APPLICATION OF THE MODIFIED WU FUNCTION TO THE CALCULATION OF SOME ATOMIC PROPERTIES

GLOSSMAN, D.[1]) DONNAMARÍA, C.[1]) CASTRO, A.[1]) FERNÁNDEZ, M.[1]), La Plata

The analytical Wu function is improved within the context of the Thomas—Fermi—Amaldi—Dirac model. The modified Wu function is then applied to calculate some neutral properties, such as interaction energies for noble gas atoms and atomic ionization energies. Comparisons with other theoretical results and available experimental data are taken into account. General trends are pointed out and advantages of the present analytical procedure are stressed.

I. INTRODUCTION

The treatment of interatomic potentials is the bottleneck of quantum mechanical calculations of atomic and molecular systems. Up to now, in atomic collision theory and its applications to stopping, range damage, sputtering, etc., mostly simple "universal" potentials have been applied [1, 2]. On a first approximation they depend on the separation R between the atoms. Bohr's screened [3] coulomb potential is a good representation of the interaction, $U(R)$, at very small distances ($R \leq 0.2 a_B$, $a_B = 5.29$ nm). In separations near the equilibrium position the empirically fitted potentials of the Lenard—Jones type [4] are applicable. Comparatively little is known as regards the interaction, $U(R)$, in the intermediate range ($R = 0.8 a_B - 7.0 a_B$) of separations, particularly important in the study of phenomena involving close atomic encounters, very high pressure or temperature. This lack of information is usually compensated by equilibrium potentials based on a reasonable physical model [5]. One of them is that proposed by Thomas [6] and Fermi [7]. Of course, such a scheme can only describe the general trends, i.e. gradual changes in the magnitude and shape depending on the atomic number Z, but not every individual wiggle due to the specific shell structure of the radius of the Seitz—Wigner cell in solid — state target atoms [1]. In a recent paper [5] we have introduced some

corrections into the interaction energy, connected with exchange and self-energy effects, which are neglected in the original Thomas—Fermi (TF) theory. The unrealistic long-range behaviour [2] of the TF screening function can be improved somewhat by the modifications suggested by Lenz and Jensen [8, 9]. The proposed Thomas—Fermi—Amaldi—Dirac (TFAD) screening function introduces the exchange energy correction [10] and the self-interaction modification as suggested by Amaldi [11]. These corrections are made evident in the screening function because of the presence of two parameters. Another optimum Z parameter arises in order to improve the total electronic energy [12, 13], since the introduction of the correction terms worsens the energy results [14]. We believe these first results on the utilization of these functionals with the optimization of Z are suggestive and interesting, because they offer a very easy alternative of improving the statistical computations. Nevertheless, before reaching a definitive conclusion about them, we consider it necessary to perform several tests in other independent trial functions and to calculate different physical quantities making the corresponding comparisons with the available experimental data. Then it is our purpose to work along these lines. Bearing this in mind, we have extended in the present paper the examination of this particular procedure to the calculation of interatomic homonuclear potentials, diamagnetic susceptibilities and the total ionization energies for rare gas atoms with another simple density function proposed by Wu [15]. The aim of our present communication was to find the appropriate dependence on Z and demonstrating the validity of some atomic properties ranging from the lightest to the heaviest atoms within the neutral atom set.

II. THEORETICAL FOUNDATIONS
INTERATOMIC POTENTIALS

Homonuclear binary potentials lend themselves most readily to a theoretical description in terms of the free electron statistical model [16]. Apart from the feasible theoretical analysis the homonuclear case has also its practical advantages: the whole field of radiation damage and sputtering is governed by low energy binary collisions between identical atoms. And the lower part of the former "universal" potential needs improvements most urgently: deviations up to an order of magnitude are quite common (notice for example, the difference between the TF and the Moliere potential in Fig. 2, Ref. 1). The most simple potential has the following form

$$U(R) = \frac{Z_1 \cdot Z_2}{R} \Phi(x),$$

(1)

where the screening $\Phi(x)$ is one and the same function for all $Z_1 \cdot Z_2$ combina-

[1]) INIFTA, Division Química Teórica, Suc. 4., C.C. 16, 1900 LA PLATA, Argentina

tions, e.g. a Thomas–Fermi [6,7], a Molière [2] or a Lenz–Jensen [7,9] function. The Z dependence enters here, only through the so-called "screening length a'", in the case of the Firsov theory [17],

$$a' = 0.8853\, a_B/(Z_1^{1/2} + Z_2^{1/2})^{2/3} \tag{2}$$

a_B = Bohr's radius,

the variable $x = R/a'$, is then used as argument of $\Phi(x)$. We restrict ourselves to study the homonuclear case:

$$Z_1 = Z_2 = Z. \tag{3}$$

We assume that the electrical potential of an atom is described in the form [17, 18]:

$$V = \frac{Ze}{R}\Phi(x) \tag{4}$$

where $\Phi(x)$ is a suitable screening function, not necessarily the TF one. If we do relate it to the TF theory, it follows that [18]:

$$\frac{d^2\Phi(x)}{dx^2} = \Phi^{3/2} x^{-1/2}, \tag{5}$$

and we adopt the scaling of r with $Z^{1/3}$,

$$x = r/a; \quad a = 0.8853\, a_B Z^{-1/3}.$$

In the framework of the TF theory the electron density ϱ is related to Φ by:

$$\varrho = \frac{Z(\Phi(x))^{3/2}}{4\pi a^3}. \tag{6}$$

This ϱ is equivalent to that determined from a variational principle by minimizing the total energy [18] with respect to the variation of the parameters included in the trial density function.

