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Improved variational solution of the Thomas-Fermi equation for atoms

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A variational solution of the Thomas-Fermi differential equation is obtained. The proposed solution is used to calculate the total ionization energy of atoms, and also the repulsive interaction energy between rare-gas atoms. It is shown that the results obtained by the proposed function are better than those obtained from Csavinszky's function for medium and high atomic number elements.

I. INTRODUCTION

The Thomas-Fermi (TF) theory of the atom[1-3] has an unsatisfactory feature in that it leads to a radial electron density which decreases as the inverse fourth power of the distance from the nucleus, whereas quantum-mechanical results show that it should decrease exponentially. Csavinszky[4,5] proposed to remedy this shortcoming by obtaining an approximate solution of a suitable form of the TF differential equation by making use of an equivalent variational principle. Csavinszky's function has found use in a number of areas.[6-14] We have been interested in the application of Csavinszky's function to describe the repulsive interaction between atoms. A close examination of the results presented by Csavinszky for the repulsive interaction between rare-gas atoms, as well as some calculations carried out by us showed that Csavinszky's proposed solution is satisfactory only for the light elements. In the present paper we propose an improved variational solution of the TF equation, which gives better results than the Csavinszky function for the total ionization energy of medium and high atomic number atoms, as well as for the repulsive interaction energy between such atoms.

II. THEORY

The TF theory leads to the differential equation

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

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, a_B is the Bohr radius, and Z is the atomic number.

The following boundary conditions should be fulfilled by a solution of Eq. (1):

$$\phi(0)=1, \tag{2}$$

and

$$\phi(\infty)=0. \tag{3}$$

The choice

$$F(\phi,\phi',x)=1/2\left(\frac{d\phi}{dx}\right)^2+2/5\left(\frac{\phi^{5/2}}{x^{1/2}}\right), \tag{4}$$

in conjunction with the variational principle

$$L(\phi)=\int_0^\infty F\,dx \tag{5}$$

is the equivalent of Eq. (1), since substitution of Eq. (4) in the Euler-Lagrange equation[15]

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

leads to the TF equation.

Csavinszky[4] suggested the following trial function:

$$\phi=(a_0\,e^{-\alpha_0 x}+b_0\,e^{-\beta_0 x})^2. \tag{6}$$

There are four parameters but these are not all independent. To satisfy the boundary condition in Eq. (2), one requires

$$a_0+b_0=1. \tag{7}$$

In addition, the subsidiary condition that the electron density be normalized must be satisfied:

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

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

$$\rho=\frac{Z}{4\pi\mu^3}\left(\frac{\phi}{x}\right)^{3/2}, \tag{9}$$

with

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

With the function (6), $L(\phi)$ can be analytically evaluated. Because of conditions (7) and (8) there are only two independent parameters. These are determined by extremalizing L with respect to these parameters. Csavinszky[5] thus obtained

$$a_0=0.721\,8337\,,\quad \alpha_0=0.178\,2559\,,$$

$$b_0=0.278\,1663\,,\quad \beta_0=1.759\,339\,.$$

In the earlier paper,[4] somewhat less accurate values were determined. As noted in the introduction, we found that the function (6) is satisfactory only for low atomic number elements. This will be considered further in Sec. III.

In the present paper, we suggest the following variational trial function for the TF equation:

$$\phi=(ae^{-\alpha x}+be^{-\beta x}+ce^{-\gamma x})^2\,, \tag{10}$$

where a, b, c, α, β, and γ are parameters. It is readily seen that the boundary condition (2) requires that

$$a+b+c=1\,. \tag{11}$$

Thus only five parameters are left; also, the boundary condition (3) is seen to be satisfied by Eq. (10). We shall determine the five remaining parameters by minimizing L with respect to these parameters subject to the subsidiary condition (8).

