QM 15-030-710-003 Spring 1999
Addendum: Thomas-Fermi Model

Problem
In the Thomas-Fermi model for a neutral atom, express the kinetic energy of the electrons, the energy of electron-electron interaction and the energy of interaction of electrons with the nucleus in terms of the electron density $n(r)$.
Using these expressions, the virial theorem, and the behavior of the electrostatic potential of the self-consistent field of the electrons and the nucleus at small distances, $r \to 0$,

$$\phi(r) \approx \frac{Z}{r} - 1.80 Z^{4/3} \tag{0.1}$$

find the numerical expression for the full ionization energy of the atom.
Solution
The maximal kinetic energy of the electron at point r is

$$T_{\max} = \frac{1}{2}\left[3\pi^2 n(r)\right]^{2/3}$$

and the mean kinetic energy is

$$\overline{T} = \frac{\int_0^{p_{\max}} \frac{p^2}{2} d^3p}{\frac{4}{3}\pi p_{\max}^3} = \frac{\frac{2}{5}\pi p_{\max}^5}{\frac{4}{3}\pi p_{\max}^3} = \frac{3}{5}\frac{p_{\max}^2}{2} = \frac{3}{5} T_{\max}$$

so that the total kinetic energy of electrons is

$$T = \frac{3}{10}\left(3\pi^2\right)^{2/3} \int \left[n(r)\right]^{5/3} dV \tag{0.2}$$

The potential $\phi_e(0)$ of electrons at the nucleus (origin, $r = 0$) is

$$\phi_e(0) = -\int \frac{n(r)}{r} dV$$

and the interaction of electrons with the nucleus is

$$U_{en} = Z\phi_e(0) = -Z\int \frac{n(r)}{r} dV \tag{0.3}$$

The energy of electron-electron interaction is

$$U_{ee} = \frac{1}{2}\int \rho_e \phi_e dV = \frac{Z}{2}\int \frac{n(r)}{r} dV - \frac{\left(3\pi^2\right)^{2/3}}{4}\int \left[n(r)\right]^{5/3} dV \tag{0.4}$$

where $\rho_e = -n(r)$ and $\phi_e = \phi - Z/r = \left[3\pi^2 n(r)\right]^{2/3}/2 - Z/r$ were used. From eqs. (0.2), (0.3) and (0.4), find

$$5T + 6U_{ee} + 3U_{en} = 0 \tag{0.5}$$

Using eq. (0.5) and the virial theorem

$$2T + U = 2T + U_{ee} + U_{en} = 0 \tag{0.6}$$

find

$$T = -\frac{3}{7}U_{en} = -\frac{3}{7}Z\phi_e(0) \text{ and } U_{ee} = -\frac{1}{7}U_{en} = -\frac{1}{7}Z\phi_e(0)$$

and (using again eq. (0.6)) the full ionization energy

$$E_{ion} = -E = -\left(T + U_{ee} + U_{en}\right) = T = -\frac{3}{7}U_{en} = -\frac{3}{7}Z\phi_e(0) \tag{0.7}$$

where, according to eq. (0.1),

$$\phi_e(0) = -1.80 Z^{4/3}$$

Consequently, $E_{ion} \approx 0.77 Z^{7/3}$ atomic units $\approx 21.0 Z^{7/3}$ eV.
Note: Z-dependence of T, U_{ee}, and U_{en} can be obtained by finding Z-dependence of the typical distance from the nucleus and typical momentum of an electron in the T-F model, as described in Problem 9 of Assignment 9.