Atomic Total Energy

The atomic total energy in the TF model and in those modified by corrections of self-interaction (FA) and exchange (D) effects are given by [5], [13], [19]:

$$E_{TF}(\varrho) = E_K(\varrho) + E_{ne}(\varrho) + E_{ee}^{TF}(\varrho) \tag{7}$$

$$E_{TFA}(\varrho) = E_K(\varrho) + E_{ne}(\varrho) + \frac{(N-1)}{N} E^{TF}(\varrho) \tag{8}$$

$$E_{TFD}(\varrho) = E_K(\varrho) + E_{ne}(\varrho) + E_{ee}^{TF}(\varrho) + E_{exch}(\varrho) \tag{9}$$

$$E_{TFAD}(\varrho) = E_{TFA}(\varrho) + E_{exch}(\varrho). \tag{10}$$

The first term, $E_K(\varrho)$, represents the kinetic energy of the electron gas, the second, $E_{ne}(\varrho)$, the interaction energy of the electron gas with the atomic nucleus, and the third, $E_{ee}(\varrho)$, the self energy resulting from the interaction of the electron gas. The FA (Fermi–Amaldi) correction appears as a simple factor $(N-1)/N$, energy results an optimum Z value is determined from the condition [3], [12], [20]:

$$E_{TF}(Z_{op}) = E_{HF}. \tag{11}$$

E_{HF} shows the self-consistent-field (SCF) energy value for the non-relativistic total electronic energy [21].

The Screening Function

The screening Wu function [15] is a modified trial solution of Robert's function [22]:

$$\Phi_{Wu} = (1 + mx^{1/2} + nx)^3 e^{-3mx^{1/2}} (x)^{-3/2} \tag{12}$$

where m, n are variational parameters, which have minimized the theory functionals (7)—(10). The infinite electron distribution of the naive TF model causes $U(R)$ to decay too slowly as the distance increases. This shortcoming can be avoided by choosing a trial electron density function with an adequate dependence on the distance, such as Φ_{Wu}. Introducing Φ_{Wu} into Eq. (6), we obtain

$$\varrho = \frac{Z}{4\pi a^3}(1 + mx^{1/2} + nx)^3 (x)^{-3/2} e^{-3mx^{1/2}}. \tag{13}$$

Replacing ϱ, Eq. (13), into the normalization condition [18]:

$$\int \varrho\, dv = N, \tag{14}$$

N being the number of electrons, then (Appendix I):

$$n^3 + a_0 n^2 + b_0 n + c_0 = 0. \tag{15}$$

With ϱ from Eq. (13), the energy functionals become (in the following we will use atomic units):

$$E_K(\varrho) = K_k \int \varrho^{5/3}\, dv. \tag{16}$$

From Appendix (II):

$$E_K(m,n) = 1.3554\, Z^{7/3}\left[0.7028\frac{1}{m} + 0.7028\frac{n}{m^3} + 0.71270\frac{n^2}{m^5} + 0.55665\frac{n^3}{m^7} + 0.28901\frac{n^4}{m^9} + 0.07432\frac{n^5}{m^{11}}\right]$$ (17)

$$E_{ne}(\varrho) = \int V_N \varrho\, dv,$$ (18)

V_N being the electron-nucleus interaction, which in an atom with nuclear charge Z is $(-Z/r)$. From Appendix III,

$$E_{ne}(m,n) = -2.25902\, Z^{7/3}\left[0.96296\frac{1}{m} + 0.96296\frac{n}{m^3} + 0.79012\frac{n^2}{m^5} + 0.32922\frac{n^3}{m^7}\right]$$ (19)

$$E_{ee}^{TF}(\varrho) = -(1/2)\int V_{ee}^{TF}\varrho\, dv$$ (20)

the electron energy $V_{ee}^{TF}(\varrho)$ is determined from the Poisson equation:

$$\frac{d^2(rV_{ee}^{TF})}{dr^2} = 4\pi\varrho r.$$ (21)

