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Repulsive Interaction Potentials between Rare-Gas Atoms. Homonuclear Two-Center Systems*

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Using a previously derived theoretical expression based on the Thomas-Fermi-Dirac statistical model of the atom, the repulsive interaction energies $U(R)$ between a homonuclear pair of neutral rare-gas atoms have been calculated at internuclear distances R ranging from $0.01a_0$ to $8.0a_0$. ($a_0=0.529$ Å.) The present calculations show that agreement with experiment is both closer as well as more extensive than was previously estimated. Specifically, for the He-He interaction, $U(R)$ nearly coincides with other theoretical and experimental results up to $R\sim 5a_0$, excepting Amdur's measurements at $R\lesssim 2a_0$. Similar and progressively closer accord with experiment is obtained for the Ne-Ne and Ar-Ar interactions. For Kr-Kr and Xe-Xe, agreement is reasonable up to separations of $\sim 6a_0$ and $\sim 7a_0$, respectively. Curves for the Rn-Rn interaction have also been obtained. Comparison of the experimental data with Bohr's screened Coulomb potential, and with a potential proposed by Firsov, shows that for $R\gtrsim 1a_0$, the former decreases far too rapidly with increasing R, while for $R\gtrsim 3a_0$, the latter falls off much too slowly. For extrapolations towards small R, the $(12-6)$ potential is found to rise rapidly to values exceeding the experimental ones by several 100%, whereas the $(\exp-6)$ potential or its repulsive part consistently remains within an order of magnitude of the empirical values and often considerably closer. Whether this latter behavior is fortuitous or not is not determined.

I. INTRODUCTION

In a previous paper,[1] hereafter referred to as (I), a theoretical expression was developed whereby the repulsive interaction potential $U(R)$ between a pair of neutral atoms, in their ground states and separated by a distance R, could be calculated with an error not exceeding 4% relative to the values predicted by the Thomas-Fermi-Dirac (TFD) approximation.[2] The latter, however, is evidently not an exact description. Moreover, in its basic, unmodified form, the model frankly disregards all effects of correlation, relativity, nonvanishing absolute temperatures, and the rapid variation of the electrostatic potential near the nucleus (inhomogeneity). In addition, it is characterized by a sharp cutoff or bounding radius r_b at which the electron density ρ abruptly drops to zero (see Fig. 1). In view of these approximations inherent in the TFD model, the question naturally arises as to the reliability of the potential curves calculated on its basis. This question assumes added significance because, although a knowledge of interatomic repulsive potentials is fundamental to the study and understanding of a very large variety of problems,[3–18] such potentials, even to an accuracy of only $\sim 30\%$, have thus far been very difficult to obtain from either theory or experiment.[19,20] Further impetus to this work came from a useful complementarity between the relevant quantum-mechanical calculations and those based on the TFD statistical model of the taom: The former, already quite complicated even for hydrogen and helium,[21–22] rapidly become less feasible for systems with higher atomic numbers Z,[23] whereas the statistical calculations not only retain their very

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much simpler formalism, but actually tend to become more reliable with increasing Z.

It is the twofold purpose of the present work, therefore, to examine the reliability of the two-center interaction potential derived in (I) and, concomitantly, to present new information on a number of specific systems.[24] The initial choice of homonuclear pairs of rare-gas atoms for this purpose was motivated by essentially four considerations: (1) The theory developed in (I) may be expected to apply optimally to atoms possessing closed-shell configurations,[2] a condition evidently best met by the noble gases; (2) the repulsive interaction energies of the rare-gas atoms are themselves of considerable interest and importance[25,26]; (3) the treatment of homonuclear pairs of such atoms can serve as the basis for a simple calculation of the corresponding heteronuclear systems[10,24,27]; (4) similarly, knowledge of the rare-gas interaction potentials can, in turn, be used to calculate those between other kinds of atoms.[28] Furthermore, knowledge of the two-body interactions is a useful starting point for the solution of the corresponding three-body problem.[29]

In Sec. II, we state and briefly discuss some analytic forms for interatomic potentials, including an improved version of the expression derived in (I), and the manner in which these potentials as well as certain related criteria (united-atom energies) may be employed to test the validity of our theoretical expression for $U(R)$. In Sec. III, a detailed description and analysis of our TFD potential in the light of other theoretical and experimental curves is given for each homonuclear pair of rare-gas atoms, and Sec. IV summarizes the conclusions reached. Numerical data, and the solutions of some related computational problems, are contained in the Appendix.

