suggestion that fundamental particles may be pictured as fabricated from quarks. It is apparent that a measurement of the decays $\varrho \to \eta + \gamma$ and $\omega \to \eta + \gamma$ are most important in this respect.

In summary, a simplified model has been investigated to illustrate the role which unstable particles may play in investigating the constituents of fundamental particles.

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Repulsive Interaction Potential between Rare-Gas Atoms in the Fermi-Amaldi Model

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Using an approximate expression based on the Fermi-Amaldi statistical model of the atom, the repulsive interaction energies $U(R)$ between a pair of nenutral rare-gas atoms have been derived. This paper contains a comparison of our numerical results for some repulsive interaction potentials between rare-gas atoms with the corresponding TFD results obtained by Abrahamson.

This paper concerns a derivation of the theoretical expression for a repulsive interaction potential between rare-gas atoms using the FERMI-AMALDI [1] model. The interaction potential was calculated with the so called screened Coulomb potential due to BOHR [2], i. e.

$$U(R) = (Z_1 Z_2 e^2/R) \exp\{-R/a'\} \qquad (1)$$

where e is the magnitude of the electronic charge; Z_1, Z_2 are respective atomic numbers of the interacting atoms; and the screening length a' is defined as

$$a' = a_0/(Z_1^{2/3} + Z_2^{2/3})^{1/2} \qquad (2)$$

with $a_0 (= 0.529$ Å) denoting the first Bohr radius in hydrogen. It has been found [3] that this interaction is fairly realistic at very small internuclear distances R, but less satisfactory elsewhere [4]. Another theoretical expression based on the Thomas-Fermi (TF) statistical model of the atom [5] is given by FIRSOV [6].

This model is applicable for small R but it gives unrealistically big values for $U(R)$ if R increases. A third theoretical potential for the repulsive interaction for the rare-gas atoms is based on the Thomas-Fermi-Dirac model (TFD). This model was considered by ABRAHAMSON [7] in a very detailed way. The numerical calculations show that the agreement with experiment is closer and more extensive than it was previously estimated.

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This model leads to troublesome numerical calculations. It seems that the Thomas-Fermi-Amaldi model is convenient for obtaining an analytical expression for the repulsive interaction potential between rare-gas atoms and gives reasonable results. For application to free atoms and ions the Thomas-Fermi equation as known reduces to

$$\varphi'' = \varphi^{3/2}/x^{1/2} \tag{3}$$

where φ is related to the potential V by

$$V(r) = -\frac{Z e^2}{r}\varphi\left(\frac{r}{\mu}\right) \tag{4}$$

and $x = r/\mu$. The solution φ_0 pertaining to the free atoms satisfies the boundary conditions $\varphi_0(0) = 1$ and $\varphi_0(\infty) = 0$ and has been computed by a number of investigators [8] or fitted by approximate solutions. As may be known the author [9] of this paper has derived an approximate solution for a free neutral atom. This solution has the form

$$\varphi_0(x) = 1/(1 + a x)^2 \text{ with } 1/a = 1.7566 . \tag{5}$$

Fermi and Amaldi have shown that Eq. (3) can be solved by help of the following boundary conditions

$$\varphi(0) = 1, \qquad \varphi(x_0) = 0 \tag{6}$$

and

$$x_0 \varphi'(x_0) = -\frac{Z-N+1}{Z} = -\left(q + \frac{1}{Z}\right) \tag{7}$$

where

$$x_0 = r_0/\mu^* \quad \text{and} \quad \mu^* = \frac{0.88534}{Z^{1/3}}\left(\frac{N}{N-1}\right)^{2/3} a_0 .$$

