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Complementary Variational Principles in the Thomas-Fermi Theory

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The normalization of the electron density associated with approximate variational solutions of the Thomas-Fermi (TF) equation for neutral atoms is discussed, and the applicability of a procedure of Anderson, Arthurs, and Robinson for obtaining the closest approximation is investigated. It is concluded that using single-parameter trial functions, the normalization requirement for the electron density cannot be strictly satisfied when the numerical value of the parameter is determined from the minimization of the difference between the complementary upper and lower bounds to the exact TF energy of a neutral atom. It is also concluded that, using multiple-parameter trial functions, this procedure is applicable since the numerical values of all but one of the parameters can be found from the minimum between the complementary bounds without violating the normalization requirement.

I. INTRODUCTION

Recently there has been a renewed interest in obtaining approximate analytical solutions of the Thomas-Fermi (TF) equation[1] both for neutral[2,3] and charged[4] atoms and for neutral diatomic molecules.[3,5] The theories behind these approximate solutions all make use of various variational principles.

By resorting to variational principles, it has been possible to eliminate a shortcoming of the original TF theory. In the case of a neutral atom, this shortcoming consists in the fact that the exact solution of the TF equation is associated with a radial electron density which decreases as the inverse fourth power of the distance from the nucleus,[6] whereas the Hartree approximation,[7] the quantum-mechanical equivalent[8] of the TF theory, gives an exponential decrease. By making use of the flexibility in imposing boundary conditions in a variational approach, i.e., by prescribing how the approximate solution of the TF equation should go to its assigned value at infinity, versus only requiring what the value of the solution should be at infinity, it has been possible to obtain approximate analytical solutions[2,3] which are associated with radial electron densities that decrease exponentially with the distance from the nucleus of an atom.

In calculating specific physical quantities for a system, such as a neutral atom, on the basis of approximate solutions of the TF equation, the correct normalization of the electron density of the system is important (see Appendix A). It appears that a recently suggested[9] variational approach for obtaining the closest approximation to the exact solution of the TF equation (for neutral atoms) cannot be applied to one-parameter trial solutions without violating the normalization requirement for the electron density. The purpose of this paper is to comment on this point. The discussion of the normalization problem at this time is believed to be needed, since calculations using a one-parameter function associated with an only approximately normalized electron density have already appeared[10] in the literature.

II. DISCUSSION

Complementary variational principles for a TF atom were first formulated by Firsov[11] and later generalized by Arthurs and Robinson[12] for a system containing an arbitrary number of electrons and nuclei. Restricting attention to a neutral atom, 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

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

In Eq. (1), Z is the atomic number, $\mu = \frac{1}{2}(\frac{3}{4})^{2/3}\pi^{2/3} Z^{-1/3} a_B$, where a_B is the first Bohr radius, and $E = -0.7687\, Z^{7/3}\, e_0^2/a_B$, where e_0 denotes the magnitude of the electronic charge.

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

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

and

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

where $G(\psi_G)$ and $J(d\psi_J/dx)$ are given[12] by the expressions

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

and

$$J\left(\frac{d\psi_J}{dx}\right) = \int_0^\infty \left[\frac{1}{2}\left(\frac{d\psi_J}{dx}\right)^2 + \frac{3}{5}\, x^{1/3} \left(\frac{d^2\psi_J}{dx^2}\right)^{5/3}\right] dx$$

$$+\left(\frac{d\psi_J}{dx}\right)_{x=0} . \qquad \text{(3b)}$$

In Eqs. (3a) and (3b) the functions ψ_G and ψ_J are trial functions depending on a number of appropriately chosen parameters, i.e.,

$$\psi_G = \psi_G(C_1^G, C_2^G, \ldots, C_i^G) \qquad \text{(4a)}$$

and

$$\psi_J = \psi_J(C_1^J, C_2^J, \ldots, C_j^J) , \qquad \text{(4b)}$$

where i and j need not be equal.

The variational principle for calculating the lower bound G, Eq. (3a), seems to have been first given by Wesselow,[13] and independently by Flügge and Marschall,[14] while that for the upper bound J, Eq. (3b), was first formulated by Firsov.[11]

The variational principle for the lower bound G has an immediate connection with the TF equation. If the negative[15] of the integral of Eq. (3a) is substituted into the Euler-Lagrange equation,[16]

$$\frac{\partial}{\partial\psi_G} F - \frac{\partial}{\partial x}\frac{\partial}{\partial\psi_G'} F = 0 ,$$

where

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

then the TF equation

$$\frac{d^2\psi_G}{dx^2} = \frac{\psi_G^{3/2}}{x^{1/2}}$$

results. 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.[12]