It is convenient to write L as

$$L=L_1+L_2\,, \tag{12}$$

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 the present work can be evaluated analytically. For carrying out the minimization of L, using Eq. (10), it is convenient to express the integrals in terms of two auxiliary variables n and m, defined by $n=\beta/\alpha$ and $m=\gamma/\alpha$. The resulting expressions for L_1 and L_2 are as follows:

$$\begin{aligned}L_1=\alpha\Big[&\tfrac{1}{2}a^4+\tfrac{1}{2}b^4n+\tfrac{1}{2}c^4m+4a^3b\left(\frac{1+n}{3+n}\right)+4a^3c\left(\frac{1+m}{3+m}\right)+4b^3a\left(\frac{n+n^2}{1+3n}\right)\\&+4c^3a\left(\frac{m+m^2}{1+3m}\right)+4b^3c\left(\frac{n^2+nm}{m+3n}\right)+4c^3b\left(\frac{m^2+nm}{n+3m}\right)+a^2b^2\left(\frac{1+4n+n^2}{1+n}\right)\\&+a^2c^2\left(\frac{1+4m+m^2}{1+m}\right)+b^2c^2\left(\frac{n^2+4nm+m^2}{n+m}\right)+4a^2bc\left(\frac{1+2n+2m+mn}{2+m+n}\right)\\&+4ab^2c\left(\frac{m+2n+2nm+n^2}{1+m+2n}\right)+4abc^2\left(\frac{n+2m+2nm+m^2}{1+n+2m}\right)\Big]\,,\end{aligned} \tag{13}$$

$$\begin{aligned}L_2=2\left(\frac{\pi}{\alpha}\right)^{1/2}\bigg(&\frac{a^5}{5^{3/2}}+\frac{b^5}{5^{3/2}n^{1/2}}+\frac{c^5}{5^{3/2}m^{1/2}}+\frac{a^4b}{(4+n)^{1/2}}+\frac{a^4c}{(4+m)^{1/2}}+\frac{b^4a}{(4n+1)^{1/2}}+\frac{c^4a}{(4m+1)^{1/2}}\\&+\frac{b^4c}{(4n+m)^{1/2}}+\frac{c^4b}{(4m+n)^{1/2}}+\frac{2a^3b^2}{(3+2n)^{1/2}}+\frac{2a^3c^2}{(3+2m)^{1/2}}+\frac{2a^2b^3}{(3n+2)^{1/2}}\\&+\frac{2a^2c^3}{(3m+2)^{1/2}}+\frac{2b^3c^2}{(3n+2m)^{1/2}}+\frac{2b^2c^3}{(3m+2n)^{1/2}}+\frac{4a^3bc}{(3+n+m)^{1/2}}+\frac{4b^3ac}{(1+3n+m)^{1/2}}\\&+\frac{4c^3ab}{(1+n+3m)^{1/2}}+\frac{6ab^2c^2}{(1+2n+2m)^{1/2}}+\frac{6bc^2a^2}{(n+2+2m)^{1/2}}+\frac{6ca^2b^2}{(m+2+2n)^{1/2}}\bigg)\,.\end{aligned} \tag{14}$$

The subsidiary condition, Eq. (8), yields

$$\begin{aligned}\frac{1}{\alpha^{3/2}}\bigg(&\frac{a^3}{3^{3/2}}+\frac{b^3}{(3n)^{3/2}}+\frac{c^3}{(3m)^{3/2}}+\frac{3a^2b}{(2+n)^{3/2}}+\frac{3a^2c}{(2+m)^{3/2}}+\frac{3b^2a}{(2n+1)^{3/2}}\\&+\frac{3c^2a}{(2m+1)^{3/2}}+\frac{3b^2c}{(2n+m)^{3/2}}+\frac{3c^2b}{(2m+n)^{3/2}}+\frac{6abc}{(1+m+n)^{3/2}}\bigg)=\frac{2}{\sqrt{\pi}}\,\frac{N}{Z}\,.\end{aligned} \tag{15}$$

For neutral atoms N/Z is, of course, equal to 1. L was minimized with respect to the parameters α, c, n, and m; the remaining two parameters being determined from Eqs. (11) and (15). The resulting values of the six parameters in Eq. (10) are

$$a=0.524\,95,\quad \alpha=0.120\,62,$$
$$b=0.435\,05,\quad \beta=0.847\,95,$$
$$c=0.04,\quad \gamma=6.7469.$$

III. DISCUSSION

Csavinszky[4] has considered three things to examine the validity of his variational function. Here we shall also consider the same three things. First, in Fig. 1 we compare ϕ [Eq. (6)] and ϕ [Eq. (10)] with the exact solution[1,16] of the TF equation. It will be noticed that Eq. (10) is in better agreement with the exact solution than Eq. (6). At large values of x there are marked deviations arising from the exponential decrease of Eq. (10).

