order terms were examined and it was found that divergences may enter. It was shown how the divergences may be avoided for the case where one of the excited states is bound and the other is in the continuum. However, the divergences have not been removed when both excitations are in the continuum, and this problem is being studied further. It was also shown that the methods of this paper are applicable to problems of multiple atomic excitations. Numerical calculations utilizing these methods are planned for several atoms.

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Approximate Variational Solution of the Thomas-Fermi Equation for Atoms

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An approximate solution of the Thomas-Fermi (TF) differential equation is obtained by making use of an equivalent variational principle. The trial solution, depending on several parameters, is chosen in such a way that it satisfies the boundary conditions imposed on the TF equation together with the subsidiary condition that the electron density be normalized. The numerical values of the parameters are determined by extremalizing the variational expression with respect to the parameters. Using the approximate solution, one finds that at large distances from the nucleus, the radial electron density decreases exponentially, as required by quantum mechanics—in contrast to the original TF theory, where the above quantity decreases as the inverse fourth power of the distance from the nucleus. The approximate TF function is then used for calculating the energy necessary to remove all electrons of an atom and for calculating the interaction energies between atoms in the Firsov approximation. In the former case the improvement upon the original TF theory is found to be substantial, and in the latter the interaction energies closely approximate Abrahamson's interaction energies based on the Thomas-Fermi-Dirac model.

I. INTRODUCTION

It is a shortcoming of the Thomas-Fermi (TF) theory of the atom[1] that it leads to a radial electron density which decreases as the inverse fourth power of the distance from the nucleus,[2] whereas the Hartree[2a] approximation, its quantum-mechanical equivalent,[3] gives an exponential decrease. The purpose of the present paper is to show that the above shortcoming can be eliminated by making use of the flexibility in imposing boundary conditions when the TF differential equation is replaced by an equivalent variational principle.

II. THEORY

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, and Z the atomic number, the TF theory leads to the differential equation

$$d^2\phi/dx^2=\phi^{3/2}/x^{1/2} \qquad (1)$$

which, for a neutral atom, is to be solved[4] with the boundary conditions

$$\phi(0)=1,\quad \phi(\infty)=0,\quad \phi'(\infty)=0. \qquad (2)$$

Choosing[5]

$$F(\phi,\phi',x)=\tfrac{1}{2}(d\phi/dx)^2+\tfrac{2}{5}(\phi^{5/2}/x^{1/2}), \qquad (3)$$

the variational principle

$$L(\phi)=\int_0^\infty F dx \qquad (4)$$

is the equivalent of Eq. (1) since substitution of Eq.

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[1] For a review of the subject see P. Gombás, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXXVI.

[2] See Ref. 1, p. 132.

[2a] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 111 (1927).

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

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

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

(3) into the Euler-Lagrange equation,[6]

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

results in the TF equation.

The problem is now the selection of a trial function ϕ which satisfies the boundary conditions in Eq. (2). Obviously, a large class of functions is admissible, and therefore, in choosing one, we resort to a form which permits computational simplicity in connection with the integral in Eq. (4).

Choosing a trial function of the form

$$\phi=[a\exp(-\alpha x)+b\exp(-\beta x)]^2, \tag{5}$$

where a, b, α, and β are as yet undetermined parameters, and requiring that

$$a+b=1,$$

the boundary conditions in Eq. (2) are satisfied. With Eq. (5) one calculates F in Eq. (3) and then evaluates the integral in Eq. (4). The resulting expression, a function of the parameters a, α, and β, is then extremalized with respect to these parameters subject to the subsidiary condition that the electron density be normalized. This is an important point since previous attempts,[5,7] based on a trial function of $\exp(-\gamma x)$, resulted in an unphysical solution since a one-parameter trial function is not compatible with a subsidiary condition.

The subsidiary condition is expressed as

$$\int\rho dv=N, \tag{6}$$

where N is the number of electrons, dv is the volume element, and ρ is the electron density which is related[8] to ϕ by

$$\rho=\frac{Z}{4\pi\mu^3}\left(\frac{\phi}{x}\right)^{3/2}, \tag{7}$$

with

$$\mu=\tfrac{1}{4}(9\pi^2/2Z)^{1/3}a_B.$$

Details of the calculation are given in the Appendix. Here the results are summarized by

$$a=0.7111,\quad \alpha=0.175,$$
$$b=0.2889,\quad n=\beta/\alpha=9.5, \tag{8}$$

where the new parameter n, as explained in the Appendix, is introduced to simplify the numerical calculations.