Here Z is the atomic number of the atom, N is the number of electrons in the atom, q is the degree of ionization and a_0 is the first Bohr radius of the hydrogen atom. For neutral atoms $Z = N$. In order to obtain an approximate solution $\varphi(x)$ which fulfills the boundary conditions (6) and (7) after Fermi and Amaldi we write $\varphi(x)$ in the form:

$$\varphi(x) = \varphi_0(x) + \delta(x) \tag{8}$$

where $\varphi_0(x)$ is given by Eq. (5) and $\delta(x)$ is a small correction to $\varphi_0(x)$. Substituting (8) into (3) and respecting that $\delta(x) \ll \varphi_0(x)$ we obtain for $\delta(x)$ the following differential equation

$$\delta''(x) = \tfrac{3}{2}\,(\varphi_0/x)^{1/2}\,\delta(x) = \tfrac{3}{2}\,(\varphi_0''/\varphi_0)\,\delta(x). \tag{9}$$

We now continue to solve (9). Setting $\varphi_0(x)$ given by (5) in the last term of (9) we obtain

$$\delta(x) = C(1 + a x)^n \tag{10}$$

where C is a constant, and $n = \frac{1}{2} + \frac{1}{2}\sqrt{37}$. Thus in our case taking into consideration Eqs. (5), (6) (7) and (8) we obtain an approximate solution.

$$\varphi(x) = \frac{1}{(1+a x)^2}\left[1 - \left(\frac{1+a x}{1+a x_0}\right)^{n+2}\right] \tag{11}$$

where $a x_0$ is given by

$$\frac{a(n+2)\, x_0}{(1+a x_0)^3} = \frac{Z-N+1}{Z} . \tag{12}$$

The first boundary condition $\varphi(0) = 1$ given by Eq. (6) is practically the better fulfilled the bigger is the value of Z. The two remaining boundary conditions $\varphi(x_0) = 0$ and the boundary condition given by Eq. (7) are exactly fulfilled by our approximate solution $\varphi(x)$ given by Eq. (11).

We compare first the values obtained in our case for x_0 when $Z = N$ with the exact numerical values of Fermi and Amaldi for some neutral atoms.

From Table 1 we see that our x_0 values gives reasonable results. In order to test the accuracy of the obtained approximate solution $\varphi(x)$ given by Eq. (11) we have calculated the molar diamagnetic sus-

Table 1. Comparison of the x_0 values for some neutral atoms with the exact numerical x_0 values of Fermi and Amaldi.

Z atomic number	10	14	19	26	31	37	42
x_0 according to Fermi and Amaldi	10.8	13.0	15.4	18.2	19.9	21.8	23.2
x_0 from our Eq. (12)	10.3	12.8	15.3	18.4	20.3	22.5	24.1
Z atomic number	47	53	58	67	74	80	92
x_0 according to Fermi and Amaldi	24.5	26.1	27.2	29.2	30.6	31.7	34.1
x_0 from our Eq. (12)	25.7	27.4	28.8	31.2	32.9	34.3	37.0

ceptibility χ using the well known formula of Langevin and Pauli

$$\chi = -\frac{e^2 L}{6 m c^2} \overline{r^2} \tag{13}$$

where $\overline{r^2}$ is the mean square distance between electrons and nucleus summed over all electrons of free neutral atom or ion and L is the Loschmidt number.

For the mean square distance we have in our case

$$\overline{r^2} = A \int_0^{x_0} \varphi''(x)\, x^3\, dx = A\left[-\frac{x_0^2 (Z-N)}{Z} + 6 \int_0^{x_0} x\, \varphi\, dx \right. \tag{14}$$

where $A = Z_\mu^{*2} \cdot N/(N-1)$. After a simple calculation we obtain for $\overline{r^2}$ in our case the following result:

$$\overline{r^2} = A\left\{-\frac{(Z-N+1)\, x_0^2}{Z} + \frac{6}{a^2}\left[\ln(1+a x_0) - \frac{(n+3)}{(n+2)} + \frac{(n+2)}{(n+1)\,(1+a x_0)} - \frac{1}{(n+1)\,(n+2)\,(1+a x_0)^{n+2}}\right]\right\}. \tag{15}$$

In Table 2 we have compared our numerical values χ for some neutral rare-gas atoms $Z = N$ in comparison with the corresponding Thomas-Fermi values and experimental ones.

Table 2. Comparison of the molar diamagnetic susceptibility in units of 10^{-6} cm^3 (absolute values).