Once trial functions, such as those in Eqs. (4a) and (4b), are chosen and the integrals in the variational principles, Eqs. (3a) and (3b), are evaluated, the quantities $G(\psi_G)$ and $J(d\psi_J/dx)$ are functions of the parameters in ψ_G and ψ_J only, i.e.,

$$G(\psi_G) = G(C_1^G, C_2^G, \ldots, C_i^G) \qquad \text{(5a)}$$

and

$$J\left(\frac{d\psi_J}{dx}\right) = J(C_1^J, C_2^J, \ldots, C_j^J) . \qquad \text{(5b)}$$

From Eqs. (5a) and (5b), the optimal values of the bounds, $G(\psi_G)_{\text{opt}}$ and $J(d\psi_J/dx)_{\text{opt}}$, are determined by finding those values of the parameters which satisfy the set of simultaneous equations

$$\frac{\partial G(C_1^G, C_2^G, \ldots, C_i^G)}{\partial C_1^G} = 0 , \cdots , \qquad \text{(6a)}$$
$$\frac{\partial G(C_1^G, C_2^G, \ldots, C_i^G)}{\partial C_i^G} = 0$$

and

$$\frac{\partial J(C_1^J, C_2^J, \ldots, C_j^J)}{\partial C_1^J} = 0 , \cdots , \qquad \text{(6b)}$$
$$\frac{\partial J(C_1^J, C_2^J, \ldots, C_j^J)}{\partial C_j^J} = 0 .$$

Calling the parameters which satisfy Eqs. (6a) and (6b) optimal parameters, and denoting them by $C_1^{Go}, C_2^{Go}, \ldots, C_i^{Go}; C_1^{Jo}, C_2^{Jo}, \ldots, C_j^{Jo}$, the optimal trial functions ψ_{Go} and ψ_{Jo} are expressed by

$$\psi_{Go} = \psi_G(C_1^{Go}, C_2^{Go}, \ldots, C_i^{Go}) \qquad \text{(7a)}$$

and

$$\psi_{Jo} = \psi_J(C_1^{Jo}, C_2^{Jo}, \ldots, C_j^{Jo}) . \qquad \text{(7b)}$$

Using Eqs. (7a) and (7b), it follows that the optimal bounds, Eqs. (2a) and (2b), can be written as

$$G = G(\psi_G)_{\text{opt}} = G(\psi_{Go}) = G(C_1^{Go}, C_2^{Go}, \ldots, C_i^{Go}) \qquad \text{(8a)}$$

and

$$J = J\left(\frac{d\psi_J}{dx}\right)_{\text{opt}} = J\left(\frac{d\psi_{Jo}}{dx}\right) = J(C_1^{Jo}, C_2^{Jo}, \ldots, C_j^{Jo}) , \qquad \text{(8b)}$$

where, in general, even if $i=j$, $C_1^{Go} \neq C_1^{Jo}$, etc.

So far we had two different functions for calculating the two different bounds, G and J. We can, however, choose one trial function ϕ for calculating both bounds by requiring that

$$\psi_G = \psi_J = \phi . \qquad \text{(9)}$$

In this case, we can write the trial function as

$$\phi = \phi(\overline{C}_1, \overline{C}_2, \ldots, \overline{C}_k) , \qquad \text{(10)}$$

where $\overline{C}_1, \overline{C}_2, \ldots, \overline{C}_k$ are appropriately chosen parameters.

Repeating the previous discussion with the trial function in Eq. (10), one obtains $G(\phi) = G(\overline{C}_1, \overline{C}_2, \ldots, \overline{C}_k)$ from Eq. (3a), and $J(d\phi/dx) = J(\overline{C}_1, \overline{C}_2, \ldots, \overline{C}_k)$ from Eq. (3b). Making use of Eq. (6a), one obtains the optimal parameters $\overline{C}_1^{Go}, \overline{C}_2^{Go}, \ldots, \overline{C}_k^{Go}$ for bound G, and by making use of Eq. (6b), one obtains the optimal parameters $\overline{C}_1^{Jo}, \overline{C}_2^{Jo}, \ldots, \overline{C}_k^{Jo}$ for bound J. With these symbols one can rewrite Eq. (1) as

$$G(\overline{C}_1^{Go}, \overline{C}_2^{Go}, \ldots, \overline{C}_k^{Go}) \leq (\mu/Z^2)E \leq J(\overline{C}_1^{Jo}, \overline{C}_2^{Jo}, \ldots, \overline{C}_k^{Jo}) . \qquad \text{(11)}$$