TABLE I. Ratio of the approximate to the exact solution of the TF equation.

x	ϕ/ϕ_{TF}	x	ϕ/ϕ_{TF}
0.00	1.000	5.50	1.082
0.05	1.008	6.00	1.042
0.10	1.009	6.50	0.9964
0.50	0.9959	7.00	0.9466
1.00	1.002	7.50	0.8943
1.20	1.013	8.00	0.8398
1.40	1.028	8.50	0.7856
1.60	1.043	9.00	0.7320
1.80	1.060	9.50	0.6787
2.00	1.077	10.00	0.6273
3.00	1.140	15.00	0.2454
4.00	1.153	20.00	0.08487
5.00	1.115	30.00	0.006170

III. DISCUSSION

To compare the approximate solution of the TF equation with the exact one, the ratio of these quantities as a function of x is tabulated in Table I. It is seen that marked deviation occurs only at large values of x reflecting the exponential decrease of the trial solution.

To test the approximate TF function of Eq. (5) with the parameter values of Eq. (8), the energy necessary to remove all electrons of an atom is calculated[9] from

$$E=(12/7)(2/9\pi^2)^{1/3}\phi'(0)Z^{7/3}(e^2/a_B).$$

The result is listed in Table II together with data obtained by the original TF equation. For comparison's sake "empirical" values are also given which were calculated by Slater's rules.[10]

It is seen from Table II that the unmodified TF theory leads to total ionization energies which are too large compared to the "empirical" values. It is also seen that the present approximation leads to a much better agreement with Slater's values, particularly for the lighter elements.

As another test of the approximate TF function the interaction energies between noble gases, both for the homo- and heteronuclear cases, are calculated in the

TABLE II. Comparison of total ionization energies (in units of e^2/a_B).

	Z	Present	TF	Empirical
H	1	0.585	0.769	0.5
He	2	2.951	3.875	2.904
Be	4	14.87	19.53	14.68
C	6	38.30	50.30	37.86
Ne	10	126.1	165.7	129.5
Ar	18	497.1	653.0	525.4
Fe	26	1172	1540	1249
Kr	36	2505	3291	2704
Xe	54	6453	8476	7079
Hg	80	16145	21210	18680
U	92	22370	29380	25520

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

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

[8] See Ref. 1, p. 125.

[9] See Ref. 1, p. 135.

[10] See Ref. 1, Table 5, p. 183; also J. C. Slater, Phys. Rev. **36**, 57 (1930).