Integrating it twice (Appendix IV):

$$E^{TF}(m,n) = -1.1295\, Z^{7/3}\left[0.5296\frac{n^6}{m^{16}} + 2.9796\frac{n^5}{m^{14}} + 5.372\frac{n^4}{m^{12}} + 8.292\frac{n^3}{m^{10}} + 7.5068\frac{n^2}{m^8} + 3.8996\frac{n}{m^6} + 0.9884\frac{1}{m^4} - \frac{26}{27m} - \frac{26n}{27m^3} - \frac{64n^2}{81m^5} - \frac{720n^3}{2187m^7}\right]$$ (22)

From Appendix V:

$$E_{exch}(\varrho) = -\frac{3(3)^{1/3}}{4\pi}\int \varrho^{4/3}\, dv.$$ (23)

$$E_{exch}(m,n) = -0.71763\, Z^{5/3}\left[0.4512\frac{1}{m^2} + 0.9023\frac{n}{m^4} + 1.1646\frac{n^2}{m^6} + 0.4614\frac{n^3}{m^8} + 0.3461\frac{n^4}{m^{10}}\right].$$ (24)

Diamagnetic Susceptibility

The atomic diamagnetic susceptibility, S, is given by [16]

$$S = -\frac{N_A}{6}\frac{\langle r^2\rangle}{c^2 m}$$ (25)

where N_A is the Avogadro number and c the light velocity, while $\langle r^2\rangle$ is given by

$$\langle r^2\rangle = \int \varrho r^2\, dv.$$ (26)

Considering (26) and (13)

$$\langle r^2\rangle = 1.56766\, Z^{1/3} a_B^2\left[\frac{10880}{729\, m^7} + \frac{76160\, n}{729\, m^9} + \frac{627200\, n^2}{2187\, m^{11}} + \frac{1971200\, n^3}{6561\, m^{13}}\right]$$ (27)

$a_B = 0.529171 \times 10^{-8}$ cm, then:

$$S = -2.82855 \times 10^{10}\,\langle r^2\rangle\, \text{cm}^3/\text{mol}.$$ (28)

Ionization Energy

The calculation of the energy necessary to remove all electrons of an atom can be easily achieved by making use of the following expression [16]:

$$IE = \frac{12}{7}\left(\frac{2}{9\pi^2}\right)^{1/3}\Phi'(0)Z^{7/3}$$ (29)

where $\Phi(x)$ satisfies the TF equation (5). In our TF-like model with the Wu function:

$$\Phi'(0) = (2n - m^2),$$ then, for IE:

$$IE_y = \frac{12}{7}\left(\frac{2}{9\pi^2}\right)^{1/3}(2n_y - m_y^2)Z^{7/3}$$

$y = $ TF, TFA, TFD or TFAD formalism, and $Z = Z$ or Z_{ap}.

III. RESULTS

First, we have completely minimized the energy functionals (7)—(10), (16)—(24) associated with the appropriate TF—Wu function, equation (13), corresponding to neutral atoms. Thus, we have obtained optimum values for the (m, n) parameters, according to the minimum energy criterion for each particular TF-like formulation, (Table 1). Then, for each (m, n) pair we have computed some atomic properties, such as total energies and atomic diamagnetic susceptibilities.

Table 1

Optimum (m, n) parameters for the modified Wu-function

Atom	Z	m_{TFA}	$-n_{TFA}$	m_{TFD}	$-n_{TFD}$	m_{TFAD}	$-n_{TFAD}$
Ne	10	1.0192	0.12407	1.0065	0.13395	0.9897	0.14618
Ar	18	1.0244	0.11995	1.0151	0.12727	1.0073	0.13324
Xe	36	1.0276	0.11738	1.0211	0.12257	1.0177	0.12525
Kr	54	1.0286	0.11657	1.0234	0.12075	1.0213	0.12242
Rn	86	1.0293	0.11601	1.0254	0.11915	1.0241	0.12019

$m_{TF} = 1.0305$, $n_{TF} = -0.11503$

Table 2

Optimum (m, n, Z_{op}) parameters for the modified Wu-function

Atom	Z_{op}	m_{TFA}	$-n_{TFA}$	m_{TFD}	$-n_{TFD}$	m_{TFAD}	$-n_{TFAD}$
Ne	9.0019	1.0178	0.12509	1.0045	0.13528	0.9850	0.14944
Ar	16.4769	1.0240	0.12019	1.0140	0.12804	1.0054	0.13460
Xe	33.4649	1.0274	0.11746	1.0206	0.12289	1.0269	0.12579
Kr	50.9301	1.0285	0.11657	1.0231	0.12091	1.0209	0.12265
Rn	81.3494	1.0292	0.11601	1.0252	0.11923	1.0238	0.12035

$m_{TF} = 1.0305$, $n_{TF} = -0.11503$

TF = Thomas–Fermi
TFD = Thomas–Fermi–Dirac
TFA = Thomas–Fermi–Amaldi
TFAD = Thomas–Fermi–Amaldi–Dirac