The energy necessary to remove all electrons of an atom can be calculated from the following equation[1]:

$$E=(12/7)(2/9\pi^2)^{1/3}\phi'(0)Z^{7/3}(e^2/a_B)\,. \tag{16}$$

We have calculated E, both by Eqs. (6) and (10), and the results are shown for some representative values of Z in Table I. Column 3 of this table shows the experimental values of the total ionization energy for $Z\leqslant 18$. For $Z>20$ experimental data for ionization potentials for all stages of ionization are not available, and in these cases, the theoretical (corrected Hartree-Fock) values of Fraga *et el.*[17] are shown. For $Z\leqslant 18$, the values of Fraga *et al.* are in good agreement with the experimental values; for higher atomic numbers, their values can be expected to be reasonably close to the correct values. It will be noticed from Table I that for light elements, in percentage terms, Csavinszky's values are better than ours, but for $Z>28$, the reverse is true.

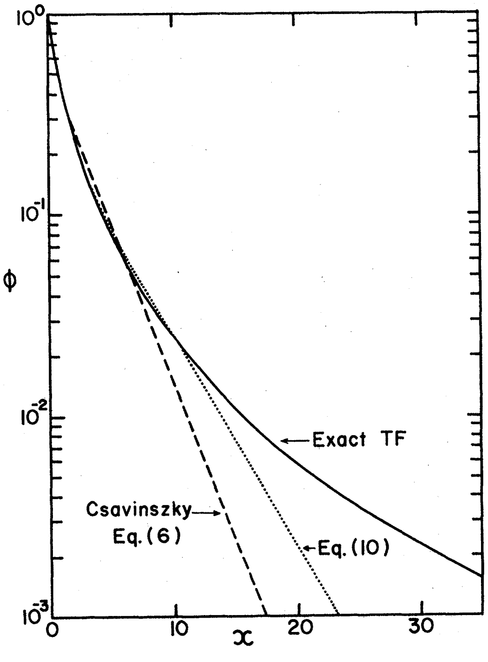

FIG. 1. ϕ [Eq. (6)] and ϕ [Eq. (10)] compared with the exact ϕ obtained from a numerical solution of the TF equation.

An interesting approach to the theory of the repulsive interaction between two atoms was initiated by Firsov.[18] In his theory, the interaction energy is given by

$$U(R)=(Z_1Z_2e^2/R)\phi(\xi)\,, \tag{17}$$

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 $R\lesssim 10^{-8}$ cm ($=1.9a_B$) mainly because the TF electron density falls off too slowly. Csavinszky[4] has calculated the interaction energies between rare-gas atoms, both for the homo and heteronuclear cases, in the Firsov approximation and making use of Eq. (6).

We have calculated repulsive interaction energies for Ne-Ne, Ar-Ar, Kr-Kr, Xe-Xe, and Rn-Rn in the Firsov approximation, from both Eqs. (6) and (10), and the results are compared with the best available experimental and theoretical potentials in Figs. 2-6. In all of these figures, $F1$ curves represent the results obtained from Eq. (6), and $F2$, represent those from Eq. (10). The dotted line curves represent the repulsive part of the empirical potentials (determined from experimental data), i.e., the dispersion energy contribution has been subtracted from the fitted potential.

There is a great amount of literature on the determination of the intermolecular potential energy functions of the inert gases from analysis of various types of experimental data on these gases. Potentials thus determined shall be referred to as empirical potentials. The early work on empirical potentials has been discussed in the well-known book by Hirschfelder *et al.*[19] There has been a considerable advance in our understanding of the potential energy functions of the inert gases during the last decade. The work on empirical potentials has been reviewed by Maitland and Smith,[20] Smith,[21] and Barker[22] during the last few years.