It is evident from Eq. (11) that, with a particular trial function ϕ, one can use either the variational principle for bound G, or the variational principle for bound J, to obtain the approximate solutions

$$\phi_{Go} = \phi(\overline{C}_1^{Go}, \overline{C}_2^{Go}, \ldots, \overline{C}_k^{Go}) \qquad \text{(12a)}$$

or

$$\phi_{Jo} = \phi(\overline{C}_1^{Jo}, \overline{C}_2^{Jo}, \ldots, \overline{C}_k^{Jo}), \qquad (12b)$$

to the exact solution of the TF equation. Anderson *et al.*,[9] however, suggest that the closest approximation to the exact solution is neither ϕ_{Go} nor ϕ_{Jo}, but the one that can be determined by minimizing the difference between the complementary upper and lower bounds J and G, i.e., by finding those parameter values which make the expression

$$H(\phi) = J\left(\frac{d\phi}{dx}\right) - G(\phi) \qquad (13)$$

a minimum. Since

$$G(\phi) = G(\overline{C}_1, \overline{C}_2, \ldots, \overline{C}_k)$$

and

$$J\left(\frac{d\phi}{dx}\right) = J(\overline{C}_1, \overline{C}_2, \ldots, \overline{C}_k),$$

it follows that $H(\phi)$, Eq. (13), can be written as

$$H(\phi) = H(\overline{C}_1, \overline{C}_2, \ldots, \overline{C}_k). \qquad (14)$$

Using Eq. (14), we find the minimum of $H(\phi)$ by solving the set of simultaneous equations

$$\frac{\partial H(\overline{C}_1, \overline{C}_2, \ldots, \overline{C}_k)}{\partial C_1} = 0, \ldots, \qquad (15)$$
$$\frac{\partial H(\overline{C}_1, \overline{C}_2, \ldots \overline{C}_k)}{\partial C_k} = 0.$$

Calling the parameters which result from Eq. (15) optimal parameters, and denoting them by $\overline{C}_1^{Ho}, \overline{C}_2^{Ho}, \ldots, \overline{C}_k^{Ho}$, we express the optimal trial function by

$$\phi_{Ho} = \phi(\overline{C}_1^{Ho}, \overline{C}_2^{Ho}, \ldots, \overline{C}_k^{Ho}). \qquad (16)$$

With these notations, the smallest difference between the bounds is given by

$$H = H(\phi)_{\text{opt}} = H(\phi_{Ho}) = H(\overline{C}_1^{Ho}, \overline{C}_2^{Ho}, \ldots, \overline{C}_k^{Ho}). \qquad (17)$$

Since, in general, $\overline{C}_1^{Ho} \neq \overline{C}_1^{Go} \neq \overline{C}_1^{Jo}$, etc., the bounds $G(\overline{C}_1^{Ho}, \overline{C}_2^{Ho}, \ldots, \overline{C}_k^{Ho})$ and $J(\overline{C}_1^{Ho}, \overline{C}_2^{Ho}, \ldots, \overline{C}_k^{Ho})$ are no longer the optimal lower and upper bounds $G(\overline{C}_1^{Go}, \overline{C}_2^{Go}, \ldots, \overline{C}_k^{Go})$ and $J(\overline{C}_1^{Jo}, \overline{C}_2^{Jo}, \ldots, \overline{C}_k^{Jo})$, respectively.

Anderson *et al.*[9] demonstrate the procedure of obtaining ϕ_{Ho} by choosing the one-parameter trial function

$$\phi = \phi(\gamma) = (1 + \gamma\sqrt{x})e^{-\gamma\sqrt{x}} \quad (\overline{C}_1 = \gamma), \qquad (18)$$

which has been suggested by Roberts.[3] [The approximate solution $\phi(\gamma)$, Eq. (18), has been obtained by Roberts by making use of a normalized approximate electron density of Jensen[17] and the complementary bounds of Firsov.[11]]

Substituting Eq. (18) into Eqs. (3a) and (3b), Anderson *et al.*[9] find that the quantities

$$G(\phi(\gamma)) = -\tfrac{1}{16}\gamma^2 - \tfrac{4}{5}\int_0^\infty [(1+\gamma y)e^{-\gamma y}]^{5/2}\, dy \qquad (19a)$$

and

$$J\left(\frac{d\phi(\gamma)}{dx}\right) = \tfrac{9}{25}\, 2^{-7/3}\gamma^4 - \tfrac{7}{16}\gamma^2 \qquad (19b)$$

have their optimum values of

$$G(\gamma^{Go}) = -0.6810\,(e_0^2/a_B) \qquad (19c)$$

and

$$J(\gamma^{Jo}) = -0.6699\,(e_0^2/a_B), \qquad (19d)$$

when the parameter γ has the values of $\gamma^{Go} = 1.905$ and $\gamma^{Jo} = 1.750$, respectively.