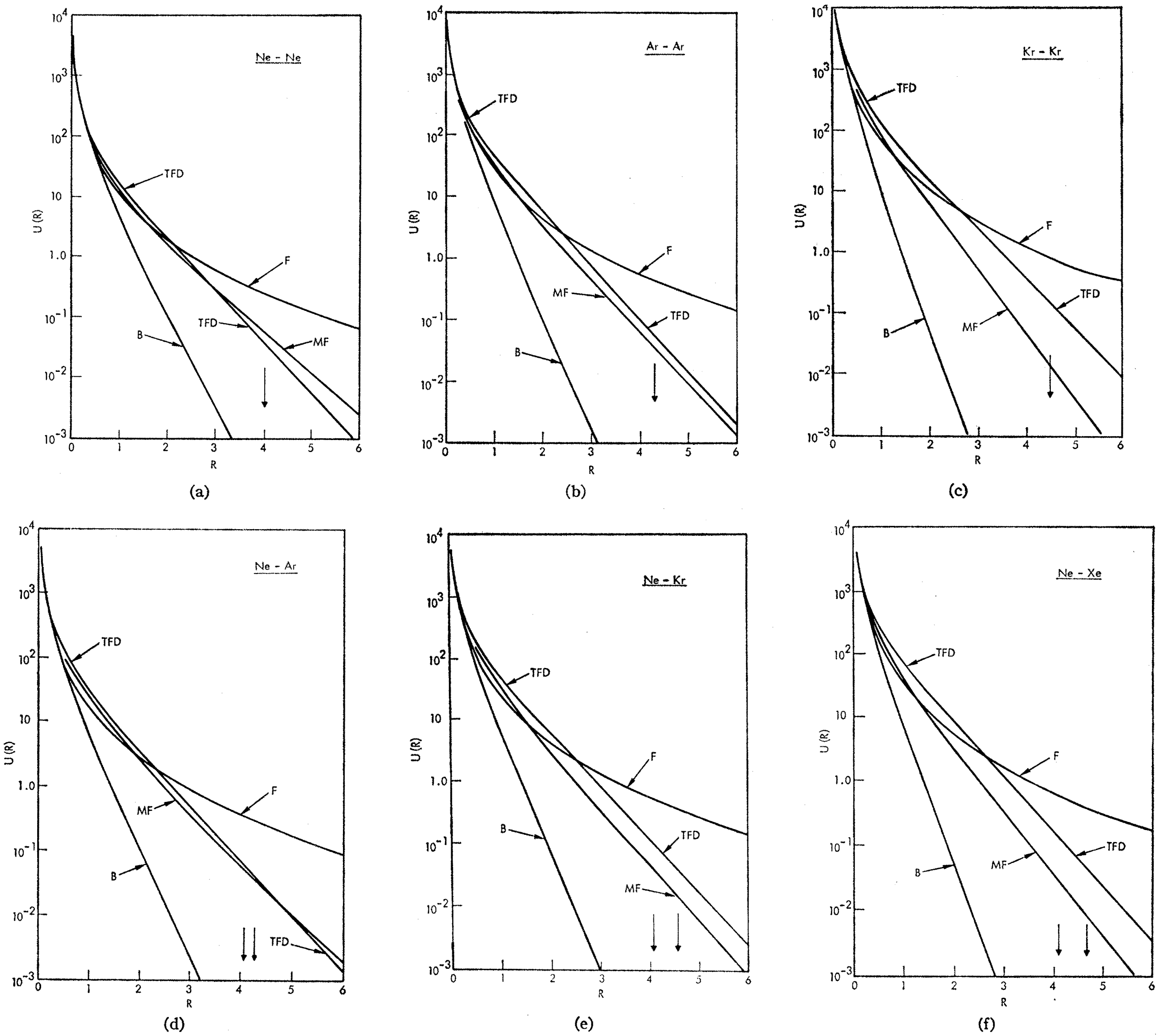

FIG. 1. Interaction energies for (a) Ne-Ne, (b) Ar-Ar, (c) Kr-Kr, (d) Ne-Ar, (e) Ne-Kr, and (f) Ne-Xe (on logarithmic scale and in units of e^2/a_B) as a function of internuclear separation (on linear scale and in units of a_B). The symbols are as follows: TFD—Thomas-Fermi-Dirac (as calculated by Abrahamson); F—Firsov; B—Bohr; MF—modified Firsov (present calculation). The vertical arrows point to the atomic radius in the TFD theory.

Firsov[11] approximation. In Firsov's theory this quantity is given by

$$U_F(R)=(Z_1Z_2e^2/R)\phi(\xi),$$

where

$$\xi=(Z_1^{1/2}+Z_2^{1/2})^{2/3}R/0.8853a_B,$$

and R is the internuclear distance. Firsov limits the validity of his approximation for $R\lesssim 1.9a_B$ mainly because the TF electron density falls off too slowly. This viewpoint was also shared by Abrahamson,[12] who calculated the interaction energies between noble gas atoms in the Thomas-Fermi-Dirac (TFD) approximation.[12,13] Since his work requires very extensive numerical calculations it is of interest to calculate the interaction energies in the Firsov approximation by making use of the TF function obtained in this paper.

Figures 1(a)–1(f) show Abrahamson's values (TFD), Firsov's values (F), the present paper's results, hereafter called the modified Firsov values (MF), and values obtained by the Bohr approximation[14] (B), i.e., by

$$U_B(R)=(Z_1Z_2e^2/R)\exp[-(Z_1^{2/3}+Z_2^{2/3})^{1/2}(R/a_B)]$$

both for some homonuclear[12] and heteronuclear[13] cases.