II. GENERAL ANALYTIC POTENTIALS

(A) Theoretical

The quantum-mechanical calculations that have been made (mainly for helium[21,22,30–38] and just a very few for neon[39] and argon[40]) will be taken up below where those specific systems are discussed. As for the more general theoretical expressions, one of the earliest is probably the so-called screened Coulomb potential due to Bohr,[41] i.e.,

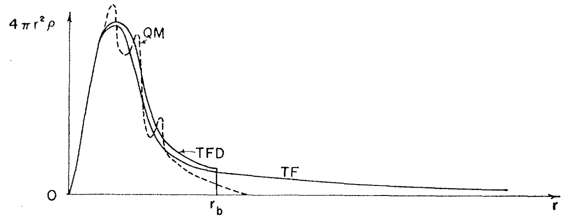

FIG. 1. Electron density distributions in TF and TFD atoms, and quantum mechanically (QM). (Schematic.)

$$U(R)=(Z_1Z_2e^2/R)\exp(-R/a'), \qquad (2.1)$$

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

$$a'=a_0/(Z_1^{2/3}+Z_2^{2/3})^{1/2}, \qquad (2.2)$$

with a_0 ($=0.529$ Å) denoting the first Bohr radius in hydrogen.[42] The negative exponential factor in (2.1) is intended to simulate the progressive screening, with increasing R, of the interacting nuclei by successively thicker "layers" of their respective electron clouds, thus reproducing the appropriate limits of $U(R)\approx Z_1Z_2e^2/R$ and zero for very small and very large values of R, respectively. This potential has been found[4,43,44] to be fairly realistic at very small internuclear distances, but less satisfactory elsewhere.[4,44–46]

Another theoretical expression, formally quite similar to (2.1), but actually based on the Thomas-Fermi (TF) statistical model of the atom,[2] is that due to Firsov[47]:

$$U(R)=(Z_1Z_2e^2/R)\chi(x), \quad R\lesssim 1.89a_0 \qquad (2.3)$$

where

$$x=(Z_1^{1/2}+Z_2^{1/2})^{2/3}R/a, \quad a=0.8853a_0, \qquad (2.4)$$

and $\chi(x)$ is the TF screening function. Partly because the TF model erroneously allows each of its electrons to interact with itself, and partly because this model ig-

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[42] Atomic units are used throughout this paper so that all lengths are expressed in units of a_0, all energies in units of e^2/a_0 $\cong$27.21 eV.

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nores all effects of exchange, its electron density distribution ρ falls off far too slowly with increasing radial distance r from the atom center.[2] Thus, the TF atom is unrealistically big and, consequently, the interaction energy between two such atoms can be expected to decrease unrealistically slowly with increasing internuclear separation R. It is essentially for this reason that Firsov restricts the applicability of his potential (2.3) to small R.

As a third theoretical potential, we cite the central result obtained in (I) and based on the TFD statistical model of the atom, i.e.,

$$U(R)=\tfrac{1}{2}(Z_1Z_2e^2/R)[\Psi(Z_1^{1/3}R/a)+\Psi(Z_2^{1/3}R/a)] +\bar{\Lambda}-C_Z, \quad (2.5)$$

where Ψ is the TFD screening function;

$$\bar{\Lambda}=\frac{1}{6}\int_{D_{12}}\{\kappa_k[(\rho_{01}+\rho_{02})^{5/3}-(\rho_{01}{}^{5/3}+\rho_{02}{}^{5/3})] -2\kappa_a[(\rho_{01}+\rho_{02})^{4/3}-(\rho_{01}{}^{4/3}+\rho_{02}{}^{4/3})]\}dv, \quad (2.6)$$

$\kappa_k=2.871e^2a_0$, $\kappa_a=0.7386e^2$; $\rho_{0i}(r_i)$ denotes the exact undistorted TFD electron density distribution due to the ith atom as a function of radial distance r_i measured from the center of this atom ($i=1,2$); D_{12} is the overlap region shared by both clouds; and

$$C_Z=(\kappa_a{}^2/120\kappa_k)(Z_1+Z_2) \quad (2.7)$$

is a parameter which remains constant for a given pair of interacting atoms.

Inasmuch as it is, essentially, the TFD potential (2.5) whose reliability and usefulness it is our purpose to determine in Sec. III below, we shall examine this expression here in some detail. The first term on the right of (2.5) is again of the screened Coulomb type, as in the preceding two potentials. Through Dirac's modification[48] of the original TF approximation,[49,50] however, the TFD model does include consideration of exchange effects and, at the same time, also eliminates the objectionable electronic self-interaction. The formal consequences of this modification were discussed in (I). Here we focus our attention on certain distinctive physical features of the TF and TFD models and their respective relationships to the quantum-mechanical description of the atom. Again referring to Fig. 1, it is seen that the exchange correction causes the unduly expansive TF electron cloud to contract so as to bring it into substantially better agreement with the quantum-mechanical density distribution. Unfortunately, however, this salutary effect is partly offset by a deleterious one, i.e., the very artificial discontinuous vanishing of the electron density $\rho(r)$ at r_b, the finite boundary radius of the TFD atom (assumed to be spherically symmetrical).

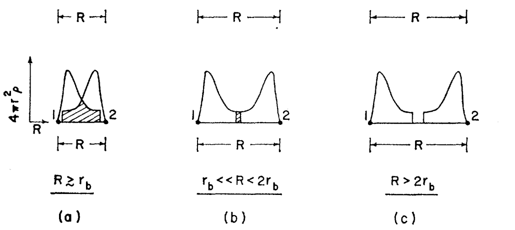

FIG. 2. TFD electron density distributions for a homonuclear pair of spherically symmetric atoms of radii r_b, internuclear separation R, and varying degrees of overlap (shown shaded).