	Ne	Ar	Kr	Xe
Thomas-Fermi	67.0	81.0	102.0	117.0
Our results	11.05	18.36	31.77	42.80
Experimental results	6.8	19.5	28.0	42.4

Table 2 shows that our results obtained from Fermi-Amaldi model agree much better with the experimental results than the results calculated from Thomas-Fermi model.

FIRSOV [10] has shown that the interaction potential between two neutral atoms in the statistical approximation may be described by the single atom Thomas-Fermi potential if one replaces the Thomas-Fermi coordinate x by

$$x = R/\mu \quad \text{with} \quad \mu = 0.88534\, a_0/(Z_1^{2/3} + Z_2^{2/3})^{1/2}. \tag{16}$$

If we apply the same scaling procedure to the Fermi-Amaldi potential we get for the interaction potential between rare-gas atoms with atomic numbers Z_1 and Z_2

$$U(R) = \frac{Z_1 Z_2 e^2}{R(1+a R/\mu)^2}\left[1 - \left(\frac{1+a R/\mu}{1+a R_0/\mu}\right)^{n+2}\right]. \tag{17}$$

In the last formula R is the internuclear distance and R_0 is the distance for which $U(R_0) = 0$. The factor $Z_1 Z_2 e^2/R$ gives the Coulomb potential.

The main difficulty in our derivation of $U(R)$ given in the last formula lies in the determination of R_0 which can be treated as a parameter to be chosen in such a way that $U(R)$ fits as close as possible the experimental results or can be obtained by reasonable assumptions.

In this paper we assume that $R_0 = x_0\, \mu^*$ where μ^* for the same neutral rare-gas atoms $Z_1 = Z_2 = Z$ according to Eq. (7) is given by

$$\mu^* = \frac{0.88534}{Z^{1/3}}\left(\frac{Z}{Z-1}\right)^{2/3} a_0. \tag{18}$$

Since $a x_0$ can be calculated from Equation (12) so $R_0 = x_0\, \mu^*$ is given ini the last equation for $U(R)$.

In Table 3 we have collected some numerical values for $a x_0$, $a R_0/\mu$ and R_0/a_0.

In the Figures 1 – 4 we have compared our numerical values of U as a function of R/a_0 in the units of e^2/a_0 with the corresponding numerical values of Thomas-Fermi-Dirac and other data for $Z_1 = Z_2 = Z = 2$, 10, 18, and 86.

Figure 1 shows that our potential closely follows the TFD curve up to $R \cong 1.5\, a_0$. From $1.5\, a_0 < R < 3\, a_0$ our results are a little higher than the corresponding results obtained from TFD. For $R_0 = 3.1678\, a_0$ our $U(R_0) = 0$. Figure 1 contains also the results of TF which are for larger R bigger than the TFD and our results. The results obtained by AMDUR et al. [11] from the analysis of gas-scattering experiments are given in this figure too. It contains also the results obtained from Lennard-Jones potential [12], modified Buckingham potential [12] and the repulsive part [12] of Exp. (6) potential. The results of PHILLIPSON [13] are also given in Figure 1.

Table 3. Some numerical values of $a x_0$, $a R_0/\mu$ and R_0/a_0.

Z	2	10	18	36	54	86
$a x_0$	1.61677	5.88199	8.44366	12.5947	15.7749	20.3119
$a R_0/\mu$	3.6294	8.9237	11.8466	18.1493	22.58888	28.9507
R_0/a_0	3.1678	4.5549	4.9709	6.0445	6.5720	7.2126