We have seen in previous papers [5], [12] that when an optimum Z value, equation (11), is introduced within the energy functionals (7)—(10), results of energy improve remarkably. With Z_{op} values, new $m(Z_{op})$, $n(Z_{op})$ are obtained from the variational procedure (Table 2). In Table 3 we present total electronic energies. As previously stated [5], additional Z_{op} constraint, equation (11), forces in a certain way a better agreement between TF and SCF electronic energy, so it is necessary to consider another independent property to judge the merits of the procedure. Atomic diamagnetic susceptibility, equation (28), seems to be a convenient alternative, because it depends on $\langle r^2 \rangle$, equation (27), Table 4. We calculate $S(Z_{op})$ and $S(Z)$ for neutral atoms for which other theoretical and experimental data exist [24, 25], Table 5. In Table 6 we have listed the corresponding ionization energies as given by formula (30). In Table 7 the comparison with other available data is made [15], [26], [27]. Finally, we have calculated the interatomic potentials between rare gas atoms in the Firsov—TFAD(Z_{op}) approximation.

Table 3

Total electronic energies (a.u.) for the modified Wu function

Atom	$-E(Z')$ TF	$-E(Z)$	$-E(Z')$ TFA	$-E(Z)$	$-E(Z')$ TFD	$-E(Z)$	$-E(Z')$ TFAD	$-E(Z)$
Ne	128.5471	164.2924	134.2754	170.8816	138.2203	175.8158	143.9815	182.4391
Ar	526.8175	647.5204	539.6386	661.9424	553.2866	678.1890	566.1444	692.6514
Xe	2752.055	3263.298	2785.035	3299.632	2838.239	3360.613	2871.255	3397.009
Kr	7332.138	8404.975	7839.740	8467.337	7505.507	8596.212	7563.273	8658.663
Rn	21866.44	24895.11	21974.15	25011.12	22244.96	25310.39	22352.77	25426.49

Table 4

$\langle r^2 \rangle$ results for the modified Wu function $(\langle r^2 \rangle \cdot 10^{-16}\,\mathrm{cm}^2)$

Atom	$\langle r_{Z'}^2 \rangle$ TF	$\langle r_Z^2 \rangle$	$\langle r_{Z'}^2 \rangle$ TFA	$\langle r_Z^2 \rangle$	$\langle r_{Z'}^2 \rangle$ TFD	$\langle r_Z^2 \rangle$	$\langle r_{Z'}^2 \rangle$ TFAD	$\langle r_Z^2 \rangle$
Ne	4.88	5.05	4.81	4.99	4.73	4.91	4.61	4.80
Ar	5.97	6.14	5.93	6.10	5.86	6.04	5.80	5.98
Xe	7.56	7.74	7.54	7.72	7.48	7.66	7.45	7.63
Kr	8.69	8.86	8.68	8.84	8.63	8.79	8.61	8.77
Rn	10.16	10.35	10.15	10.34	10.61	10.29	10.09	10.28

$Z' = Z$ optimum

Table 5

Diamagnetic susceptibilities ($-S.10^{-6}\,cm^3/mol$) for the modified Wu function

Atom	$-S_{SCF}$	$-S_{exp.}$	$-S(Z')_{TF}$	$-S(Z)$	$-S(Z')_{TFA}$	$-S(Z)$	$-S(Z')_{TFD}$	$-S(Z)$	$-S(Z')_{TFAD}$	$-S(Z)$
Ne	5.77	6.7	13.80	14.29	13.61	14.11	13.39	13.89	13.03	13.58
Ar	17.42	19.6	16.88	17.38	16.77	17.27	16.54	17.08	16.40	16.92
Xe	26.75	28.8	21.90	21.90	21.31	21.83	21.15	21.67	21.06	21.59
Kr	42.69	43.9	24.58	25.07	24.59	25.02	24.40	24.87	24.34	24.82
Rn	55.72	—	28.74	29.27	28.71	29.23	28.59	29.11	28.55	29.07

Table 6

Ionization energies (a.u.) for the modified Wu function

Atom	E_{HF}	$IE(Z')_{TF}$	$IE(Z)$	$IE(Z')_{TFA}$	$IE(Z)$	$IE(Z')_{TFD}$	$IE(Z)$	$IE(Z')_{TFAD}$	$IE(Z)$
Ne	129.1	105.4	134.7	104.9	134.2	104.4	133.6	103.6	132.6
Ar	529.4	432.1	531.1	431.1	530.0	429.5	528.1	428.1	526.6
Xe	2786	2257	1676	2254	2674	2249	2668	2246	2664
Kr	7424	6013	6893	6008	6900	5997	6877	5993	6871
Rn	23523	17934	20418	17924	20410	17899	20382	17891	20373

