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Complementary variational principles in the Thomas-Fermi theory

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The relative merits of the complementary variational principles for the upper and lower bounds to the exact Thomas-Fermi energy of a neutral atom, and of a suggestion of Anderson, Arthurs, and Robinson for the determination of the parameters in a variational function from the minimization of the difference between the upper and lower bounds, are examined by applying these to two variational functions. It appears that the variational principle for the lower bound is of the most practical value. The suggestion of Anderson *et al.* appears to have little merit.

In a paper with the same title as the present one, Csavinszky[1] has emphasized the importance of the normalization of the electron density associated with approximate variational solutions of the Thomas-Fermi (TF) equation for normal atoms, and has also discussed a suggestion of Anderson, Arthurs, and Robinson for the determination of the parameters in a variational function from the minimization of the difference between the complementary upper and lower bounds to the exact TF energy of a neutral atom. In the present paper we discuss the relative merits of the two complementary bounds and of the suggestion of Anderson *et al.* by applying these to two variational functions.

Firsov[2] formulated complementary variational principles for a TF atom. If we consider a neutral atom, using atomic units, the complementary variational principles establish an upper bound J and a lower bound G for a particular approximate solution of the TF equation in such a manner that the exact TF energy E of the atom lies in the interval

$$G \leqslant (\mu/Z^2)E \leqslant J\,, \tag{1}$$

where Z is the atomic number, and $\mu = \frac{1}{2}(3\pi/4)^{2/3} \times Z^{-1/3}$. In the TF theory, μ is involved in the definition of a dimensionless variable x, which is given by $x = r/\mu$.

The complementary bounds G and J are defined as (using opt for optimum)

$$G = G(\phi)_{\text{opt}} \tag{2a}$$

and

$$J = J\left(\frac{d\phi}{dx}\right)_{\text{opt}}, \tag{2b}$$

where $G(\phi)$ and $J(d\phi/dx)$ are given[3,4] by the expressions

$$G(\phi) = \int_0^\infty \left[-\frac{1}{2}\left(\frac{d\phi}{dx}\right) - \frac{2}{5}\,\phi^{5/2}x^{-1/2}\right]dx \tag{3a}$$

and

$$J\left(\frac{d\phi}{dx}\right) = \int_0^\infty \left[\frac{1}{2}\left(\frac{d\phi}{dx}\right)^2 + \frac{3}{5}x^{1/3}\left(\frac{d^2\phi}{dx^2}\right)^{5/3}\right]dx + \left(\frac{d\phi}{dx}\right)_{x=0}. \tag{3b}$$

In Eqs. (3a) and (3b), the function ϕ is a trial function depending on a number of parameters which are determined by maximizing $G(\phi)$ and minimizing $J(d\phi/dx)$; the respective optimized trial functions shall be denoted by ϕ_G and ϕ_J. The trial functions may be chosen to be different for determining G and J. Equations (3a) and (3b) were generalized by Arthurs and Robinson[3] for a system containing an arbitrary number of electrons and nuclei.

The variational principle for calculating the lower bound G, Eq. (3a), appears to have been first given by Wesselow[5] and independently by Flügge and Marschall.[6] This variational principle has a direct connection with TF equation. If the negative of the integral of Eq. (3a) is substituted into the Euler-Lagrange equation,[7]

$$\frac{\partial F}{\partial \phi} - \frac{d}{dx}\left(\frac{\partial F}{\partial \phi'}\right) = 0\,,$$

where

$$F = \tfrac{1}{2}\left(\frac{d\phi}{dx}\right) + \tfrac{2}{5}\,\phi^{5/2}x^{-1/2}\,,$$

then we get the TF equation

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}}. \tag{4}$$

The variational principle for the upper bound J does not have such a direct interpretation. Also, while the variational principle for bound G is exact, that for bound J is only approximate, in the sense that in obtaining Eq. (3b) certain terms have been neglected.[3] Anderson *et al.*[4] have suggested that the closest approximation to the exact solution of ϕ is that which is obtained by minimizing $H(\phi)$, where

$$H(\phi)=J\left(\frac{d\phi}{dx}\right)-G(\phi)\,. \tag{5}$$

We note here that this suggestion, while intuitively appealing, is not a proven variational principle and can only be considered as a plausible conjecture. The optimum value of $H(\phi)$ shall be denoted by H and the corresponding optimized trial function by ϕ_H. Anderson *et al.*[4] applied Eqs. (3a), (3b), and (5) to a single-parameter trial function suggested by Roberts.[8] However, as pointed out by Csavinszky,[1] single-parameter trial functions, in general, cannot satisfy simultaneously both the requirement of the normalization of the electron density and the requirement of extremalization of one of Eqs. (3a), (3b), and (5). In view of the fact that the trial function for ϕ used by Anderson *et al.*[4] is not associated with a normalized electron density, no definite conclusions are possible from their results.