Next, Anderson *et al.*[9] find that $H(\gamma^{Ho}) = 0.0148 \times (e_0^2/a_B)$ when, from Eq. (15),

$$\gamma^{Ho} = 1.7822.$$

From the fact that

$$H(\gamma^{Ho}) = J(\gamma^{Ho}) - G(\gamma^{Ho}) = 0.0148(e_0^2/a_B)$$

is smaller than either

$$H(\gamma^{Go}) = J(\gamma^{Go}) - G(\gamma^{Go}) = 0.0341(e_0^2/a_B)$$

or

$$H(\gamma^{Jo}) = J(\gamma^{Jo}) - G(\gamma^{Jo}) = 0.0159(e_0^2/a_B),$$

Anderson *et al.*[9] conclude that $\phi(\gamma^{Ho})$ is a closer approximation to the exact solution of the TF equation (for a neutral atom) than either $\phi(\gamma^{Go})$ or $\phi(\gamma^{Jo})$.

In this author's view none of the three possible approximate solutions is rigorously normalized, since all three of them are one-parameter functions. The point that one-parameter functions, determined from variational principles, cannot be rigorously normalized has been raised earlier,[2] but Anderson *et al.*[9] seem to have taken the contrary view.

In order to show that $\phi(\gamma^{Go})$, $\phi(\gamma^{Jo})$, and $\phi(\gamma^{Ho})$ are, indeed, not rigorously normalized, let us start out with a general discussion of the normalization problem.

Introducing the dimensionless variable x by

$$x = 4(2Z/9\pi^2)^{1/3}(r/a_B),$$

where r is the distance from the nucleus, in units of the Bohr radius a_B, the TF theory[1] for a nucleus of charge Ze_0 surrounded by N electrons leads to the (nonlinear) differential equation

$$\phi''(x) = \phi(x)^{3/2}/x^{1/2}, \qquad (20)$$

where the double prime on ϕ denotes the second derivative of ϕ with respect to x. For a neutral atom, $N = Z$, Eq. (20) is to be solved[1] with the boundary conditions

$$\phi(0)=1\ , \tag{21a}$$

$$\phi(\infty)=0\ , \tag{21b}$$

$$\phi'(\infty)=0\ , \tag{21c}$$

where the prime on ϕ denotes the first derivative of ϕ with respect to x. The above boundary conditions, as shown by Gombás,[18] assure that the normalization condition

$$\int \rho\, dv = Z\ , \tag{22}$$

where ρ is the electron (number) density, and the integration is over all space, is satisfied.

When Eq. (20) is solved exactly,(by a numerical procedure[19]), then ρ can be expressed either as

$$\rho_L = (Z/4\pi\mu^3)(\phi''/x) \tag{23a}$$

or as

$$\rho_R = (Z/4\pi\mu^3)\,(\phi/x)^{3/2}\ , \tag{23b}$$

where the subscripts L and R on ρ refer to the left-hand side and right-hand side of Eq. (20), respectively.

Obviously, with the exact solution of Eq. (20), the normalization condition in Eq. (22), which can also be written (since we have spherical symmetry) as

$$4\pi\int_0^\infty \rho\, r^2\, dr = Z\ , \tag{24}$$

is satisfied both for $\rho=\rho_L$ and for $\rho=\rho_R$. In the case of the exact solution of Eq. (20), as shown by Gombás,[18] the normalization condition in Eq. (24) is equivalent to the boundary condition in Eq. (21c). For the exact solution of Eq. (20), therefore, the boundary conditions in Eqs. (21a), (21b); and (21c) automatically guarantee the normalization of the electron density ρ.

In the case of an approximate solution ϕ_a to ϕ, however, Eq. (20) becomes

$$\phi_a'' \approx \phi_a^{3/2}/x^{1/2}\ ,$$

and the quantity

$$\Delta = \phi_a'' - \phi_a^{3/2}/x^{1/2}$$

is a function of x. In this case the equivalency of Eqs. (23a) and (23b) is lost because $\Delta \neq 0$. This is true for any approximate solution ϕ_a, without regard to the number of parameters it depends on. This fact is also responsible for a loss of the equivalency of Eqs. (21c) and (24) since the proof,[18] that one follows from the other, was based on the equivalency of Eqs. (23a) and (23b). This means, that unless additional steps are taken, so that Eq. (24) is satisfied with both $\rho=\rho_L$ and $\rho=\rho_R$, the approximate solution ϕ_a, satisfying Eqs. (21a)–(21c), cannot be normalized. That this is so can be seen by writing down the explicit expressions for Eq. (24). Using Eqs. (23a) and (23b), we find that