The theory of intermolecular forces was reviewed by Hirschfelder *et al.*[19] in 1954 and by

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

Element	Z	Expt. and corrected Hartree-Fock	Calc. from Eq. (6)	Percent difference from col. 3	Calc. from Eq. (10)	Percent difference from col. 3
He	2	2.905	3.016	3.8	3.426	17.9
C	6	37.88	39.14	3.3	44.47	17.4
Ne	10	129.1	128.9	−0.2	146.4	13.4
Ar	18	529.4	508.1	−4.0	577.2	9.0
Ni	28	1 519	1 424	−6.2	1 618	6.5
Kr	36	2 786	2 561	−8.1	2 909	4.4
Pd	46	5 036	4 537	−9.9	5154	2.3
Xe	54	7 427	6 595	−11.2	7 492	0.9
Hf	72	14 977	12 905	−13.8	14 659	−2.1
Hg	80	19 431	16 501	−15.1	18 745	−3.5
Rn	86	23 253	19 535	−16.0	22 191	−4.6
U	92	27 506	22 864	−16.9	25 972	−5.6
Fm	100	33 896	27 774	−18.1	31 550	−6.9

Margenau and Kestner[23] in 1969. More recently, Murrell[24] has discussed the short- and intermediate-range forces, and Bell and Zucker[25] have discussed long-range forces. There have been numerous calculations[26-41] of the repulsive interaction energy between rare-gas atoms by a variety of methods. We shall now consider individual gases.

A. Neon

Siska *et al.*[42] have used the following potential, known as the Morse-spline-van der Waals (MSV) potential:

$$V(R)/\epsilon = \begin{cases} \exp[-2\beta(x-1)] - 2\exp[-\beta(x-1)], & 0<x\leqslant x_1 \\ b_1 + (x-x_1)\{b_2 + (x-x_2)[b_3 + (x-x_1)b_4]\}, & x_1<x<x_2 \\ -C_6x^{-6} - C_8x^{-8} - C_{10}x^{-10}, & x_2\leqslant x \end{cases} \tag{18}$$

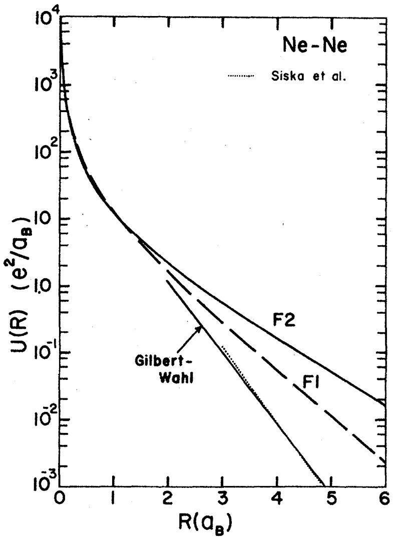

FIG. 2. Repulsive interaction potential for the Ne–Ne system. $F1$ and $F2$ are explained in the text.

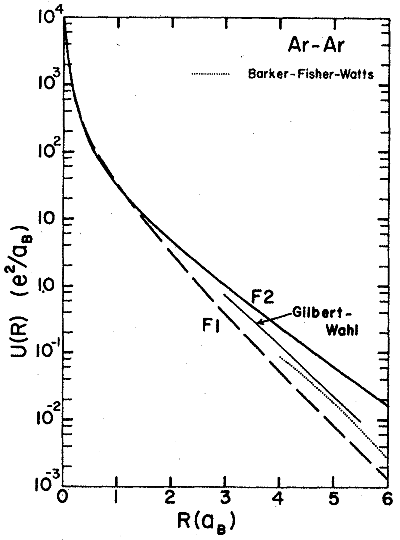

FIG. 3. Repulsive interaction potential for the Ar–Ar system.