From a practical point of view, one would like to know: (a) which one of the two equations, (3a) or (3b), is more useful for calculating E, and (b) which one of the three equations, (3a), (3b), or (5), will give the closest approximation to the screening function ϕ.

We consider here two different multiparameter variational functions for ϕ and calculate the values of G, J, and H therefrom. We compare G and J with the exact value of $\mu E/Z^2$. The resulting ϕ's are compared with the exact ϕ and also between themselves.

The first variational function examined in this paper is due to Csavinszky[9,10] who proposed the following variational function for ϕ:

$$\phi=(ae^{-\alpha x}+be^{-\beta x})^2, \tag{6}$$

where a, b, α, and β are parameters; a and b are related by

$$a+b=1,$$

in order to satisfy the boundary condition,

$$\phi(0)=1\,. \tag{7}$$

The parameters in Eq. (6) were determined by extremalizing $G(\phi)$ with respect to these parameters subject to the subsidiary condition that the electron density be normalized:

$$\int \rho\, dv=N, \tag{8}$$

where N is the number of electrons, dv is the volume element, and ρ is the electron density which is related to ϕ by

$$\rho=\frac{Z}{4\pi\mu^3}\left(\frac{\phi}{x}\right)^{3/2}.$$

The values of the parameters determined by Csavinszky together with the value of G are shown in Table I. The number of significant figures in G has been truncated.

For the second function, we assume

$$\phi=\frac{e^{-ax}}{1+bx}, \tag{9}$$

where a and b are parameters. This type of function was first proposed by Gáspár[11] to represent Z_p/Z, where Z_pe is the effective charge in the usual notation of the self-consistent field theory.

There are three integrals involved in the evaluation of $G(\phi)$, $J(d\phi/dx)$, and $H(\phi)$. We shall find it convenient to represent them by

$$L_1=\int_0^\infty \tfrac{1}{2}\left(\frac{d\phi}{dx}\right)^2 dx\,, \tag{10a}$$

$$L_2=\int_0^\infty \tfrac{2}{5}\phi^{5/2}x^{-1/2}\,dx\,, \tag{10b}$$

and

$$L_3=\int_0^\infty \tfrac{3}{5}x^{1/3}\left(\frac{d^2\phi}{dx^2}\right)^{5/3} dx\,. \tag{10c}$$

The integrals L_1 and L_2 for the function in Eq. (6) have been analytically evaluated by Csavinszky.[9] It is possible to evaluate analytically these two integrals for the Gáspár function, Eq. (9), also.

TABLE I. Optimized values of the parameters in the Csavinszky function and the corresponding values of G, J, and H.

	a	b	α	β	
From $G(\phi)$	0.721 833 7	0.278 166 3	0.178 255 9	1.759 339	$G=-0.681\,964\,81$
From $J(d\phi/dx)$	0.908 3	0.091 7	0.256 5	5.002	$J=-0.616\,57$
From $H(\phi)$	0.885 1	0.114 9	0.245	4.189	$H=0.070\,69$

The final expressions are as follows:

$$L_1 = \frac{a}{3} + \frac{b}{6} - \frac{a^2}{6b} + \frac{a^3}{3b^2} e^{2a/b} \int_{2a/b}^{\infty} \frac{e^{-t}}{t}\, dt\,, \tag{11}$$

$$\begin{aligned} L_2 &= \frac{2}{5\sqrt{b}} U\left(\tfrac{1}{2}, -1, \frac{5a}{2b}\right) \\ &= \frac{8}{15\sqrt{b}} \left\{ 1 - \frac{1}{2}\left(\frac{5a}{2b}\right) + \frac{1}{\sqrt{\pi}} \sum_{k=0}^{\infty} \frac{\Gamma(\frac{5}{2}+k)}{(2+k)!k!} \left[\psi(3+k) + \psi(1+k) - \psi(\tfrac{5}{2}+k) - \ln\left(\frac{5a}{2b}\right)\right] \left(\frac{5a}{2b}\right)^{k+2} \right\}, \end{aligned} \tag{12}$$

where $U(\alpha,\beta,x)$ is the confluent hypergeometric function, and $\psi(x)$ is the digamma function, defined by $\psi(x) = \Gamma'(x)/\Gamma(x)$. From the subsidiary condition, Eq. (8), we obtain

$$\frac{\Gamma(3/2)}{b^{3/2}} U\left(\frac{3}{2}, 1, \frac{3a}{2b}\right) = \frac{N}{Z}$$

or

$$\frac{2}{\sqrt{\pi}\, b^{3/2}} \sum_{k=0}^{\infty} \frac{\Gamma(\frac{3}{2}+k)[2\psi(1+k) - \psi(\frac{3}{2}+k) - \ln(3a/2b)]}{(k!)^2} \left(\frac{3a}{2b}\right)^k = \frac{N}{Z}. \tag{13}$$

For neutral atoms, the right-hand side of Eq. (13) is equal to one. The expression for $G(\phi)$ was maximized with respect to the parameter b, the other parameter, a, being determined from Eq. (13). The resulting values of a, b, and G are given in Table II.

