (6.9.3) and second-order gradient-expansion approximations to it have been made (Yang, Parr, and Lee 1986).

There are many other studies on kinetic energy involving the local behavior of kinetic energy density (for example, the important early paper by Goodisman 1970, Baltin 1972, Alonso and Girifalco 1978a, Tal and Bader 1978, Murphy and Parr 1979, Zorita, Alonso, and Balbás 1985, Pearson and Gordon 1985). Various forms of kinetic energy functional have been proposed (Haq, Chattaraj, and Deb 1984, Ghosh and Balbás 1985, Herring 1986, Yang, Parr, and Lee 1986, DePristo and Kress 1986, Herring and Chopra 1988, Plindov and Pogrebnya 1988).

If one forgets the Thomas-Fermi reference point for a moment and just asks what amount of $T_w[\rho]$ one would expect in a *good* kinetic energy functional, the answer at first glance would appear to be "all of it," for the correct long-range behavior and the correct cusps at nuclei both follow from such a term [if other terms are not present that swamp the effect of (6.7.1)]. Also, there is an argument from information theory that this term should be a leading component of $T[\rho]$ (Sears, Parr, and Dinur 1980; see also Gázquez and Ludena 1981). So one might conjecture that $T[\rho] = T_w[\rho] + \text{"rest."}$ What would be the rest? Hopefully, or at least perhaps, a "statistical" estimate will suffice for it. $T_0[\rho]$ itself is too much. But a formula for atoms and ions,

$$T[\rho] = T_w[\rho] + \gamma(N, Z)T_0[\rho] \quad (6.9.5)$$

does well (Acharya, Bartolotti, Sears, and Parr 1980). Figure 6.4 shows the $\gamma(N, N)$ that exactly fit the Hartree-Fock kinetic energies of neutral

atoms. To high accuracy, as the figure shows, $\gamma(N, N)$ has a nice functional form,

$$\gamma(N, N) = 1 - \frac{1.412}{N^{1/3}} \quad (6.9.6)$$

This was discovered empirically, but Gázquez and Robles (1982) later provided a derivation of much the same result (see also Acharya 1983). Variational calculations with (6.9.5) have been done (Bartolotti and Acharya 1982), giving modest but not impressive accuracy: no shell structure is obtained. The good fit in Figure 6.4 provides no assurance, of course, that variational calculations using (6.9.5) will give good results.

One gets considerably improved results, including shell structure, if one replaces (6.9.5) with a formula of the form

$$T[\rho] = T_w[\rho] + C_F \int f(\mathbf{r}) \rho^{5/3}(\mathbf{r}) d\mathbf{r} \quad (6.9.7)$$

where $f(\mathbf{r})$ is suitably determined (Deb and Ghosh 1983). An instructive rationale for (6.9.7) [or the less accurate (6.9.5)] (Acharya, Bartolotti, Sears, and Parr 1980) is that $T_w[\rho]$ is a correct estimate of the kinetic energy of the atomic $1s^2$ shell and $C_F \int [1 - f(\mathbf{r})] \rho^{5/3}(\mathbf{r}) d\mathbf{r}$ is an incorrect statistical estimate of that energy. If we rewrite (6.9.7) in the form

$$T[\rho] = T_0[\rho] - C_F \int [1 - f(\mathbf{r})] \rho^{5/3}(\mathbf{r}) d\mathbf{r} + T_w[\rho] \quad (6.9.8)$$

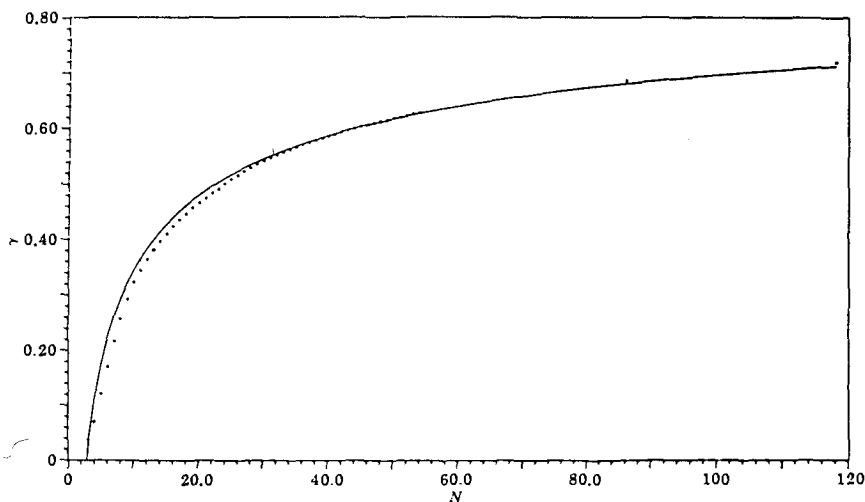


Figure 6.4. Values of $\gamma(N, N)$ for neutral atoms, calculated from Hartree-Fock electron densities and (6.9.5). The curve is the one-parameter fit of (6.9.6).

