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# Modified variational solution of the Thomas-Fermi equation for atoms

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A modified trial solution of Roberts's function, depending on two parameters, is chosen in such a way that it can satisfy the boundary conditions and the subsidiary condition that the electron density be normalized. The proposed solution is used to calculate the total ionization energy of atoms, and also the repulsive interaction energy between rare-gas atoms. The results obtained by the proposed function are better than those obtained from Csavinszky's function and from Kesarwani and Varshni's function for medium-atomic-number elements, and the numerical values of the parameters are easier to optimize.

## I. INTRODUCTION

Recently there has been a renewed interest in the approximate analytical solution of the Thomas-Fermi (TF) equation.[1-3] Csavinszky[4] has proposed the trial function

$$\phi_1=(a_0e^{-\alpha_0 x}+b_0e^{-\beta_0 x})^2\ , \tag{1}$$

where $a_0=0.721\,8337$, $\alpha_0=0.178\,2559$, $b_0=0.278\,1663$, and $\beta_0=1.759\,339$, while Kesarwani and Varshni[3] suggest

$$\phi_2=(ae^{-\alpha x}+be^{-\beta x}+ce^{-\gamma x})^2\ , \tag{2}$$

where $a=0.524\,95$, $\alpha=0.120\,62$, $b=0.435\,05$, $\beta=0.847\,95$, $c=0.04$, $\gamma=6.7469$. These approximate solutions of the TF equation have been obtained by making use of an equivalent Firsov's variational principle[5] which has been rigorously justified.[6] When they are used to calculate the total ionization energy of atoms and the repulsive interaction energy between rare-gas atoms, the Csavinszky function is more suited for light elements, while the Kesarwani and Varshni function is more suited for high-atomic-number elements. But the work involved in determining the numerical values of the parameters is cumbersome especially for a six-parameter fit. In the present paper, we propose a modified variational solution of the TF equation, which gives better results for the total ionization energy of medium-atomic-number atoms, as well as for the repulsive interaction energy between such atoms. The numerical values of the two-parameter function are easier to optimize than those obtained from Csavinszky's and from Kesarwani and Varshni's functions, respectively.

## II. THEORY

The TF differential equation for a neutral atom is

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

where $x$ is a dimensionless variable, defined 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 $Z$ is the atomic number. The boundary and subsidiary conditions are

$$\phi(0)=1,\ \ \phi(\infty)=0,\ \ \phi'(\infty)=0\ , \tag{4}$$

and

$$\int \rho\, dv=N\ , \tag{5}$$

where $N$ is the number of electrons, $dv$ is the volume element, and $\rho$ is the electron density which is related to $\phi$ by

$$\rho=\frac{Z}{4\pi\mu^3}\left[\frac{\phi}{x}\right]^{3/2} \tag{6}$$

with $\mu=\frac{1}{4}(9\pi^2/2Z)^{1/3}a_B$. The choice

$$F(\phi,\phi',x)=\frac{1}{2}\left[\frac{d\phi}{dx}\right]^2+\frac{2}{5}\left[\frac{\phi^{5/2}}{x^{1/2}}\right]\ , \tag{7}$$

in conjunction with the variational principle

$$L(\phi)=\int_0^\infty F\,dx\ , \tag{8}$$

is the equivalent of Eq. (3) since substitution of Eq. (7) into the Euler-Lagrange equation

$$\frac{d}{dx}\left[\frac{\partial F}{\partial \phi'}\right]-\frac{\partial F}{\partial \phi}=0$$

leads to the TF equation.

Roberts[7] suggests the following one-parameter trial function:

$$\phi=(1+\eta x^{1/2})e^{-\eta x^{1/2}}\ , \tag{9}$$

where $\eta=1.905$. Anderson *et al.*[8] choose $\eta=1.7822$ by considering complementary variational principles. But the one-parameter functions, determined from variational principles, cannot be rigorously normalized 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.[9] It is important that the electron density be normalized when one calculates specific physical quantities for a neutral atom on the basis of approximate solutions of the TF equation.