The integral L_3 cannot be evaluated analytically for either of functions (6) or (9); consequently, numerical integration was resorted to for calculating this integral. Both, for the Csavinszky and the Gáspár function, $J(d\phi/dx)$ and $H(\phi)$ were minimized separately, subject to condition (8), and the parameters in the two functions thus determined are shown in Tables I and II, respectively, together with the corresponding values of J and H.

An accurate value of $\mu E/Z^2$ can be found from the numerical solution[12,13] of the TF equation, and is

$$\mu E/Z^2 = -0.6806. \tag{14}$$

A comparison of this value with the values of G and J in Table I and II shows that for both the trial functions, G is much closer to the exact value than J. It would appear that for calculating E, Eq. (3a) provides a better approximation than Eq. (3b).

To compare the different ϕ's with the exact[13] ϕ (represented by ϕ_{TF}), in Fig. 1, we show the ratio ϕ (Csavinszky)/ϕ_{TF} as a function of x for the three sets of parameters obtained from optimizing $G(\phi)$, $J(d\phi/dx)$, and $H(\phi)$. It will be noticed from Fig. 1 that ϕ_G is the best of the three. Also, ϕ_J and ϕ_H are rather close.

TABLE II. Optimized values of the parameters in the Gáspár function and the corresponding values of G, J, and H.

	a	b	
From $G(\phi)$	0.114 32	1.1455	$G = -0.681\,2755$
From $J(d\phi/dx)$	0.075 06	1.412	$J = -0.607\,91$
From $H(\phi)$	0.088 77	1.366	$H = 0.076\,20$

A similar comparison for the Gáspár function is made in Fig. 2. The TF theory is considered to be most valid for small values of x. Thus to compare the various curves, we shall confine ourselves, somewhat arbitrarily, to $x < 15$. Here also, in Fig. 2, we notice that ϕ_G is the best of the three. However, contrary to the Csavinszky case, here ϕ_J and ϕ_H are rather different.

It is of interest to compare the two variational functions, Eqs. (6) and (9). In Fig. 3, we show a plot of ϕ_G(Csavinszky), ϕ_G(Gáspár), and ϕ_{TF} against

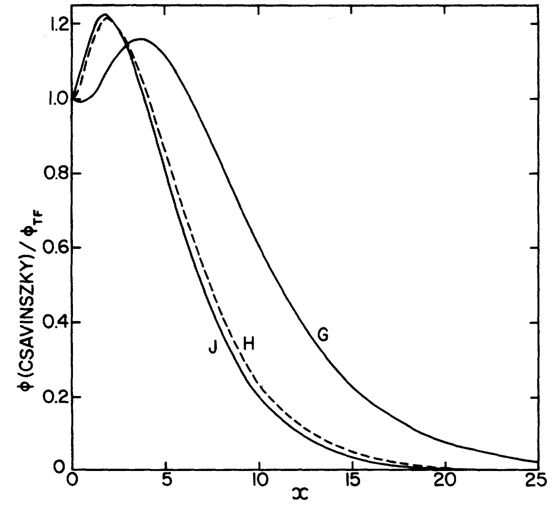

FIG. 1. Ratio ϕ(Csavinszky)/ϕ_{TF} as a function of x. The labels G, J, and H correspond to the parameters obtained from optimizing Eqs. (3a), (3b), and (5), respectively.

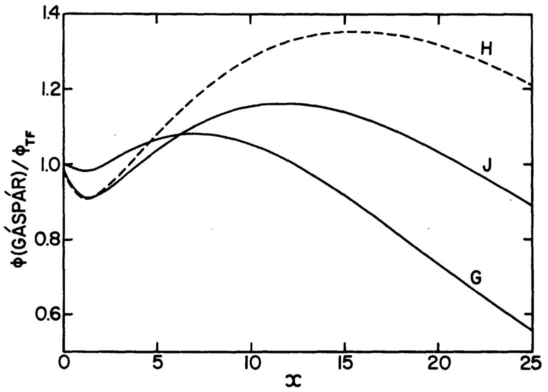

FIG. 2. Ratio ϕ(Gáspár)/ϕ_{TF} as a function of x. The labels G, J, and H correspond to the parameters obtained from optimizing Eqs. (3a), (3b), and (5), respectively.

x. It is noticed that the Gáspár function is closer to the exact TF function than the Csavinszky function. To give an idea of what this figure means in physical terms, we note that up to about $x=8$, the exact TF, the Csavinszky and the Gáspár solutions just about coincide. For a moderately heavy atom, such as Kr, this limit corresponds to $r=2.1a_B$, the "interior" of the atom.