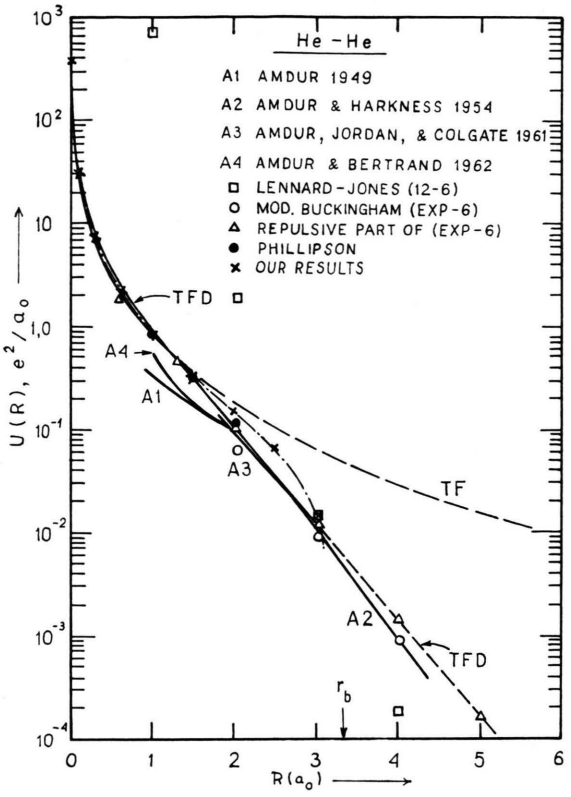

Fig. 1. Repulsive interaction potentials for the He–He system.

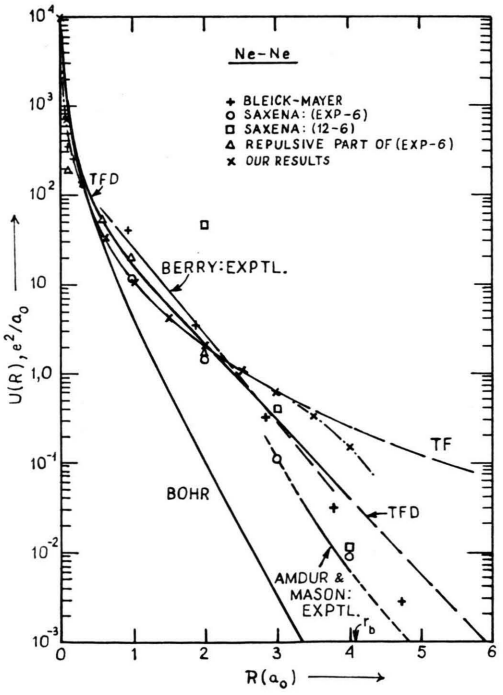

Fig. 2. Repulsive interaction potentials for the Ne–Ne system.

In Fig. 2 we have compared our results with the corresponding TFD and TF results. We notice that our potential closely follows the TFD curve up to $R \cong 2\,a_0$. From $2\,a_0 < R < 4.5\,a_0$ our results lie between the results of TF and TFD. For $R = 4.5549\,a_0$ our $U(R_0) = 0$. Figure 2 contains the experimental curve obtained from gas-scattering analysis by BERRY [14] and experimental curve at large separations given by AMDUR and MASON [15].

In this figure we find the theoretical results given by BLEICK-MAYER [16], SAXENA [17] and the repulsive part of the Exp. (6) potential. Figure 2 shows that for $0 < R < 2\,a_0$ our results agree well with the corresponding experimental results. For $2\,a_0 < R < 4.2\,a_0$ according to Fig. 2 the agreement with experiment is not as good as one may wish.