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[11] O. B. Firsov, Zh. Eskperim. i Teor. Fiz. **32**, 1464 (1957); **33**, 696 (1957) [English transls.: Soviet Phys.—JETP **5**, 1192 (1957); **6**, 534 (1958)].

[12] A. A. Abrahamson, Phys. Rev. **130**, 693 (1963).

[13] A. A. Abrahamson, Phys. Rev. **133**, A990 (1964).

[14] N. Bohr, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **18**, No. 8 (1948).

It is seen from the figures that the agreement between the modified Firsov approximation and the Abrahamson approximation is very good at smaller internuclear separations and is reasonably good over all nuclear separations considered. This behavior is interesting since the Abrahamson approximation is beset with a difficulty, namely the fact that in the TFD model the electron density of neutral atoms extends only to a given distance from the nucleus, the so-called atomic radius, and there it abruptly drops to zero. This physically unattractive aspect of the TFD model has also been criticized by March.[15] Consequently, interaction-energy calculations based on the TFD model should not predict any interaction energy for internuclear separations larger than the sum of the radii of the atoms. For this region Abrahamson obtained his values by extrapolations. These values, therefore, are probably not more reliable than the modified Firsov values which are based on Eq. (5), or expressed otherwise, on an electron distribution whose asymptotic behavior is more in accordance with the requirements of quantum mechanics than that of the TFD model. Finally, it is also seen from the figures that the unmodified Firsov approximation and the Bohr approximation can only be used for small values of R.

APPENDIX

Substituting Eq. (3) into Eq. (4) and introducing the notations

$$L=L_1+L_2, \tag{A1}$$

where

$$L_1=\int_0^\infty \tfrac{1}{2}(d\phi/dx)^2dx,$$

and

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

a straightforward evaluation of the integrals leads to

$$L_1=\alpha\left[\tfrac{1}{2}a_4+4a^3b\left(\frac{1+n}{3+n}\right)+a^2b^2\left(\frac{1+4n+n^2}{1+n}\right)+4ab^3\left(\frac{n+n^2}{1+3n}\right)+\tfrac{1}{2}b^4n\right], \tag{A2}$$

and

$$L_2=\frac{2\sqrt{\pi}}{\alpha^{1/2}}\left[\frac{a^5}{5^{3/2}}+\frac{a^4b}{(4+n)^{1/2}}+\frac{2a^3b}{(3+2n)^{1/2}}+\frac{2a^2b^3}{(2+3n)^{1/2}}+\frac{ab^4}{(1+4n)^{1/2}}+\frac{b^5}{5(5n)^{1/2}}\right]. \tag{A3}$$

It should be remarked here that to facilitate numerical calculations a new variable has been introduced defined by $n=\beta/\alpha$. It is also remarked that the formula displayed in Eq. (A3) has been obtained by making use of the recurrence relations between Γ functions which appear on account of the fractional powers of x in the integrand of L_2.

To evaluate the integral of the subsidiary condition in Eq. (6) one makes use of Eqs. (5) and (7) and obtains

$$\frac{1}{\alpha^{3/2}}\left[\frac{a^3}{3^{3/2}}+\frac{3a^2(1-a)}{(2+n)^{3/2}}+\frac{3a(1-a)^2}{(1+2n)^{3/2}}+\frac{(1-a)^3}{(3n)^{3/2}}\right]=\frac{2}{\sqrt{\pi}}\frac{N}{Z}, \tag{A4}$$

where use has again been made of the properties of Γ functions. It is seen from Eq. (A4) that for neutral atoms $N/Z=1$ and, for this reason, the solution of the TF equation remains universal.

To extremalize L in Eq. (A1), subject to the subsidiary condition in Eq. (A4), the following procedure is carried out. A value is picked for α at random and then a value for n is picked and modified in succession until for each value of n one finds values for a with which Eq. (A4) is satisfied. Using the fixed α value and the various n and a values L is calculated. When that value of n is found which makes L a minimum then it is kept constant and α is varied. This lowers the magnitude of the minimum. This cycling is continued until the minimum of L as a function of α, n, and a is found. The numerical values are displayed in Eq. (8).

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[15] N. H. March, Advan. Phys. **6**, No. 21 (1957).