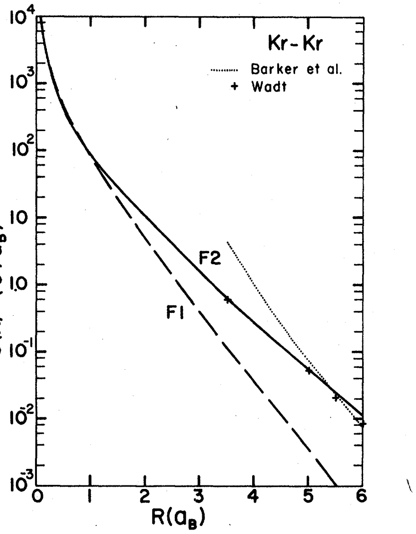

FIG. 4. Repulsive interaction potential for the Kr–Kr system.

where $x=R/R_m$, R_m being the interatomic separation at the minimum of the potential; ϵ, β, and b's are constants. C_6, C_8, and C_{10} are dispersion energy coefficients. These authors determined the parameters, occuring in the potential from their scattering data, second virial coefficients and known long-range behavior; the resulting values being $\epsilon=(0.633\pm0.024)\times10^{-14}$ erg, $R_m=3.03\pm0.02$ Å, $\beta=6.93\pm0.18$, $x_1=1.1000$, $x_2=1.4000$, $b_1=-0.7500$, $b_2=1.870$, $b_3=-5.185$, $b_4=5.797$, $C_6=1.282$, $C_8=0.278$, and $C_{10}=0$. The dispersion energy constant C_6 was given the theoretical value and C_8 was estimated. This potential gives good agreement with experimental viscosity data.[43] A slightly improved potential has been proposed by Farrar *et al.*[44]; however, the values of all the parameters occurring in the latter potential are not available. The potential of Siska *et al.* (after subtracting the dispersion energy contribution) is shown in Fig. 2 by the dotted line curve.

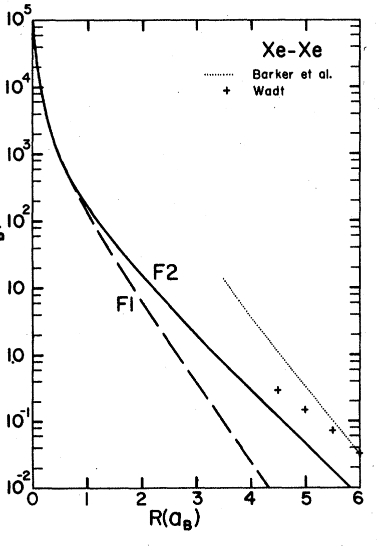

FIG. 5. Repulsive interaction potential for the Xe–Xe system.

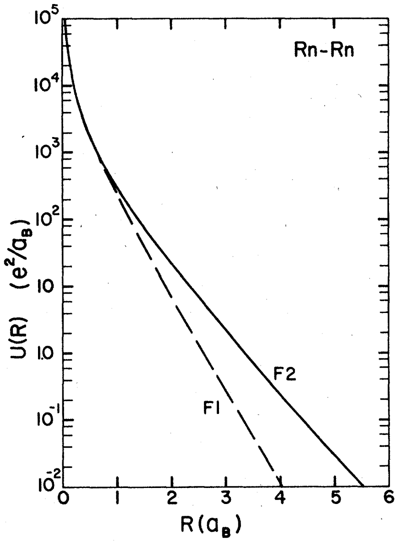

FIG. 6. Repulsive interaction potential for the Rn–Rn system.

Gilbert and Wahl[30] have carried out self-consistent field (SCF) calculations for the Ne-Ne interaction and their results are shown in Fig. 2. *Ab initio* configuration-interaction calculations have been made by Cohen and Schneider[36]; their results are in good agreement with those of Gilbert and Wahl. It will be noticed from Fig. 2 that there is good agreement between the empirical and Gilbert-Wahl potentials. Csavinszky's function is seen to give better results than Eq. (10).