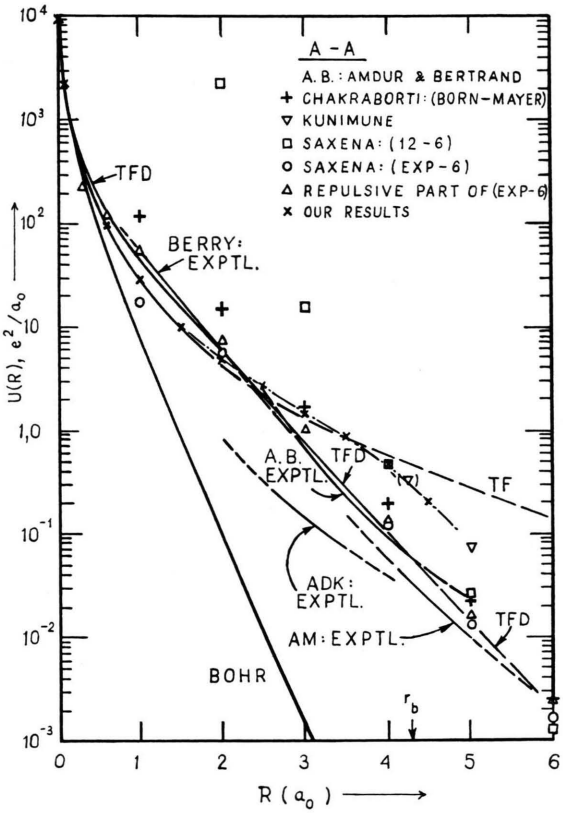

Fig. 3. Repulsive interaction potentials for the Ar–Ar system.

Figure 3 for the argon interaction compares our potential given by Eq. (17) with TFD potential, experimental curves to BERRY [18] and with several others due to AMDUR and his coworkers [19]. The agreement with Berry's curve is satisfactory and that with

Bertrand's most recent measuremenst is not so good since our results are higher.

Figure 3 contains also the results of CHAKRABORTI's [20] empirical potential, the quantum mechanical calculations of KUNIMUNE [21] which are very close to our results.

In this figure we have also the results of SAXENA [22] (12 – 6), SAXENA [22] Exp. (6) and the results of the repulsive part [22] of Exp. (6). In summary we conclude that our potential for the A – A interaction gives results up to $R \cong 2.5\, a_0$ which are close to the corresponding results of TFD. For higher R values, our results lie between the results of TFD and TF. For $R_0 = 6.445\, a_0$ our potential $U(R_0) = 0$.

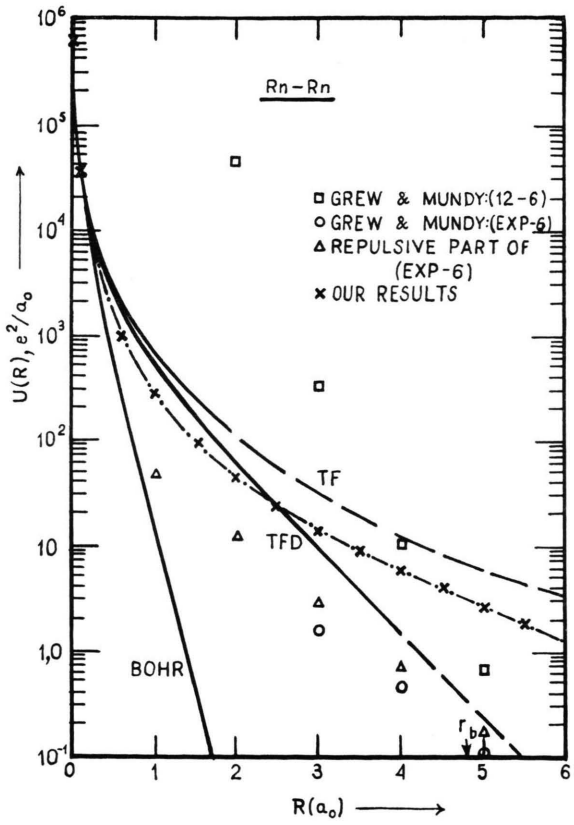

Fig. 4. Repulsive interaction potential for the Rn–Rn system.

In the last Fig. 4 we have a comparison of our results with TFD potential for $Rn - Rn$ interaction and the corresponding results of the TF interaction are given too.

Unfortunately, experimental data for this case are exceedingly scant. Figure 4 shows that our results up to $R \cong 2.5\, a_0$ are very close to TFD results and for higher R values our results lie between TFD and TF results. For the potential $R_0 = 7.2126$ our potential $U(R_0) = 0$. This figure contains the semi-empirical results of GREW and MUNDY [23], Exp. (6), and the results of the repulsive part of the potential Exp. (6).

In order not to extend this paper we do'nt give figures for Kr – Kr interaction and Xe – Xe interaction since the numerical values are already given in tables.