$Z' = Z$ optimum

Table 7

Comparison of ionization energies (atomic energies)

| Atom		E_{HF}	IE_1	$\% D_1$	IE_2	$\% D_2$	IE_3	$\% D_3$	$m(Z)_{TFAD}$	$-n(Z)$	IE_4	$\% D_4$
C	6	37.88	39.14	2.3	44.47	17.4	41.76	10.2	0.9591	0.16695	39.70	4.8
Ne	10	129.1	128.9	−0.2	146.4	−13.4	137.5	6.5	0.9897	0.14618	132.6	2.7
Ar	18	529.4	508.1	−4.0	572.2	9.0	542.1	2.4	1.0073	0.13324	526.6	−0.6
Ni	28	1519	1924	−6.2	1618	6.5	1520	0.1	1.0147	0.12758	1480	−2.6
Kr	36	2786	2561	−8.1	2909	4.4	2732	−1.9	1.0177	0.12525	2663	−4.4
Xe	54	7424	6595	−11.2	7492	0.9	7036	−5.3	1.0213	0.12242	6870	−7.5
Hf	72	14977	12905	−13.8	14699	−2.1	13767	−8.1	1.0231	0.12099	13477	−10.0
Hg	80	19431	16501	−15.1	18745	−3.5	17604	−9.4	1.0237	0.12051	17207	−11.0
Rn	86	23253	19535	−16.0	22191	−4.6	20840	−10.4	1.0241	0.12019	20373	−12.0

$\% D$ = Percent difference from column 3
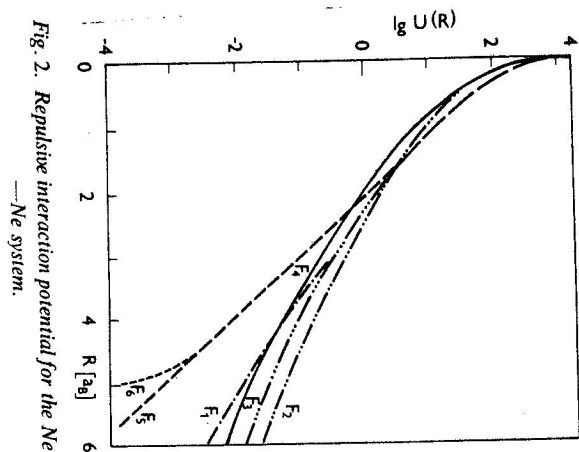
Fig. 2. Repulsive interaction potential for the Ne — Ne system.
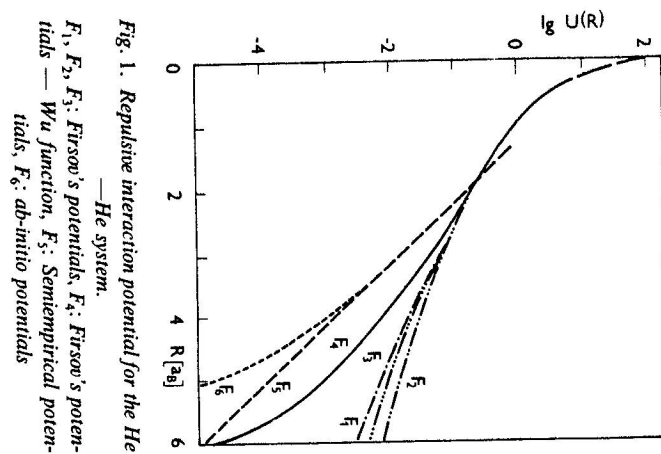
Fig. 1. Repulsive interaction potential for the He — He system. F_1, F_2, F_3: Firsov's potentials, F_4: Firsov's potentials — Wu function, F_5: Semiempirical potentials, F_6: ab-initio potentials

The comparison of results in Table 3 shows the existence of a poor agreement between statistical and SCF energy data. In addition, we can see that the introduction of the different corrections, considered here, worsens the TF results even more, as it was pointed out by Goodisman [14]. When an effective Z is introduced within the energy functionals (16)—(24), and the new $(m, n)_{Z_{op}}$ parameters are employed, energy results improve greatly. In addition, the notable contractions, becomes noticeable in Table 4. The Z optimization produces the same effect of decreasing $\langle r^2 \rangle$. As regards statistical values of S, there are no marked differences among them, but $|S(Z_{op})| < |S(Z)|$, (Table 5). It is important to point out that in judging the parallelism between theoretical and experimental susceptibilities, the experimental data are not the results of the true measurements of particular atoms, but they are determined by measurements of compounds and the use of somewhat indirect considerations [24]. In Table 6, we can see that the best ionization energy results, IE, are those corresponding to the TFAD(Z) formalism, so we have used these values in Table 7. Column 4 presents the experimental values for Z > 18, while for Z < 28 the theoretical ones of Fraga et al. [28] are shown. By IE_i, $i = 1$—3, we denote other available ionization energy data, obtained with the same statistical formula (30), but by means of other screening functions due to Csavinszky [26], IE_1, Kesarwani and Varshni [27], IE_2, and Wu [15], IE_3. With the subscript 4 we refer to the modified Wu function equation (13). The latter allows us to extend the range of the Wu function to the light Z elements. The best Z medium values are those for IE_2.