$$4\pi\int_0^\infty \rho_L\, r^2\, dr = Z\int_0^\infty x\,\phi_a''\, dx$$
$$= Z\,[x\,\phi_a'(\infty) - \phi_a(\infty) + \phi_a(0)\,] \tag{25a}$$

and

$$4\pi\int_0^\infty \rho_R r^2\, dr = Z\int_0^\infty x^{1/2}\,\phi_a^{3/2}\, dx\ . \tag{25b}$$

From inspection of Eq. (25a), using Eqs. (21a)–(21c), it is seen that the quantity in the square brackets has the value of unity and, therefore, the normalization condition with $\rho=\rho_L$ is always satisfied. This is true for any approximate function ϕ_a, regardless of how many parameters it depends on.

From an inspection of Eq. (25b), however, one concludes that the normalization condition with $\rho=\rho_R$,

$$\int_0^\infty x^{1/2}\,\phi_a^{3/2}\, dx = 1\ , \tag{26}$$

can only be satisfied for special values of the parameters on which ϕ_a depends.

Consequently, if $\phi_a = \phi(\gamma)$, as given in Eq. (18), then the normalization requirement in Eq. (26) can only be satisfied either with a unique value of γ, let us say γ^N, or perhaps with a possible "spectrum" of values of γ, let us say γ^i, γ^j, ... For the present, we assume, that there is only one unique value of γ, $\gamma=\gamma^N$, which satisfies Eq. (26). (For a discussion of the possible existence of a set of such values of γ, $\gamma=\gamma^i$, $\gamma=\gamma^j$, . . . , see Appendix B). If γ^N is determined from Eq. (26), then no undetermined parameter is left in Eq. (18), and no use can be made of any of the three variational principles discussed earlier. Conversely, if the optimal value of γ is determined either from the variational principles for the bounds G and J, or from their minimum H, then one cannot expect that Eq. (26) is satisfied unless by coincidence γ^{Go}, γ^{Jo}, or γ^{Ho} happens to be also γ^N. This, however, is not the case and, for this reason, $\phi(\gamma^{Go})$, $\phi(\gamma^{Jo})$, and $\phi(\gamma^{Ho})$ are not associated with a normalized electron density.

Numerical integration of Eq. (26) leads to the values

$$\int_0^\infty x^{1/2}\,\phi(\gamma^{Go}=1.905)^{3/2}\, dx = 0.9382\ ,$$
$$\int_0^\infty x^{1/2}\,\phi(\gamma^{Jo}=1.750)^{3/2}\, dx = 1.210\ , \tag{27}$$
$$\int_0^\infty x^{1/2}\,\phi(\gamma^{Ho}=1.7822)^{3/2}\, dx = 1.146\ ,$$

which clearly show that, contrary to the assertion of Anderson *et al.*,[9] the one-parameter function $\phi(\gamma)$ is not associated with a normalized electron density, regardless which one of the three variational principles is used to fix the value of γ.

Inspection of Eqs. (27) also shows that Eq. (26) may be satisfied when

$$\gamma^{Ho} < \gamma^N < \gamma^{Go} \quad \text{or} \quad \gamma^{Jo} < \gamma^N < \gamma^{Go}\ ,$$

but in this case no use can be made of variational principles.

For a multiple-parameter function, the finding of the extremum of either G, J, or H can be carried out with the simultaneous consideration of the normalization requirement. This procedure was followed earlier by the author[2] using the four-parameter trial function

$$\phi = \phi(a, b, \alpha, \beta) = (ae^{-\alpha x} + be^{-\beta x})^2 , \qquad (28)$$

and the variational principle for G in Eq. (3a). This resulted in the approximate solution $\phi\ (a^{Gos}, b^{Gos}, \alpha^{Gos}, \beta^{Gos})$ where

$$a^{Gos} = 0.7111 , \quad \alpha^{Gos} = 0.175 , \qquad b^{Gos} = 0.2889 , \quad \beta^{Gos} = 1.6625 . \qquad (29)$$

In Eq. (29) the s on the superscript Go means that the optimal values of the parameters have been obtained not only from Eq. (6a), but by the simultaneous consideration of Eq. (6a) and Eq. (26), i. e.,

$$\int_0^\infty x^{1/2}\, \phi(a, b, \alpha, \beta)^{3/2}\, dx = 1 . \qquad (30)$$

