TF approximation for unbound electrons

The density of unbound electrons in a hybrid quantum / TF model is (Rozsnyai 1972):

$$\rho_{ub}(r) = \frac{\sqrt{2}}{\pi^2 c^3}\left[T q(r)\right]^{3/2}\left\{ I_{1/2}(z) + \frac{5}{4}\frac{\cancel{k}T}{q(r)} I_{3/2}(z) + \frac{7}{32}\frac{\cancel{k}T^2}{q^2(r)} I_{5/2}(z) + 6\left(\frac{T}{q(r)}\right)^3 \right\},$$

where
$$q(r) = \{M^2 c^4 + [r' V'(r)]^2\}^{1/2},$$

$$I_\nu(z) = \int_{-\frac{V(r)}{T}}^{\infty} \frac{t^\nu}{e^{(t-z)}+1}\, dt,$$

$$V(r) = V_{en}(r) + V_{Hxc}(r),$$

$$z(r) = \frac{\mu - V(r) + Mc^2 - q(r)}{T}.$$

We work in the non-relativistic limit, so:

$$\cancel{k}T \ll M_e c^2 \quad \& \quad |r' V'(r)| \ll M_e c^2$$

$$\Rightarrow q(r) \simeq M_e c^2, \quad M_e = 1 \text{ in atomic units}$$

Hence in this limit, $\rho_{ub}(r)$ is equal to:

$$\rho_{ub}(r) = \frac{\sqrt{2}}{\pi^2} T^{3/2} \int_{-V(r)/T}^{\infty} dx\, \frac{x^{1/2}}{e^{(x - [\mu - V(r)]/T)}+1}$$

We make the following change of variables:
~~$x = y$~~

$$x = \frac{y}{T} \Rightarrow dx = \frac{dy}{T}$$

$$\Rightarrow \boxed{\rho_{u0}(r) = \frac{\sqrt{2}}{\pi^2} \int_{-V(r)}^{\infty} dy \, \frac{y^{1/2}}{e^{(y-(\mu - V(r)))/T} + 1}}$$

This is very similar to the density of the ideal electron gas, which is a special case of the above when $V(r) = 0$.

The ~~tot~~ number of unbound electrons is then given by

$$N_{u0} = \int r^2 \rho_{u0}(r) \, dr$$

And μ found in the usual manner by enforcing $N_{u0}(r) + N_b(r) = Z$.

Now we compute the energy of the unbound electrons. ~~Again~~, In the relativistic limit this is given by:

$$\rho_E^{ub}(r) \cancel{E_{sub}} = \frac{1}{\pi^2 c^3} T^2 \int_{x_0}^{\infty} dx \frac{[T^2 x^2 + 2xTq(r)]^{1/2} [Tx + q(r)] [x - x_0(r)]}{e^{x - z(r)} + 1}$$

$$\xrightarrow{q(r) >> xT} \simeq \frac{1}{\pi^2 c^3} T^2 \int_0^{\infty} \frac{\sqrt{2}\, q^{3/2}(r) \, (Tx)^{1/2} \, [x - x_0(r)]}{e^{x - z(r)} + 1} dx$$

$$\xrightarrow{q(r) \simeq mc^2} = \frac{\sqrt{2}}{\pi^2} T^{5/2} \int_0^{\infty} \frac{x^{1/2} [x - x_0(r)]}{e^{x - z(r)} + 1} dx$$

~~Making the substitution $x = y/T$ yields:~~

The unbound energy E_{ub} is equal to:

$$E_{ub} = 4\pi \int_0^L dr\, r^2\, \rho_E^{ub}(r)$$

Making the change of variables $x = y/T$ yields:

$$\rho_E^{ub}(r) = \frac{\sqrt{2}}{\pi^2} \int_{-V(r)}^{\infty} \frac{y^{1/2}\,(y + V(r))}{e^{[y-(\mu-V(r))]/T} + 1}\, dy$$

$$= \frac{\sqrt{2}}{\pi^2} \left\{ \int_{-V(r)}^{\infty} \frac{y^{3/2}}{e^{[y-(\mu-V(r))]/T} + 1}\, dy \right.$$

$$\left. + V(r) \cancel{+V(r)} \int_{-V(r)}^{\infty} \frac{y^{1/2}}{e^{[y-(\mu-V(r))]/T} + 1}\, dy \right\}$$

$$= \frac{\sqrt{2}}{\pi^2} \int_{-V(r)}^{\infty} \frac{y^{3/2}}{e^{[y-(\mu-V(r))]/T} + 1}\, dy + V(r)\, \rho_{ub}(r)$$

And hence:

$$\boxed{\begin{aligned} E_{ub} = 4\pi\, \frac{\sqrt{2}}{\pi^2} \int_0^L dr\, r^2 \int_{-V(r)}^{\infty} \frac{y^{3/2}}{e^{[y-(\mu-V(r))]/T} + 1} \\ + 4\pi \int_0^L dr\, r^2\, V(r)\, \rho_{ub}(r) \end{aligned}}$$

Again, this reduces to the ideal expression for $V(r) = 0$.