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Modified Weizsäcker Corrections in Thomas-Fermi Theories

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We consider theories in which a kinetic-energy correction $(\lambda \hbar^2/32\pi^2 m)[(\nabla\rho)^2/\rho]$ (ρ = density) is
added to the usual Thomas-Fermi term. A treatment based on the WKB method and expected
to be valid for large r shows $\lambda = 1$ here, as found experimentally. For small r, $\lambda = 1$ is needed
to give proper behavior of ρ, but other arguments suggest that the Thomas-Fermi term be
dropped here.

The Thomas-Fermi and related theories,[1] at-
tractive because of their simplicity, are not sat-
isfactory for atomic problems because they yield
an electron density with incorrect behavior very
close to and very far away from the nucleus. Von
Weizsäcker[2] suggested the addition of an inhomo-
geneity correction

$$U_W = (\hbar^2/32\pi^2 m)(\Delta\rho)^2/\rho \tag{1}$$

to the kinetic-energy density. Here, ρ is the den-
sity in Weizsäcker's theory. The differential equa-
tion for ρ now becomes

$$\frac{5}{3}\kappa_k\rho^{2/3} + \frac{\hbar^2}{32\pi^2 m}\left[\left(\frac{\nabla\rho}{\rho}\right)^2 - \frac{2\nabla^2\rho}{\rho}\right] + V = E \ , \tag{2}$$

with E as a Lagrange multiplier. This leads to a
density which has the proper qualitative behavior
in both the large and small r limits ($\rho \rightarrow$ const and
$\rho \rightarrow$ decreasing exponential, respectively), but is
quite unsatisfactory from a quantitative point of
view.[3] It seems that simply by adding the Weizsäcker
term to the usual Thomas-Fermi kinetic-energy
term, $\kappa_k\rho^{5/3}$ gives too much kinetic energy. The
original derivation of U_w has been questioned,[4-6]
and it was suggested by Berg and Wilets[4] that a
term λU_w be used with $\lambda < 1$. It was found that
$\lambda \sim \frac{1}{8}$ works well for the harmonic oscillator, and
$\frac{1}{2} < \lambda < 1$ for the square-well problem.

There have been attempts to calculate correc-
tions to the simple Thomas-Fermi theory as ex-

pansions in $\hbar$, and some of these derive terms of the form λU_w. For instance, Golden[7] found $\lambda = \frac{13}{45}$ and several Russian authors[8] $\lambda = \frac{1}{9}$. It seems, however, that the expansions are not valid[9,10] for very large or very small r, just where the correction is important. In fact, poor results are obtained[5,11,12] for energies with these corrected theories. Taking an experimental point of view, Yonei and Timoshima[10] considered noninteracting electrons in a Coulombic field using the correction λU_w with λ varying from 0 to 1 in steps of 0.2. They found that $\lambda = 1$ led to densities in good accord with quantum-mechanical ones for large r, while $\lambda = 0.2$ gave the best results with respect to the small-r density. Later work on the rare gases with $\lambda = 0.2$ by these authors[13] confirmed this: ρ was accurate near $r = 0$ but not for $r \to \infty$. In this paper we wish to make several observations which suggest a slightly different way of using the Weizsäcker correction.

We first consider large r, using a "derivation" of the Weizsäcker term given by Fényes[14] in terms of the WKB method. We employ the formalism of Brillouin[15] here. At some point in space, let the potential be locally separable along axes x, y, z. Then the WKB one-electron wave functions are written in the form

$$\Psi_n = \left(\frac{\nu_x \nu_y \nu_z}{v_x v_y v_z}\right)^{1/2}$$
$$\times \exp\left[\frac{i}{\hbar}\left(\int^x p_x dx + \int^y p_y dy + \int^z p_z dz\right) + \theta\right] , \quad (3)$$

where ν_x is the classical frequency, given by the size of the energy quantum divided by h, and $v_x = p_x/m$ is the speed at the point in question. The density, making the correspondence

$$\sum_n \to h^{-3} \int v_x v_y v_z / \nu_x \nu_y \nu_z \, dp_x dp_y dp_z , \quad (4)$$

is $\quad \rho = 2\sum_n |\Psi_n|^2 \to 2h^{-3} \int d^3p = 8\pi p'^3/3h^3 , \quad (5)$

where it is assumed that the distribution in momentum is spherically symmetric at each point, $p'(\vec{r})$ being the maximum value of momentum. In the zeroth approximation, the speeds are taken as constant in (3) and the kinetic-energy density, using (5), is

$$\frac{\hbar^2}{m}\sum_n \left|\vec{\nabla}\Psi_n\right|^2 = \frac{\hbar^2}{m}\sum_n \left(\frac{\nu_x \nu_y \nu_z}{v_x v_y v_z}\right)^{1/2} \frac{i\vec{p}}{\hbar}\Big|^2$$

$$\to (mh^3)^{-1} \int p^2 d^3p , \quad (6)$$

and we recover the Thomas-Fermi term

$$\frac{4\pi}{mh^3}\frac{p'^5}{5} = \frac{3h^2}{40m}\left(\frac{3}{\pi}\right)^{2/3}\rho^{5/3} = \kappa_k \rho^{5/3} \equiv U_{TF} \quad . \quad (7)$$

One might as well have used plane waves here. In the next approximation, we must consider that dv_x/dx is not zero (inhomogeneity), although our choice of axes means that v_x does not depend on y or z, and so on. Then

$$\frac{\hbar^2}{m}\sum_n |\vec{\nabla}\Psi_n|^2 = \frac{\hbar^2}{m}\sum_n \left|\left(\frac{\nu_x \nu_y \nu_z}{v_x v_y v_z}\right)^{1/2}\left(\frac{i\vec{p}}{\hbar} - \frac{\vec{\nabla}v_x}{2v_x}\right)\right|^2$$

$$\to (mh^3)^{-1} \int \left|i\vec{p} - \tfrac{1}{2}\hbar\vec{\nabla}\ln(w)\right|^2 d^3p ,$$

where $w = p_x p_y p_z$. We again obtain (7) but also an additional term, which we may write

$$U' = (16\pi^2 mh)^{-1} \int \left|\ln(w)\right|^2 dw . \quad (8)$$

Some calculations by Gombás[5] bear much resemblance to the above up to this point.