The trial function in Eq. (28) is a four-parameter function, but not all four parameters are independent since by virtue of the boundary condition in Eq. (21a) it follows that $a + b = 1$. Consequently, one has to determine the optimal values of only a, α, and β. The optimal values for these parameters, displayed above, have been obtained by a numerical procedure. For numerical calculations it was convenient to introduce the variable $n = \beta/\alpha$, so that the task was the finding of the extremum of $G(\alpha, n, a)$. This has been done in the following way. First a value for α was picked at random. Then a value for n was picked. Finally, Eq. (30) was used to find that value of a with which the normalization condition is satisfied. This was followed by picking different values for n, in succession, and by the determination of the corresponding a values. When those values of a and n were found which made $G(\alpha, n, a)$ a minimum, with the fixed α value, then n has been kept constant and the value of α has been modified, in succession, and new values for a were computed from Eq. (30). This further lowered the magnitude of $G\ (\alpha, n, a)$. This cycling has been repeated until the minimum of $G\ (\alpha, n, a)$ has been found which corresponds to the parameter values displayed in Eq. (29).

It has been necessary to dwell on this procedure at some length, since finding the minimum of $G(\alpha, n, a)$ without the simultaneous consideration of Eq. (30) would result in a different set of parameters, say $a^G, b^G, \alpha^G, \beta^G$, and the approximate solution $\phi\ (a^G, b^G, \alpha^G, \beta^G)$ would not satisfy Eq. (30).

In summary, we can say that for an m-parameter function, the finding of the extremum of either G, J, or H can be carried out with the simultaneous consideration of the normalization requirement, and one can obtain the optimal values of $(m-1)$ parameters from any of the three variational principles and find the value of the mth parameter from the normalization condition.

Anderson *et al.*,[9] using the parameter values in Eq. (29), also calculate

$$J(a^{Gos}, b^{Gos}, \alpha^{Gos}, \beta^{Gos}) = -0.5728(e_0^2/a_B) , \qquad G(a^{Gos}, b^{Gos}, \alpha^{Gos}, \beta^{Gos}) = -0.6816(e_0^2/a_B) , \qquad (31)$$

and from these values they find that

$$J - G = 0.1088(e_0^2/a_B) . \qquad (32)$$

They compare Eq. (32) with the corresponding quantity from the trial function in Eq. (18), i. e., with

$$J - G = J(\gamma^{Go}) - G(\gamma^{Go}) = 0.0341(e^2/a_b) , \qquad (33)$$

and conclude that the solution in Eq. (18) is a better approximation to the exact solution than the approximate solution in Eq. (28). Apart from the fact that Eq. (18) is associated with an electron density which is not strictly normalized, while Eq. (28) with one that is strictly normalized, it is doubtful that such a comparison is very meaningful, since the bounds $J\ (a^{Gos}, b^{Gos}, \alpha^{Gos}, \beta^{Gos})$, in Eq. (31), and $J\ (\gamma^{Go})$, in Eq. (33), are not optimal bounds.

If we have a number of approximate solutions ϕ_1, $\phi_2, \phi_3, \ldots$, each depending on any number of parameters, then it is a meaningful question to ask which one of these functions is the best approximation to the exact solution of the TF equation. Should one obtain the optimal values for each of these functions from the minimum between the complementary bounds, i. e., calculate

$$H_1, H_2, H_3, \ldots ,$$

then the best approximation should be the one for which the magnitude of $H_i (i = 1, 2, 3, \ldots)$ is the smallest.

III. CONCLUSIONS

It is concluded, that for multiple-parameter trial functions, the finding of the minimum between the complementary bounds, as suggested by Anderson *et al.*,[9] can serve as a procedure for determining the best approximation to the exact solution of the TF equation (for a neutral atom), provided that the normalization condition is simultaneously considered. It is also concluded, that for single-parameter functions this procedure cannot be carried out.

APPENDIX A

The question of normalization of ρ. In quantum mechanics, using the variational technique, the expectation value $\bar{\Omega}$ of a measurable quantity Ω of an N-electron system is calculated from[20]

$$\bar{\Omega} = \int \Psi_t^* \Omega_{\rm op} \Psi_t \, d\tau \;, \tag{A1}$$

where $\Omega_{\rm op}$ is the operator associated with the quantity Ω, Ψ_t is a trial function with optimal parameters, and $d\tau$ stands for the volume element of all coordinates. If the trial function is not normalized, i.e., if

$$\int \Psi_t^* \Psi_t \, d\tau \neq N \;, \tag{A2}$$

then Eq. (A1) has to be rewritten as

$$\bar{\Omega} = \int \Psi^* \Omega_{\rm op} \Psi_t \, d\tau \Big/ \int \Psi_t^* \Psi_t \, d\tau \;. \tag{A3}$$