In the present paper, we suggest the following modified variational trial solution of Roberts's function for the TF equation

$$\phi_3=[(1+mx^{1/2}+nx)e^{-mx^{1/2}}]^2\ . \tag{10}$$

This is a two-parameter function, so the finding of the extremum of $L$ [Eq. (8)] can be carried out with the simultaneous consideration of the normalization requirement.

Now we shall determine $m$ and $n$ by minimizing $L$ with respect to these parameters subject to the subsidiary condition Eq. (5). It is convenient to write $L$ as

$$L=L_1+L_2\ , \tag{11}$$

where

$$L_1=\int_0^\infty \frac{1}{2}\left[\frac{d\phi}{dx}\right]^2 dx$$

and

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

All the integrals involved in Eq. (11) can be evaluated analytically. The resulting expressions for $L_1$ and $L_2$ are as follows:

$$\begin{aligned}L_1=&\ (2n-m^2)^2/(4m)^2+4m(2n-m^2)(n-m^2)/(4m)^3\\&+6[m^2n^2-4m^2n(2n-m^2)+(m^2+2n)(2n-m^2)^2]/(4m)^4\\&+48[m^3n^2-mn(2n-m^2)(m^2+2n)+mn(2n-m^2)^2]/(4m)^5\\&+120[m^2n^2(m^2+2n)-4m^2n^2(2n-m^2)+n^2(2n-m^2)^2]/(4m)^6\\&+2880mn^3(m^2-n)/(4m)^7+5040m^2n^4/(4m)^8\ ,\end{aligned} \tag{12}$$

$$\begin{aligned}L_2=&\ 8/(25m)+8(n+2m^2)/(5m)^3+48(m^3+2mn)/(5m)^4+96(m^4+2n^2+6m^2n)/(5m)^5\\&+96(m^5+20m^3n+30mn^2)/(5m)^6+2880(m^4n+2n^3+6m^2n^2)/(5m)^7\\&+40\,320(m^3n^2+2mn^3)/(5m)^8+4\times 8!(n^4+2m^2n^3)/(5m)^9+4\times 9!mn^4/(5m)^{10}\\&+4\times 10!n^5/[5(5m)^{11}]\ .\end{aligned} \tag{13}$$

The subsidiary condition Eq. (5) yields

$$\begin{aligned}&16/(3m)^3+144(m^2+n)/(3m)^5+240(m^3+6mn)/(3m)^6+4320(n^2+m^2n)/(3m)^7\\&\qquad+30\,240mn^2/(3m)^8+80\,640n^3/(3m)^9=N/Z\ .\end{aligned} \tag{14}$$

For a neutral atom $N/Z$ is equal to 1. We can rewrite Eq. (14) into the following form:

$$n^3+an^2+bn+c=0\ , \tag{15}$$

where $a=129\,600m^2/80\,640$, $b=89\,424m^4/80\,640$ and $c=(29\,808m^6-19\,683m^9)/80\,640$. It is easy to show that Eq. (15) has one real root and two imaginary roots for any real values of $m$.[10] The real root $n$ of Eq. (15) is

$$n=\left[-\frac{q}{2}+D^{1/2}\right]^{1/3}+\left[-\frac{q}{2}-D^{1/2}\right]^{1/3}-\frac{a}{3}\ , \tag{16}$$

where $q=c-ab/3+2a^3/27$, $D=q^2/4+p^3/27$, and $p=b-a^2/3$.

Therefore the numerical procedure for obtaining the optimal values of $m$ and $n$ is simple. We vary $m$ in succession and determine the corresponding $n$

value of Eq. (16) until those values of $m$ and $n$ are found which make $L(m,n)$ [Eq. (11)] a minimum. The minimization is carried out with double precision. The resulting values of the two parameters in Eq. (10) are

$$m = 1.148\,37 \text{ and } n = 4.0187\times 10^{-6}\,.$$

Although a value renders the term $nx$ in Eq. (10) almost negligible compared to the terms 1 and $mx^{1/2}$ for any practical value of $x$, it is still necessary to satisfy the subsidiary condition that the electron density is normalized.