B. Argon

The following potential was proposed by Barker and Pompe[45]:

$$V(R)=\epsilon\left(e^{\alpha(1-r)}\sum_{i=0}^{5}A_i(r-1)^i-\frac{C_6}{(r^6+\delta)}-\frac{C_8}{(r^8+\delta)}-\frac{C_{10}}{(r^{10}+\delta)}\right),\qquad(19)$$

where $r=R/R_m$, and α and A_i's are constants. The constant δ, which prevents a spurious maximum in the potential at small distances, has always been given the value 0.01. Successive refinements of the argon potential using the form

(19) and related forms were made by Barker and co-workers.[46-48] The potential of Barker, Fisher, and Watts[48] appears to be the best available potential for argon. The following data were used to fix the parameters in Eq. (19): high-energy molecular-beam data, zero-temperature and -pressure lattice spacing, energy and Debye parameter θ_0, derived from specific heat measurements of solid argon, the known long-range coefficients of R^{-6}, R^{-8}, and R^{-10} (the two latter coefficients are approximate values), second virial coefficients, the liquid-phase pressure at one temperature and density, and the known coefficients of the Axilrod-Teller interaction. The values of the parameters in Eq. (19), as listed by Barker,[22] are given in Table II. This pair potential has been used to calculate a wide range of thermodynamic properties of solid, gaseous, and liquid argon, and the results are in excellent agreement with experiment. The repulsive part of this potential is shown by the dotted line curve in Fig. 3.

Gilbert and Wahl[30] and Wadt[40] have performed SCF calculations on the Ar-Ar interaction. The two sets are in reasonable agreement with each other. Gilbert-Wahl results are shown in Fig. 3. The theoretical results of Gilbert and Wahl are seen to be in reasonable agreement with the empirical potential. The results from Eqs. (6) and (10) have about the same sort of deviation, but in opposite directions, from the Gilbert-Wahl results.

C. Krypton

An extended version of potential (19) has been quite successful for krypton. This potential has the form

$$V(R)=\epsilon[V_0(r)+\Delta V(r)], \qquad (20)$$

where $V_0(r)$ is given by the expression inside the large parentheses in Eq. (19) and $\Delta V(r)$ is defined by

$$\Delta V(r)=\begin{cases}[P(r-1)^4+Q(r-1)^5]e^{\alpha'(1-r)}, & r>1\\ 0, & r\leqslant 1\,.\end{cases} \qquad (21)$$

Barker *et al.*[49] determined the parameters of this potential using scattering data, vibrational levels of Kr_2, solid-state data, second virial coefficients, and gas viscosities. The *K*2 set of their parameters is given in Table II. The repulsive part of this potential is plotted in Fig. 4. Barker *et al.*[49] estimate the range of validity of their potential to be roughly $V(R)<1.3\times10^{-2}$ a.u. Thus the major portion of the plotted curve can only be considered as an extrapolation. There is a potential due to Buck *et al.*,[50] which gives results almost as good as those from the potential of Barker *et al.*[49]; the two potentials are in excellent agreement with each other.

TABLE II. Parameters for argon, krypton, and xenon potantials.

	Argon[a]	Krypton[b]	Xenon[b]
ϵ/k (*K*)	142.095	201.9	281.0
R_m (Å)	3.761 2	4.006 7	4.3623
A_0	0.277 83	0.235 26	0.2402
A_1	−4.504 31	−4.786 86	−4.8169
A_2	−8.331 215	−9.2	−10.9
A_3	−25.269 6	−8.0	−25.0
A_4	−102.019 5	−30.0	−50.7
A_5	−113.25	−205.8	−200.0
C_6	1.107 27	1.063 2	1.0544
C_8	0.169 713 25	0.170 1	0.1660
C_{10}	0.013 611	0.014 3	0.0323
α	12.5	12.5	12.5
δ	0.01	0.01	0.01
P		−9.0	59.3
Q		68.67	71.1
α'		12.5	12.5

[a] Reference 22.

[b] Reference 49.

Wadt[40] has carried out SCF calculations for Kr_2, and his results are included in Fig. 4. At very small values of R, i.e., $R<a_B$, the results from Bohr's screened Coulomb potential, Firsov's TF results, *F*1, and *F*2, are all very close to each other and there are good theoretical reasons to believe that these results are correct. The *F*2 curve is in excellent agreement with the quantum-mechanical results and it would appear that it is close to the true potential in the repulsive region.