Our results for the He—He, Ne—Ne, Ar—Ar, Xe—Xe, Kr—Kr and Rn—Rn interatomic potentials are compared in Figures 1—6, respectively, with the best theoretical and empirical ones [5], [29—31]. The "empirical" data are obtained from "semiempirical potentials". These empirical atomic interactions are in most cases based on a simple analytical expression, which contains one or more parameters adjusted to an experimental situation [2]. In all cases F_1 curves represent the Csavinszky results, F_2 curves show the Kesarwani and the Varshni values, the F_3 curves are those corresponding to the Wu and the F_4 ones and the related to the TFAD(Z_{op})—Wu function, Φ_4. In the Firsov treatment we have only used the TFAD(Z_{op}) values in order to unify working criteria, as we did in a previous paper [5]. We must point out that in using Firsov's formulation there is no need to perform an explicit two-centre calculation. The successive TF-like modifications are not basically different, while the Z optimization introduces the real improvement as regards the Wu potentials [15]. The F_5 curves show the theoretical results from SCF calculations [31], [32]. It can be seen from Fig. 1—2 for He—He and Ne—Ne that the small R agreement between SCF and the "empirical" results is excellent. As regards theoretical results, Gilbert
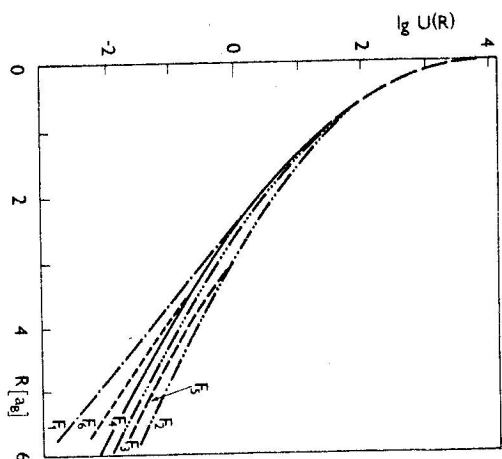

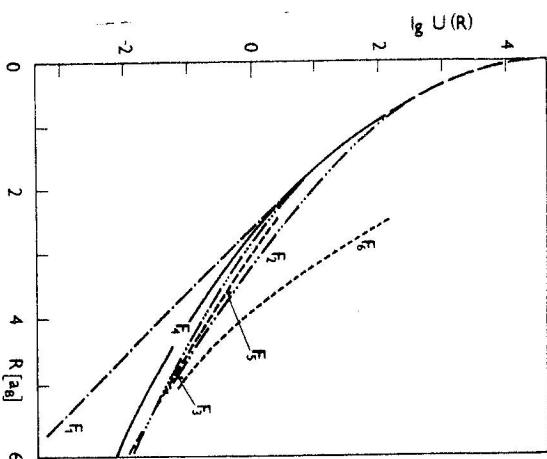Fig. 3. Repulsive interaction potential for the Ar—Ar system.

Fig. 4. Repulsive interaction potential for the Xe—Xe system.

and Wahl [31] have calculated the potential energy curves for these gases using single configuration — wave-functions constructed from a molecular orbital. The "empirical" results are obtained with the Morse-spline-van der Waal — potential [29]. In Firsov's formulation, our F_4 potentials give in both cases the best results. For R < 2, F_1 to F_4 are almost the same (represented by dotted lines); this feature is common to all the rare gases. For Ar—Ar, Fig. 3, and Xe—Xe, Fig. 4, we have used empirical parameters, for F_5 from a previous paper [5] as listed by Barker [30a, 30b]. For Ar—Ar, Fig. 3, the empirical results are in reasonable accordance with the theoretical ones given by Gilbert and Wahl [31]. As regards Firsov's results the Wu ones, F_3, seem to be the best (see the SCF values). There is a little divergence for R > 5, but in this region it is a feature of the SCF data (see Fig. 1). For Kr—Kr, Fig. 4 and Xe—Xe, Fig. 5, the SCF calculations have been carried out by Wadt [32]. In both cases there is a noticeable discrepancy between the SCF and the empirical potentials. The available evidence [26] indicates that the latter potentials are inadequate to describe the high-energy repulsion region. It can be noticed from Figs. 4—5 that the Kesarwani and the Varshni results are in good agreement with the theoretical ones. From the trend of SCF calculations it would be evident that for Rn—Rn, Fig. 6, the repulsive potential may lie above F_2. So, in general, for intermediate values of intermolecular separations (R =
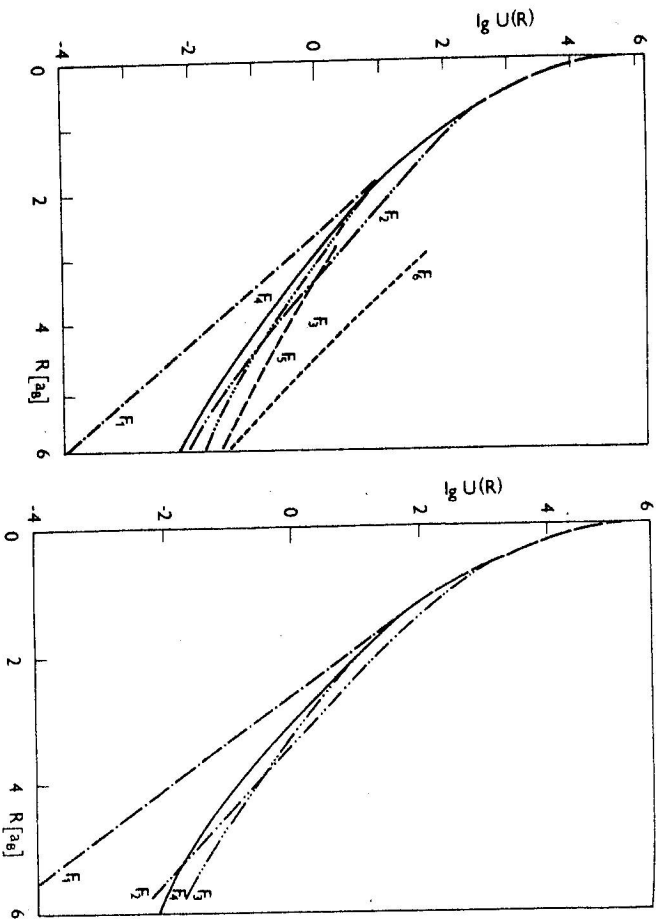
Fig. 5. Repulsive interaction potential for the Kr —Kr system.