When Ψ_t is not normalized, and instead of Eq. (A3) only Eq. (A1) is used, then the calculated value of $\bar{\Omega}$ is not only in error numerically, but may be meaningless. That this is so can be seen by choosing

$$\Omega = E_0 \quad \text{and} \quad \Omega_{\rm op} = \mathcal{H} \;,$$

where E_0 is the ground-state energy of a system whose Hamiltonian is $\mathcal{H}$. When Ψ_t is not normalized, then the calculated ground-state energy $\bar{E}_0$ might turn out to be lower than the true ground-state energy, which is not a permissible result.

In the TF theory, the particular physical quantity $\bar{\Omega}$ is calculated from

$$\bar{\Omega} = \int f_\Omega(\rho) dv = 4\pi \int_0^\infty f_\Omega\big(\rho(r)\big) r^2 \, dr \;, \tag{A4}$$

where ρ is the spherically symmetric electron (number) density and r is the distance from the nucleus. The detailed form of the function f_Ω depends, of course, on the particular quantity Ω, so that for two different quantities, Ω_1 and Ω_2, we have $f_{\Omega 1} \neq f_{\Omega 2}$ etc.

Since the electron density $\rho(r)$ can be expressed in terms of the solution of the TF equation ϕ, and ϕ depends on a number of parameters, it is seen from Eq. (A4) that the value of $\bar{\Omega}$ depends on the variational parameters. Consequently, if these variational parameters have been obtained with an unnormalized electron density then, in this author's opinion, no significance can be attached to a comparison of calculated and measured values of $\bar{\Omega}$.

What an unnormalized electron density means can also be illuminated from a different viewpoint. In the TF model, the electrons are regarded as a perfect gas obeying Fermi-Dirac statistics and occupying a sphere in phase space of radius P. For a given atom, i.e., for a given number of electrons, this radius P in phase space is a fixed quantity. An unnormalized electron density now means that an atom is assigned a volume of phase space which is not the correct one. Also, since the Hartree approximation can be shown[8] to yield the TF approximation, this correspondence can only be meaningful if the number of electrons is the same in both cases.

APPENDIX B

The uniqueness of the parameter γ^N. One might ask the question "Is there a proof that there exists only a single value of γ, $\gamma = \gamma^N$, rather than a "spectrum" of values of γ, $\gamma = \gamma^i, \gamma^j, \ldots$, for which the normalization condition, Eq. (26), is satisfied?" To answer this question, we follow the procedure of assuming the opposite of what we want to prove and then show that it leads to unreasonable requirements.

First, we assume that with $\gamma = \gamma^N$ the normalization integral in Eq. (25b),

$$4\pi \int_0^\infty \rho_R(\gamma^N) \, r^2 \, dr = Z \;, \tag{B1}$$

is satisfied. Next, we assume that Eq. (25b) is also satisfied with another value of γ, $\gamma = \gamma^i$, where $\gamma^i = \gamma^N + \Delta\gamma$. This assumption demands that

$$4\pi \int_0^\infty \rho_R(\gamma^N + \Delta\gamma) \, r^2 \, dr = Z \;. \tag{B2}$$

A Taylor-series expansion of $\rho_R(\gamma^i)$ in $\Delta\gamma$ results in

$$\rho_R(\gamma^i) = \rho_R(\gamma^N + \Delta\gamma) = \rho_R(\gamma^N) + \Delta\gamma \, \rho_R'(\gamma^N) + \cdots \;, \tag{B3}$$

where the prime on ρ_R denotes the derivative of ρ_R with respect to γ^N. If $|\Delta\gamma| \ll \gamma^N$, then the above series expansion, with only a linear term in $\Delta\gamma$, is a sufficiently good approximation to $\rho_R(\gamma^i)$. If $|\Delta\gamma| < \gamma^N$, then terms higher than linear in $\Delta\gamma$ must also be included in Eq. (B3). This, however, would only unnecessarily complicate the proof without adding anything to it so that we shall restrict attention to Eq. (B3).[21]

Since the left-hand sides of Eqs. (B1) and (B2) are both equal to the same quantity Z, it follows that

$$\int_0^\infty \rho_R(\gamma^N) \, r^2 \, dr = \int_0^\infty \rho_R(\gamma^N + \Delta\gamma) \, r^2 \, dr \;. \tag{B4}$$

