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[1]E. Allin, A. May, B. Stoicheff, J. Stryland, and H. Welsh, Appl. Opt. 6, 1597 (1967).
[2]J. V. Foltz, D. H. Rank, and T. A. Wiggins, J. Mol. Spectry. 21, 201 (1966).
[3]J. Fiutak and J. Van Kranendonk, Can. J. Phys. 40, 1085 (1962).
[4]J. Fiutak and J. Van Kranendonk, Can. J. Phys. 41, 21 (1963).
[5]P. J. Brannon, C. H. Church, and C. W. Peters, J. Mol. Spectry. 27, 44 (1968).
[6]J. Van Kranendonk, Can. J. Phys. 41, 433 (1963).
[7]R. H. Dicke, Phys. Rev. 89, 472 (1953).
[8]D. H. Rank and T. A. Wiggins, J. Chem. Phys. 39, 1348 (1963).
[9]P. Lallemand, P. Simova, and G. Bret, Phys. Rev. Letters 17, 1239 (1966).
[10]J. I. Gersten and H. M. Foley, J. Opt. Soc. Am. 58, 933 (1968).
[11]P. J. Brannon, J. Quant. Spectry. Radiative Transfer 8, 1615 (1968).
[12]C. J. Tsao and B. Curnutte, J. Quant. Spectry. Radiative Transfer 2, 41 (1962).
[13]See, for example, *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U.S. Department of Commerce, Nat'l. Bur. Std., Washington, D.C., 1964) Appl. Math. Ser. 55.
[14]R. H. Hunt, C. W. Robertson, and E. K. Plyler, Appl. Opt. 6, 1295 (1967).
[15]W. Boyd, P. J. Brannon, and N. M. Gailar, Appl. Phys. Letters 16, 135 (1970).
[16]P. A. Jansson, J. Opt. Soc. Am. 60, 184 (1970).

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# Modified Weizsäcker Corrections in Thomas-Fermi Theories

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We consider theories in which a kinetic-energy correction $(\lambda h^2/32\pi^2 m)[(\nabla\rho)^2/\rho]$ ($\rho$ = 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 $\rho$, but other arguments suggest that the Thomas-Fermi term be dropped here.

The Thomas-Fermi and related theories,[1] attractive because of their simplicity, are not satisfactory 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 inhomogeneity correction

$$U_W = (h^2/32\pi^2 m)(\Delta\rho)^2/\rho \qquad (1)$$

to the kinetic-energy density. Here, $\rho$ is the density in Weizsäcker's theory. The differential equation for $\rho$ now becomes

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

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 ($\rho \to$ const and $\rho \to$ 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 $\lambda U_w$ 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 corrections to the simple Thomas-Fermi theory as ex-

pansions in $\hbar$, and some of these derive terms of the form $\lambda U_w$. 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 $\lambda U_w$ with $\lambda$ 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: $\rho$ 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 $\nu_x$ 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 $$\rho = 2\sum_n |\Psi_n|^2 \to 2h^{-3} \int d^3p = 8\pi p'^3/3h^3 , \quad (5)$$

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

$$\frac{\hbar^2}{m}\sum_n \left|\vec{\nabla}\Psi_n\right|^2 = \frac{\hbar^2}{m}\sum_n \left(\frac{\nu_x \nu_y \nu_z}{v_x v_y v_z}\right)^{1/2} \frac{i\vec{p}}{\hbar}\Psi_n \Big|^2 \to (mh^3)^{-1} \int p^2 d^3p , \quad (6)$$

and we recover the Thomas-Fermi term

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

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

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

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

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

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 $\rho$ 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 1$s$ 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 $U_{\mathrm{W}}$ by $\lambda$. 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 $U_{\mathrm{W}}$, 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 $\Psi$, 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 1*s* 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 $U_{TF}$, perhaps 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 $\int \kappa_k \rho^{5/3} d\tau$ 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 1*s* 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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[1] P. Gombás, *Die Statistische Theorie des Atoms und Ihre Anwendungen* (Springer-Verlag, Vienna, 1949).

[2] C. F. Von Weizsäcker, Z. Physik 96, 431 (1934).

[3] Reference 1, p. 116.

[4] R. Berg and L. Wilets, Proc. Phys. Soc. (London), 68, 16 (1955).

[5] P. Gombás, Acta Phys. Acad. Sci. Hung. 25, 361 (1968) and previous work by this author.

[6] N. H. March, Advan. Phys. 6, 1 (1957), Secs. 9.1 and 9.2.

[7] S. Golden, Phys. Rev. 105, 604 (1957); 107, 1283 (1957).

[8] A. S. Kompaneets and E. S. Pavlovskii, Zh. Eksperim. i Teor. Fiz. 31, 427 (1956) [Soviet Phys. JETP 4, 328 (1957)]; D. A. Kirznits, *ibid.* 32, 115 (1957) [*ibid.* 5, 64 (1957)].

[9] H. Payne, Phys. Rev. 132, 2544 (1963); N. Bâlàzs, *ibid.* 134, A841 (1964).

[10] K. Yonei and Y. Tomishima, J. Phys. Soc. Japan 20, 1051 (1965).

[11] H. M. Schey and J. L. Schwartz, Phys. Rev. 137, A709 (1965).

[12] P. Gombás, Phys. Letters 28A, 585 (1969).

[13] Y. Tomishima and K. Yonei, J. Phys. Soc. Japan 21, 142 (1966).

[14] I. Fényes, Z. Physik 125, 336 (1949).

[15] L. Brillouin, Actualités Sci. et Ind. 160, 1 (1934).

[16] E. Steiner, J. Chem. Phys. 39, 2365 (1963).

[17] T. Kato, Commun. Pure Appl. Math 10, 151 (1957).

[18] Reference 1, p. 110.

[19] L. D. Landau and E. M. Lifschitz, *Quantum Mechanics: Non-Relative Theory* (Addison-Wesley, Reading, Mass., 1959), p. 238.