It will also be noticed in Fig. 4 that there is an increasing divergence between the empirical and quantum-mechanical results as $R\rightarrow 0$. As we go away from $R=R_m$ to smaller values of R, the shape of the empirical potential becomes increasingly less influencial in determining most of the physical properties which are usually employed for determining such potentials. (An important exception is high-temperature second virial coefficient data). Thus the empirical potential is accurate only in the attractive and low-energy repulsive region. The available evidence indicates that the empirical potential is inadequate to describe the high-energy repulsive region.

D. Xenon

The determination of an interatomic potential for xenon consistent with all experimental data has proved to be difficult, possibly because of a real inconsistency in the experimental data. The best compromise appears to be a potential of the form (20) whose parameters have been obtained by Barker *et al.*[49] (their set $X2$). These parameters are listed in Table II and the repulsive part of this potential is shown in Fig. 5. For xenon also, the estimated range of validity of Eq. (20) is $V(R)<1.3\times10^{-2}$ a.u.

Wadt[40] has performed SCF calculations on the ground state of Xe_2 also, and his results are shown in Fig. 5. It will be noticed from Fig. 5 that the results from Eq. (10) are closer to Wadt's values than those obtained from Eq. (6). Also we notice that, as was the case for Kr, there is an increasing divergence in the empirical and SCF potentials as R tends towards zero. In this case also the empirical potential is inadequate in the high-energy repulsive region.

E. Radon

The experimental data for radon are very scant. While attempts have been made to estimate[51,52] the values of ϵ/k and R_m for the intermolecular potential for radon, reliable information on the repulsive region is lacking. The only previous theoretical calculation on the Rn-Rn interaction is that of Abrahamson.[26] However, his results are suspect as his method of calculation has been criticized by Gunther[29] and the criticism has been substantiated by Junker and Menendez.[37] From the trend of relative positions of $F2$ and *ab initio* calculations for the previous four cases, it would appear that the actual repulsive potential for radon will lie above the $F2$ curve (Fig. 6).

Summarizing, we find that for Ne-Ne interaction Csavinszky's function gives better results than Eq. (10); for Ar-Ar, the results from the two have about the same sort of deviation from the *ab initio* theoretical curve. But as we go to heavier pairs, namely, Kr-Kr, Xe-Xe, and Rn-Rn, the results obtained from Eq. (10) become increasingly better than those from Csavinszky's function.

We have also carried out calculations for heteronuclear pairs of rare gases. The results are analogous to those for homonuclear pairs. The results from Eq. (6) are better than those from Eq. (10) for Ne-Ar, the results from the two are comparable for Ne-Kr, but for all other heteronuclear pairs between Ne, Ar, Kr, and Xe, the results from Eq. (10) are better than those from Eq. (6). In conclusion, we find that for medium and high atomic number elements, Eq. (10) provides a more satisfactory approximation for ϕ than Eq. (6). In a sense the two solutions are complementary, one is more suited for light elements, while the other for medium and high atomic number elements.

At first sight it may appear rather surprising that a six-parameter fit [Eq. (10)] does more poorly than a four-parameter fit [Eq. (6)] for low-Z elements. A reference to Fig. 1 will help to clarify the situation. It is known that if one uses the exact ϕ obtained from the TF equation, the calculated atomic and interatomic properties are in poor agreement with experiment. A sharper decrease of ϕ with x is indicated. How much sharper? The results of the present paper show that for low-Z elements a rapid decrease of ϕ with x, Eq.(6), is needed, while for medium-and high-Z elements, a less rapid decrease of ϕ with x, Eq. (10), is satisfactory. Extrapolating, one could conjecture that as Z becomes very large, atomic and interatomic properties calculated from the exact TF solution will tend to the "correct" values. One could argue that after all the TF model is a statistical model and can be expected to be best applicable only when Z is very large. The results of the present paper also indicate that probably it is not possible to find a "universal" repulsive potential of the form of Eq. (17) such that $\phi(\xi)$ is some suitable function of ξ alone.

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