Fig. 6. Repulsive interaction potential for the Rn —Rn system.

$= 2a_B - 4a_B)$ the empirical and the SCF curves are very nearly straight lines in a logarithmic scale. In smaller separations there is a rapid deviation from this behaviour, the energy varying as $(1/R)$. This is a familiar Bohr type dependence on distance which occurs because of the dominance of the nuclear-nuclear interaction [33]. At a larger distance there is a tendency for the energy to become negative. The reliability of "empirical" potentials is restricted to the interval of separation, in which the corresponding measurements were made. With respect to distances greater than $R = 4a_B$, the energy curves are extrapolated ones.

IV. CONCLUSIONS

Concluding we have found, as regards interatomic potentials, that the modified Wu function provides a more suitable approximation for the screening function than Csavinszky's, for light elements. The original Wu function is the best for medium Z elements, while Kesarwani's results are the best for high atomic number elements. Such a statistical scheme can only describe general

trends depending on the atomic number Z, but not every individual feature that is due to the specific shell structure.

Our modified Wu function is also appropriate to describe the ionization energy for light and medium atomic number elements.

In both cases we have introduced that TFAD self-interaction correction and exchange effects through the presence of only three parameters (in Φ) instead of the awkward Φ and Φ' calculations. This treatment is a complement to the treatments of Wu, Kesarwani and Varshni. The main advantage of the present method seems to be in that it can easily be extended to any other element, while the other approaches such as the SCF and the empirical calculations are likely to involve a greater computational effort.

V. APPENDICES

Appendix I

From the normalization condition (14) and from the expression of $\varrho(\Phi)$, equation (6):

$$Z \int \Phi^{3/2} x^{1/2} \, dx = N \qquad (1.1)$$

for a neutral atom $N = Z$ and then

$$\int \Phi^{3/2} x^{1/2} \, dx = 1 \qquad (1.2)$$

by using the relation (12)

$$\int (1 + mx^{1/2} + nx)^3 \, e^{-3mx^{1/2}} \, dx = 1$$

if

$$x^{1/2} = y, \; x = y^2, \; dx = 2y \, dy \qquad (1.3)$$

and using the following relation (34):

$$(d + e)^n = \sum_{k=0}^{n} \binom{n}{k} x^k a^{n-k} \qquad (1.4)$$

$$\int e^{-ax} . x^n \, dx = n!/a^{n+1} , \qquad (1.5)$$

for (1.2) we obtain:

$$2\left[\frac{4480\,n^3}{2187\,m^9} + \frac{800\,n^2}{243\,m^7} + \frac{184\,n}{81\,m^5} + \frac{184}{243\,m^3}\right] = 1.$$ (1.6)

It can be written as:

$$n^3 + a_0 n^2 + b_0 n + c_0 = 0,$$ (1.7)

where

$$a_0 = 129600\,m^2/80640;\quad b_0 = 89424\,m^4/80640$$
$$c_0 = (29808\,m^6 - 19683\,m^8)/80640.$$

It is easy to show that equation (1.8) has only one real root and two imaginary ones for any real value of m. The real root is then:

$$n = [-(q/2) + H^{1/2}]^{1/3} + [-(q/2) - H^{1/2}]^{1/3} - (a_0/3)$$ (1.8)

with

$$q = c_0 - (a_0 b_0/3) + (2a_0^3/27),$$
$$p = b_0 - (a_0^2/3),$$
$$H = (q^2/4) + (p^3/27).$$ (1.9)