## III. DISCUSSION

It is well known that if one uses the exact $\phi$ obtained from the TF equation, the calculated atomic and interatomic properties are in poor agreement with experiment. Because the Thomas-Fermi theory of the atom leads to a radial electron density which decreases as the inverse fourth power of the distance from the nucleus, whereas the Hartree approximation, its quantum-mechanical equivalent, gives an exponential decrease, the TF electron density falls off too slowly. A sharper decrease of $\phi$ with $x$ is needed. But the question is how much sharper? Kesarwani and Varshni have shown that for low-$Z$ elements a rapid decrease of $\phi$ with $x$ is needed, while for medium- and high-$Z$ elements, a less rapid decrease of $\phi$ with $x$ is satisfactory. In Fig. 1 we compare $\phi_1,\phi_2$ with our approximate solution $\phi_3$. The results of Eq. (10) decrease more sharply than Eq. (2) and less rapidly than Eq. (1), so we can predict our solution is more suited for medium-$Z$ elements.

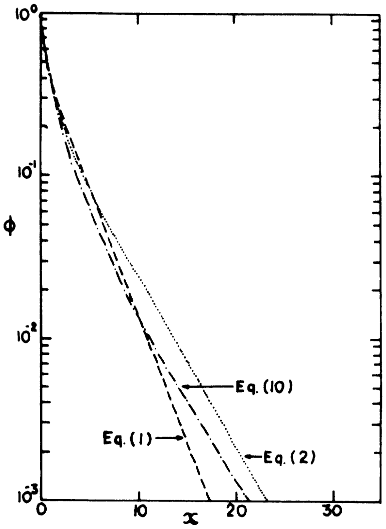

FIG. 1. Comparison of $\phi$ obtained from Eqs. (1), (2), and (10).

To test the validity of the approximate TF function of Eqs. (1), (2), and (10), the energy necessary to remove all electrons of an atom is calculated from[11]

$$E=\left[\frac{12}{7}\right]\left[\frac{2}{9\pi^2}\right]^{1/3}\phi'(0)Z^{7/3}\left[\frac{e^2}{a_B}\right]. \quad (17)$$

We have calculated $E$ by Eqs. (1), (2), and (10), and the results are listed in Table I. Column 3 of this table shows the experimental values of the total ionization energy for $Z \le 18$. For $Z > 20$ the theoretical (corrected Hartree-Fock) values of Fraga *et al.*[12] are shown. It is seen from Table I that

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

| | $Z$ | Standard | Eq. (1) | Errors | Eq. (2) | Errors | Eq. (10) | Errors |
|---|---|---|---|---|---|---|---|---|
| He | 2 | 2.905 | 3.016 | 3.8% | 3.426 | 17.9% | 3.217 | 10.7% |
| C | 6 | 37.88 | 39.14 | 3.3% | 44.47 | 17.4% | 41.76 | 10.2% |
| Ne | 10 | 129.1 | 128.9 | −0.2% | 146.4 | 13.4% | 137.5 | 6.5% |
| Ar | 18 | 529.4 | 508.1 | −4.0% | 577.2 | 9.0% | 542.1 | 2.4% |
| Ni | 28 | 1519 | 1424 | −6.2% | 1618 | 6.5% | 1520 | 0.07% |
| Kr | 36 | 2786 | 2561 | −8.1% | 2909 | 4.4% | 2732 | −1.9% |
| Pd | 46 | 5036 | 4537 | −9.9% | 5154 | 2.3% | 4840 | −3.9% |
| Xe | 54 | 7427 | 6595 | −11.2% | 7492 | 0.9% | 7036 | −5.3% |
| Hf | 72 | 14 977 | 12 905 | −13.8% | 14 659 | −2.1% | 13 767 | −8.1% |
| Hg | 80 | 19 431 | 16 501 | −15.1% | 18 745 | −3.5% | 17 604 | −9.4% |
| Rn | 86 | 23 253 | 19 535 | −16.0% | 22 191 | −4.6% | 20 840 | −10.4% |
| U | 92 | 27 506 | 22 864 | −16.9% | 25 972 | −5.6% | 24 392 | −11.3% |
| Fm | 100 | 33 896 | 27 774 | −18.1% | 31 550 | −6.9% | 29 631 | −12.6% |