Using Eq. (B3), we may rewrite Eq. (B4) as

$$\int_0^\infty \rho_R(\gamma^N) \, r^2 \, dr = \int_0^\infty \rho_R(\gamma^N) \, r^2 \, dr + \Delta\gamma \int_0^\infty \rho_R'(\gamma^N) \, r^2 \, dr \;. \tag{B5}$$

If $\rho_R(\gamma^N)$ is a continuous function of γ^N, which is a reasonable assumption to make, then $\rho_R'(\gamma^N)$ will also be a continuous function of γ^N. If $\rho_R'(\gamma^N) \neq 0$, then Eq. (B5) can only be satisfied if $\Delta\gamma = 0$, which means that $\gamma^i = \gamma^N$, so that there is no "spectrum" of values of γ, but only a single value, $\gamma = \gamma^N$, which satisfies the normalization condition in Eq. (25b).

It would appear from Eq. (B5) that the value of $\gamma = \gamma^i$ may still be assumed if $\rho_R'(\gamma^N) = 0$. This, however, is not the case since Eq. (B5) is based only on the first two terms of the Taylor expansion of $\rho_R(\gamma^N + \Delta\gamma)$. If terms higher then linear in $\Delta\gamma$ are also taken into account, then integrals of the type

$$\frac{(\Delta\gamma)^m}{m\,!}\int_0^\infty \rho_R^{(m)}(\gamma^N)\,r^2\,dr\,, \quad m=2,3,\ldots$$

would also appear on the right-hand side of Eq. (B5). The demand that Eq. (25b) be satisfied with $\gamma = \gamma^i$ can now be met only if the derivatives of all orders of $\rho_R(\gamma^N)$ with respect to γ^N vanish which, certainly, is an unreasonable requirement.

Since ρ_R is related to ϕ_a by Eq. (23b), i.e., by

$$\rho_R(\gamma) = (Z/4\pi\mu^3)\,[\phi_a(\gamma)/x]^{3/2}\,, \tag{B6}$$

we can say that Eq. (26) is satisfied only at a single value of γ, $\gamma = \gamma^N$, provided that the derivatives of all orders of $\rho_R(\gamma)$ with respect to γ, at $\gamma = \gamma^N$, do not vanish.

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[1] For a review of the subject (and references) see (a) P. Gombás, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXXVI; (b) P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949); (c) N. H. March, Advan. Phys. 6, No. 21 (1957).

[2] P. Csavinszky, Phys. Rev. 166, 53 (1968). There are two misprints in this paper. In Eq. (A2) the first term in the brackets should read $\frac{1}{2}a^4$. In Eq. (A3) the numerator of the third term in the brackets should read $2a^2b^2$.

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

[4] P. Csavinszky, J. Chem. Phys. 50, 1176 (1969).

[5] P. Csavinszky, J. Phys. Soc. Japan 28, 1302 (1970).

[6] See Ref. 1(a), p. 132.

[7] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 111 (1927).

[8] P. A. M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930).

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

[10] S. Kumar and A. Jain, J. Phys. Soc. Japan 28, 1046 (1970).

[11] O. B. Firsov, Zh. Eksperim. i Theor. Fiz. 32, 1464 (1957) [Sov. Phys. JETP 5, 1192 (1957)]; 33, 696 (1958) [6, 534 (1958)].

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

[13] M. G. Wesselow, Zh. Eksperim. i Theor. Fiz. 7, 829 (1937).

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

[15] Minus signs are chosen in the integrand of Eq. (3a) so that the lower bound G is negative, as is the energy E.

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

[17] H. Jensen, Z. Physik 77, 722 (1932).

[18] See Ref. 1(b), p. 39.

[19] The most accurate numerical solution is given by S. Kobayashi, T. Matsukuma, S. Nagai, and K. Umeda, J. Phys. Soc. Japan 10, 759 (1955).

[20] P. A. Tipler, *Foundations of Modern Physics* (Worth, New York, 1970), p. 248ff.

[21] The proof just given would fail (since the Taylor expansion is no longer meaningful) in the event that $|\Delta\gamma| > \gamma^N$, a possibility that cannot be ruled out, *a priori*. Ideally, the proof should further be generalized so as to cover this latter case, too. A brief reflection, however, shows that this conceivable lack of "uniqueness" on the part of the γ value that satisfies Eq. (26) does not materially affect the fundamental conclusions stated in the text in the two sentences just above Eqs. (27). Whether there is just one unique value of γ, satisfying Eq. (26), or a "spectrum" of such values, the fact still remains, that determination of a particular value of γ from Eq. (26) excludes the possibility of making use of any of the three variational principles discussed. Hence, the conclusions referred to remain valid in either case.