Appendix II

For the kinetic energy

$$E_K(\varrho) = \frac{K_k Z^{5/3}}{a^2(4\pi)^{2/3}} \int_0^\infty (1 + mx^{1/2} + nx)^5 e^{-5mx^{1/2}}\,dx$$ (II.1)

with the variable change (1.3):

$$a = 0.8853\,Z^{-1/3},\quad K_k = (3/10)(3\pi^2)^{2/3}$$

$$E_K(\varrho) = 2C_1 \int_0^\infty (1 + my + ny^2)^5 e^{-5my}\,dy$$ (II.2)

$$2C_1 = 1.35541\,Z^{7/3}$$

with (1.4) and (1.5) we obtain

$$E_K(m,n) = 1.35541\,Z^{7/3}\left[0.70208\frac{1}{m} + 0.70208\frac{n}{m^3} + 0.71270\frac{n^2}{m^5} + 0.55665\frac{n^3}{m^7} + 0.2901\frac{n^4}{m^9} + 0.07432\frac{n^5}{m^{11}}\right].$$ (II.3)

Appendix III

$$E_{ne}(\varrho) = -\frac{Z^2}{a}\int_0^\infty \frac{(1 + mx^{1/2} + nx)^3 e^{-mx^{1/2}}}{x^{1/2}}\,dx$$ (III.1)

with (1.3)

$$E_{ne}(\varrho) = -\frac{2Z^2}{a}\int_0^\infty (1 + my + ny^2)^3 e^{-3my}\,dy$$ (III.2)

by using (14) and (1.5)

$$E_{ne}(m,n) = -2.25902\,Z^{7/3}\left[0.96296\frac{1}{m} + 0.96296\frac{n}{m^3} + 0.79012\frac{n^2}{m^5} + 0.32922\frac{n^3}{m^7}\right].$$ (III.3)

Appendix IV

$$E^{TF}(\varrho) = -(1/2)\int V_{ee}^{TF}\varrho\,dv$$ (IV.1)

from the Poisson equation

$$\frac{d^2(rV_{ee}^{TF})}{dr^2} = 4\pi\varrho r$$ (IV.2)

and from the following boundary conditions:

$$r \to \infty,\; x \to \infty,\; y \to \infty \text{ and } rV_{ee}^{TF} \to -Z$$ (IV.3)

by integrating the Poisson equation it is possible to obtain V_{ee}^{TF}, then

$$E_{ee}^{TF}(m,n) = -1.1295\,Z^{7/3}\left[0.5296\frac{n^6}{m^{16}} + 2.9796\frac{n^5}{m^{14}} + 5.372\frac{n^4}{m^{12}} + 8.292\frac{n^3}{m^{10}} + 7.5068\frac{n^2}{m^8} + 3.8996\frac{n}{m^6} + 0.9884\frac{1}{m^4} - \frac{26}{27m} - \frac{26n}{27m^3} - \frac{64\,n^2}{81\,m^5} - \frac{720\,n^3}{2187\,m^7}\right]$$ (IV.4)

Appendix V

For the exchange energy

$$E_{exch}(\varrho) = \frac{-3(3)^{1/3}}{4\pi^{1/3}}\int \varrho^{4/3}\,dv$$ (V.1)

as in the former cases

with (1.3):

$$E_{exch}(\varrho) = -3\left[\frac{6}{36\pi^4}\right]^{1/3} Z^{5/3} \cdot \int_0^\infty \Phi^2 dx. \qquad (V.2)$$

With (1.4) and (1.5) it is possible to obtain

$$E_{exch}(m,n) = -0.71763\, Z^{5/3}\int_0^\infty (1+my+ny^2)^4\, y\, e^{-4my}\, dy. \qquad (V.3)$$

$$E_{exch}(\varrho) = -0.71763\, Z^{5/3}\left[0.4512\frac{1}{m^2} + 0.9023\frac{n}{m^4} + 1.1646\frac{n^2}{m^6} + 0.4614\frac{n^3}{m^8} + 0.3461\frac{n^4}{m^{10}}\right] \qquad (V.4)$$

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ПРИМЕНЕНИЕ МОДИФИЦИРОВАННОЙ ФУНКЦИИ ВУ ДЛЯ ВЫЧИСЛЕНИЯ НЕКОТОРЫХ ХАРАКТЕРИСТИК АТОМОВ

В работе в рамках модели Томаса—Ферми—Амальди—Дирака предложена модификация аналитической функции Ву, которая затем применяется для расчета некоторых характеристик атомов, таких как энергии взаимодействия для атомов инертных газов и атомные энергии ионизации. Приводится сравнение с другими теоретическими результатами и доступными экспериментальными данными. Отмечаются общие черты и подчеркиваются преимущества предложенного аналитического метода.