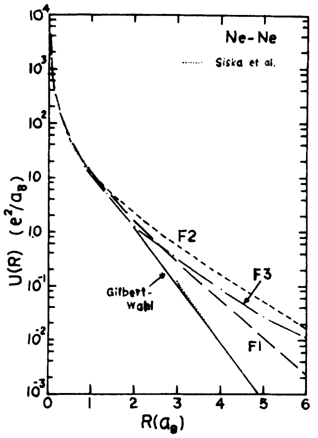

FIG. 2. Repulsive interaction potential for the Ne-Ne system. $F1$, results obtained from Eq. (1). $F2$, results obtained from Eq. (2). $F3$, results obtained from Eq. (10).

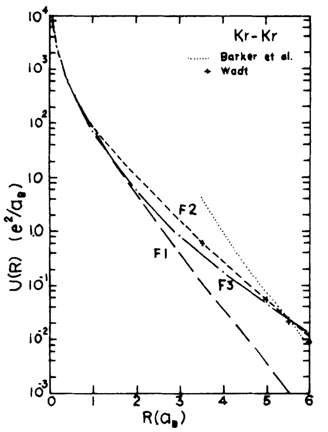

FIG. 4. Repulsive interaction potential for the Kr-Kr system.

for light elements Csavinszky's values are better, for medium-$Z$ elements our values are better, and for high-$Z$ elements Kesarwani and Varshni's values are better. In a sense the three solutions are mutually complementary.

As another test of the approximate TF function, the interaction energies between noble-gas atoms are calculated in the Firsov approximation.[5] In Firsov's theory this quantity is given by

$$U(R)=(Z_1Z_2e^2/R)\phi(\epsilon)\ , \tag{18}$$

where

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

and $R$ is the internuclear distance. It has been known for a long time that two TF atoms do not lead to binding.[13,14] For this reason, atomic interaction potentials calculated in the Firsov approximation can be considered reliable only at small internuclear separation where the interaction energy is much larger than several electron volts. We have calculated repulsive interaction energies for Ne-Ne, Ar-Ar, Kr-Kr, and Xe-Xe in the Firsov approximation from Eqs. (1), (2), and (10), and the results are compared with the experimental and theoretical potentials[15–19] in Figs. 2–5. In all of these figures, the $F1$ curves represent the results obtained from Eq. (1), the $F2$ curves represent those from Eq. (2), and the $F3$ curves represent those from Eq. (10). The dotted-line curves represent the repulsive part of the empirical potentials. It is seen from the figures that for Ne-Ne in-

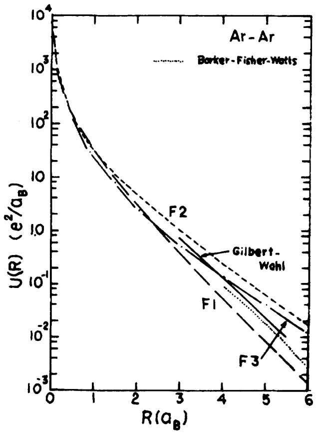

FIG. 3. Repulsive interaction potential for the Ar-Ar system.

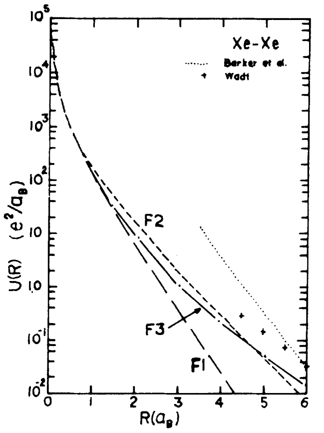

FIG. 5. Repulsive interaction potential for the Xe-Xe system.

teraction, Csavinszky's function gives better results; for Ar-Ar, our function gives better results. As we go to heavier pairs, namely, Kr-Kr, Xe-Xe, Kesarwani and Varshni's function gives better results. In conclusion, we find that for medium-atomic-number elements, Eq. (10) provides a more satisfactory approximation for $\phi$ than Eqs. (1) and (2).

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