Table 3 and figures show that our results concerning the six homonuclear pairs of rare-gas atoms studied here lie for smaller values of R/a_0 below the corresponding values of TFD and for larger values our numerical values lie above the TFD values. It seems that the obtained interaction given by Eq. (17) gives us realistic values. This interaction allows to obtaini too the interaction between rare-gas atoms if $Z_1 \neq Z_2$.

The weak point of the derivation of the repulsive interaction potential between the rare-gas atoms lies in the assumption $R_0 = x_0\, \mu^*$. In order to obtain closer agreement with experimental data R_0 appearing in $U(R)$ given by Eq. (17) can be treated as a free parameter fitted in such a way that there might be obtained the best agreement with experiment.

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Ab-initio-Berechnung von Molekülen. II.

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Ab-initio-Calculation of Molecules. II.

By means of the FSGO-method calculations of the molecules CH_3NH_2 and CH_3OH have been performed. A recent method, proposed by Lim and Whitehead in 1967, which is very similar to the FSGO-method, has been applied to CO respectively CH_3NH_2. A comparison with the exact SCF-theory has shown that the method of Lim and Whitehead can only be used for the calculation of ionization energies.

I. Einleitung

In einer vorangegangenen Arbeit wurden mit Hilfe der FSGO-Methode [1, 2] Bindungsverhältnisse und Geometrie zweiatomiger Moleküle untersucht. Dabei hat sich gezeigt, daß die Brauchbarkeit dieser Methode, in der ein minimaler Basisansatz von reinen Gauß-Funktionen vom Typ [3]

$$\chi_p = (2\,\eta_p/\pi)^{3/4} \exp\{-\eta_p (r - r_p)^2\} \qquad (1)$$

verwendet wird, im wesentlichen auf diese Informationen beschränkt ist. Obwohl die erhaltene Gesamtenergie eines Moleküls ca. 15% vom HF-Limit entfernt ist, sind die Energieunterschiede bei der Darstellung von Bindungen beträchtlich, so daß eine eindeutige Aussage darüber möglich ist, ob eine Doppelbindung oder Dreifachbindung energetisch günstiger ist. Dasselbe gilt auch für die Geometrie eines Moleküls und, wie von JANOSCHEK [4] gezeigt werden konnte, für die Elektronendichten an den einzelnen Atomrümpfen.

Wie in der vorangegangenen Arbeit auch gezeigt wurde, erlaubt die FSGO-Methode eine besonders anschauliche Darstellung der Bindungsverhältnisse eines Moleküls, denn dieses mit Minimalbasis arbeitende quantenmechanische Näherungsverfahren liefert dasselbe Modell von der chemischen Bindung, wie es dem Chemiker von der Formelsprache her gewohnt ist. Die Tatsache, daß durch die Verwendung einer minimalen Funktionsbasis auch die Rechenzeit klein gehalten werden kann und die Moleküle aus Atomrümpfen und Bindungsorbitalen dargestellt werden können, hat die FSGO-Methode zu einem brauchbaren Ausgangspunkt zur Berechnung größerer Moleküle werden lassen, wenn man sich zuvor geeignete Informationen über die Parameter kleinerer Moleküle verschafft. In dieser Arbeit werden zunächst CH_3NH_2 und CH_3OH behandelt.

Die weiteren Vorteile der FSGO-Methode als Spezialfall eines HF-SCF-LCGO-Verfahrens [5] bestehen darin, daß sie keine SCF-Iterationen und damit auch keine Speicherungsproble der Vierzentrenintegrale kennt. Es wurde jedoch 1967 von LIM und WHITEHEAD [6] ein Verfahren angegeben, das auch bei einer Funktionsbasis $T > n$, wenn $2n =$ Zahl der Elektronen, ohne SCF-Iterationen auskommt und deshalb einer Methode, die mit Minimalbasis arbeitet, sehr ähnlich ist. Diese Autoren [6] gehen von Voraussetzungen aus, die in Abschnitt III kurz erläutert werden sollen, und die nur bei Minimalbasis erfüllt sind.