Some years ago, Umeda[14] had proposed a measure for the "closeness" of an approximate solution of ϕ to the exact one. He proposed that the smaller the value of $(-G)$, the better the approximate solution of ϕ is. The results obtained here from Eq. (3a) support Umeda's suggestion. The value of $(-G)$ for the Gáspár function is smaller than that for the Csavinszky function, and as noted above, ϕ_G(Gáspár) is closer to ϕ_{TF} than ϕ_G(Csavinszky). We may note here that several other approximations[15] to the TF function, besides those of Csavinszky[9] and Gáspár,[11] have been proposed.

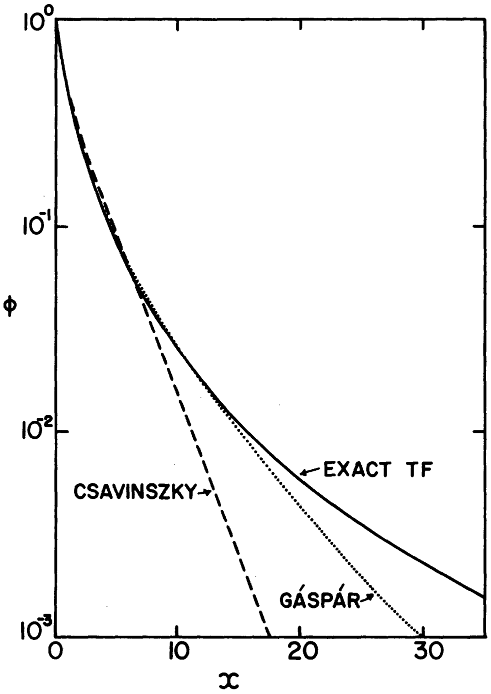

FIG. 3. Comparison of the functions ϕ_G(Csavinszky), ϕ_G(Gáspár), and ϕ_{TF}.

In conclusion, we find that the $G(\phi)$ variational principle is the best, both for obtaining the energy as well as for obtaining an approximate solution for ϕ. The $H(\phi)$ minimization conjecture, Eq. (5), appears to have little merit.

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[1] P. Csavinszky, Phys. Rev. A 5, 2198 (1972).

[2] O. B. Firsov, Zh. Eksp. Teor. Fiz. 32, 1464 (1957); 33, 696 (1957) [Sov. Phys.—JETP 5, 1192 (1957); 6, 534 (1958)].

[3] A. M. Arthurs and P. D. Robinson, Proc. Cambridge Philos. Soc. 65, 535 (1969).

[4] N. Anderson, A. M. Arthurs, and P. D. Robinson, Nuovo Cimento 57B, 523 (1968).

[5] M. G. Wesselow, Zh. Eksp. Teor. Fiz. 7, 829 (1937).

[6] S. Flügge and H. Marschall, *Rechenmethoden der Quantentheorie* (Springer, Berlin, 1952), p. 262ff.

[7] R. Courant, *Differential and Integral Calculus* (Interscience, New York, 1951), Vol. II, p. 497ff.

[8] R. E. Roberts, Phys. Rev. 170, 8 (1968).

[9] P. Csavinszky, Phys. Rev. 166, 53 (1968).

[10] P. Csavinszky, Phys. Rev. A 8, 1688 (1973).

[11] R. Gáspár, J. Chem. Phys. 20, 1863 (1952); Acta Phys. 2, 151 (1952).

[12] P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer, Wien, 1949).

[13] S. Kobayashi, T. Matsukuma, S. Nagai, and K. Umeda, J. Phys. Soc. Jpn. 10, 759 (1955).

[14] K. Umeda, J. Phys. Soc. Jpn. 9, 290 (1954).

[15] A. Sommerfeld, Z. Phys. 78, 283 (1932); S. Rozental, *ibid.* 98, 742 (1936); H. C. Brinkman, Physica (Utrecht) 20, 44 (1954); T. Tietz, J. Chem. Phys. 22, 2094 (1954); Nuovo Cimento 1, 955 (1955); 4, 1192 (1956); R. Latter, Phys. Rev. 99, 510 (1955); H. A. Buchdahl, Ann. Phys. (Leipzig) 17, 238 (1956); R. N. Kesarwani and Y. P. Varshni, Phys. Rev. A 23, 991 (1981).