we see that this amounts to replacing the incorrect statistical estimate for the innermost shell with an improved value, accepting the statistical picture for the rest of the electrons. This idea is present in recent work by Englert and Schwinger (1982, 1984a,b,c), and was anticipated in a study by Tal and Bader (1978), who used $T_w[\rho]$ close to the nucleus and $T_0[\rho]$ outside. Nyden and Acharya (1981) did away with the "core" entirely. Many other works also favor the use of $T_w[\rho]$ as a kinetic energy component (Ludena 1983, Levy, Perdew, and Sahni 1984, Plumer and Stott 1985, March 1986a,b, Baltin 1987).

Deb and Chattaraj (1988) have proposed a first-order gradient correction to the kinetic energy of the form $-(1/40) \int \mathbf{r} \cdot (\nabla \rho / r^2) d\mathbf{r}$. This amounts to a generalization of a proposal by Langer (1937) to include a term $\int (\rho / r^2) d\mathbf{r}$ for atoms, studied also by Cummins and Nordholm (1984). Chattaraj and Deb (1984) have written an excellent review of the $T[\rho]$ problem.

The exchange energy $K[\rho]$ also possesses gradient expansions. To second order, the standard form is

$$K^{(2)}[\rho] = K_0[\rho] + K_2[\rho] \quad (6.9.9)$$

where

$$K_0[\rho] = K_{\text{TFD}}[\rho] = C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad (6.9.10)$$

and

$$K_2[\rho] = \beta \int \frac{\nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r})}{\rho^{4/3}(\mathbf{r})} d\mathbf{r} \quad (6.9.11)$$

with β a constant. A purely theoretical value of β (Sham 1971; Gross and Dreizler 1981) is

$$\beta_s = \frac{7}{144} (81\pi^5)^{-1/3} = 1.667 \times 10^{-3} \quad (6.9.12)$$

Kleinman (1984) gave a value of $\frac{8}{7}\beta_s$ for infinite systems. Empirically, a value for β of about 5.5×10^{-3} is better (Herman, Van Dyke, and Ortenburger 1969, Shih, Murphy, and Wang 1980). The derivation given by Gross and Dreizler (1981) is very similar to the derivation in §6.7 for the second-order gradient correction to Thomas-Fermi kinetic energy. However, to do away with an apparent divergence. Gross and Dreizler replace the Coulomb interaction $1/r$ by a screened interaction $\exp(-\alpha r)/r$ and take the limit $\alpha \rightarrow 0$ at the end of the calculation.

There exist various other approximate exchange-energy functionals. Indeed, for atoms, a generally better form for $K[\rho]$ than (6.9.9) is (Bartolotti 1982a).

$$K[\rho] = \int \rho^{4/3}(\mathbf{r}) [C(N) + D(N)y^2] d\mathbf{r}, \quad y = \frac{d \ln \rho}{d \ln r} \quad (6.9.13)$$

with $C(N) = C_F - 0.3599N^{-2/3}$, $D(N) = 2.009 \times 10^{-3}N^{-2/3}$. From a real-space analysis following Gross and Dreizler (1981), Perdew (1985a) provided a model that approximates the Hartree-Fock exchange energy to within 1%. Ghosh and Parr (1986) developed a phase-space approach based on a maximum entropy principle and obtained the nonlocal form (6.5.13). And both DePristo and Kress (1987) and Cedillo, Robles, and Gázquez (1988) construct rational-function approximations for the exchange energy functional. In §8.7, the effects of electron exchange will be readdressed in the context of a full exchange-correlation functional.

Efforts to find an accurate functional $T[\rho]$ by extensions of the Thomas-Fermi-Dirac-Weizsacker model have continued for many years—the problem is a very difficult one at best. An alternative approach is developed in the following chapter, the Kohn-Sham (1965) formulation of the density-functional theory, in which there is introduced the concept of corresponding non-interacting system, with kinetic energy $T_s[\rho]$ that can be accurately computed and is close to the exact $T[\rho]$. The Kohn-Sham idea dominates present-day density-functional calculations.