Fényes[14] noted that if $\vec{\nabla}\ln(w)$ is constant it can be taken out of the integral and evaluated for w equal to its maximum value, which is $\frac{4}{3}\pi p'^3$, and this is $\frac{1}{2}h^3\rho$ according to (5). Then we have

$$U' \sim (16\pi^2 mh\rho^2)^{-1}(\vec{\nabla}\rho)^2 \int dw = U_W ,$$

the Weizsäcker correction. When can $\vec{\nabla}\ln(w)$ be considered constant? When the range of integration in (8) is small, i.e., when p' and hence ρ is small. This is for large values of r, which may help explain Yonei and Tomishima's results: The full Weizsäcker correction should be used for large r.

Turning to small r, we note that the singularity of the Coulomb field places a restriction on the behavior of the correct density. It is reasonable to demand that the modified Thomas-Fermi theory give a density obeying this restriction. One can show[16] that the correct density obeys

$$\left[\frac{\partial\rho}{\partial r}\right]_{r=0} = -2Za_0^{-1}[\rho]_{r=0} , \quad (9)$$

where a_0 is the Bohr radius. This follows from a theorem by Kato[17] concerning the wave functions, and is valid for the n-electron system, whether or not the electrons are interacting. It is easily understood when one realizes that, when very near a nucleus, the electrons see essentially a pure Coulombic field, and the electron density is essentially that of one or two $1s$ electrons:

$$\rho = (CZ^3/\pi)e^{-2Zr/a_0} , \quad (10)$$

with $C = 1$ or 2. Differentiating, we recover (9). Now we consider the modified Thomas-Fermi equation (2) near the nucleus, multiplying U_W by λ. All potential energy terms are negligible compared to that due to the nucleus, $-Ze^2/r$. The only other terms which are not finite come from U_W, and such terms must cancel the $-Ze^2/r$ according to (2). Thus we require

$$\frac{\lambda h^2}{32\pi^2 m}\left[\left(\frac{\rho_r}{\rho}\right)^2 - \frac{4r\rho_r + 2r^2\rho_{rr}}{\rho r^2}\right] - \frac{Ze^2}{r} = 0.$$

It suffices to keep the most singular term, and we find

$$\lambda[\rho_r/\rho]_{r=0} = -2Ze^2 m^{-1}\hbar^{-2} \quad,$$

which agrees with (9) if $\lambda = 1$. Thus one should use the full Weizsäcker correction for small r.

Now this argument says nothing about the other term (7), and one knows that adding U_W to that term gives too much kinetic energy. In particular, if there are n electrons in one quantum state with wave function Ψ, so that the density is given by

$$\rho = n|\Psi|^2 \quad,$$

the kinetic-energy density is

$$(n\hbar^2/2m)|\nabla\Psi|^2 = (\hbar^2/8m)[(\nabla\rho)^2/\rho] \quad.$$

Thus the Weizsäcker term gives *all* the kinetic energy in this case.[18] As noted above, close to the nucleus one has essentially two electrons in a $1s$ orbital. This suggests that the Thomas-Fermi term should be corrected, by writing it as $f(r)U_{TF}$ where $f(r)$ goes to zero for $r \to 0$ and approaches unity when r is such that the assumptions of the Thomas-Fermi theory are valid, say for $r \gtrsim Z^{-1}a_0$.[19] Here the Weizsäcker term becomes relatively unimportant. For large r, we have argued that $U_W + U_{TF}$ be used. Eventually, U_W will dominate U_{TF}, per-

haps due to the fact that the density is due to electrons all in one quantum state.

To summarize, our arguments suggest that the full Weizsäcker correction ($\lambda = 1$) be used throughout along with the Thomas-Fermi kinetic-energy term, except that the Thomas-Fermi term be dropped near the nucleus. Tomishima and Yonei[13] have given the electron density for calculations on the rare gases where $U_{TF} + U_W$ was used. One can use their results to get a rough estimate of the validity of our method, by calculating $\int \kappa_B\rho^{5/3}d\tau$ over a sphere of radius $Z^{-1}a_0$ around the nucleus. We find this quantity to be roughly half of the difference between the calculated and correct energies. This suggests that $f(r)$ be essentially zero out to r larger than $Z^{-1}a_0$. The correct cutoff should in fact be such that the $1s$ density no longer dominates the total density.

Gombás has in fact suggested[5,12] that the Thomas-Fermi term U_{TF} be multiplied by a correction factor. For the electrons with principal quantum number n, the kinetic energy would be the Weizsäcker contribution plus $(2n-2)/(2n+1)$ times the Fermi contribution [Eq. (7)]. In the present interpretation, the factor of $\lambda = 0.2$ in the Weizsäcker term near the nucleus (while keeping the full Fermi term) found by Yonei and Tomishima has no deep significance. It is suggested that $0.2\,U_W + U_{TF}$ is roughly equivalent to $U_W + f(r)U_{TF}$ over the important region.

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