Some of the difficulties which this discontinuity in $\rho(r)$ tends to produce in $U(R)$ can be appreciated by reference to Fig. 2. From there it is apparent that, in this approximation and for $R\sim r_b$, the two nuclei are shielded from each other far more completely than would be the case if the electron density did not fall off as abruptly as demanded by this model. Indeed, when $R>r_b$, the nuclei no longer "see" each other at all. An extreme case of this situation is shown in Fig. 2(c) where $R>2r_b$ (typically[51] $\sim 8a_0$), so that in the complete absence of overlap (and polarization), we have a juxtaposition of two effectively neutral entities and hence, a *spurious* vanishing of the interaction between them. Again, this would clearly not be the case if, instead of the artificially cutoff TFD atom, one were to consider the more correct quantum-mechanical electron density distribution (QM) indicated in Fig. 1. One effect on $U(R)$ to be expected in the neighborhood of $R=r_b$, therefore, is an underestimate of the internuclear repulsive energy. Another effect arises at $R\gtrsim r_b$ in conjunction with the two-center integral $\bar{\Lambda}$ given by (2.6). Since the domain of integration for $\bar{\Lambda}$ extends over the overlap region D_{12} only, it is clear that for $r_b\ll R<2r_b$, the contributions of the spuriously high electron densities $\rho(r)$ near the atom edge are emphasized, thereby tending to yield a similarly unrealistic value for $\bar{\Lambda}$ [see Fig. 2(b)].

In the light of the preceding paragraphs it is evidently desirable to achieve some compromise between the TF and TFD models which would tend to preserve the advantages (gradual density decrease and realistic extent) and to minimize the disadvantages (excessive size and abrupt density decrease) of each. This objective may be realized, albeit crudely, if we recall from reference 2 and the discussion in (I), that it is essentially the term C_Z which (a) is formally responsible for maintaining the electron density so unrealistically high near $r=r_b$, and (b) is of such small magnitude as to be practically insignificant in the interior of the atom. We, therefore,

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delete this troublesome term from the expression (2.5) henceforth and, accordingly, take

$$U(R)_{\mathrm{TFD}}=\tfrac{1}{2}(Z_1Z_2e^2/R) \times[\Psi(Z_1^{1/3}R/a)+\Psi(Z_2^{1/3}R/a)]+\bar{\Lambda} \quad (2.8)$$

as our working formula for the improved TFD potential.

As will be shown in detail in Sec. III below, the form (2.8) results in our $U(R)$ being practically linear, on a semilogarithmic plot, over a considerable range of R in which the potential is essentially repulsive. In these intervals, therefore, U_{TFD} falls off exponentially, in agreement with the form *approximately* suggested by theory and confirmed by experiment.[13,17,26,52] In addition to thus furnishing independent theoretical and experimental support for our potential (2.8), this feature of linearity also turns out to be useful in the extrapolation of $U(R)$ to values of R exceeding r_b. The actual merit of this procedure will be described in more detail in conjunction with its application to the specific systems treated in Sec. III below.

(B) Empirical[53]

A simple way of analytically representing the presence of repulsive and attractive interaction energies at small and large interatomic distances, respectively, is the form

$$U(R)=(A/R^m)-(B/R^n), \quad (2.9)$$

where A, B, m, n are positive parameters to be determined empirically.[10] One very commonly employed[10] version of (2.9) is the Lennard-Jones (12-6) potential[54]

$$U(R)=4\epsilon[(\sigma/R)^{12}-(\sigma/R)^6], \quad (2.10)$$

where ϵ is the depth of the potential well, and σ is the finite value of R for which U vanishes. The inverse twelfth power assignment to the repulsive term is not unique and, in fact, not based on physical considerations, but is made merely for the sake of mathematical convenience.[10,11] The inverse sixth power for the attractive term, on the other hand, is chosen deliberately so as to agree with the quantum-mechanical result for the induced dipole-dipole interaction.[10] The two parameters ϵ and σ are generally determined from experimental measurements of the thermodynamic or transport properties of nonpolar gases or liquids.[10]

Although the (12-6) potential has been very widely used, its intrinsic validity as a realistic representation of $U(R)$ has lately been seriously doubted on the basis of a rather exhaustive analysis by Guggenheim and McGlashan.[55] Also, as Amdur[25] has pointed out, use of the parameters determined empirically (for argon) in the approximate range $6.80a_0\leq R\leq 9.07a_0$ fails to reproduce the potential as determined by molecular-beam techniques[56] at $R\simeq 4.12a_0$ by $\sim 700\%$. This weakness of the Lennard-Jones (12-6) potential is probably attributable, at least in part,[57] to the inadequacy of the inverse power form of the repulsive term. Indeed, it was observed long ago,[58–61] and has since been verified by many workers,[13,17,26,62–67] that this term, on both quantum-mechanical as well as empirical grounds, should instead be represented by an exponential form. Accordingly, the Born-Mayer[58] type

$$U(R)=Ae^{-R/R_0} \quad (2.11)$$

has been proposed in place of the repulsive part of (2.9). Here A is an "amplitude" factor, and R_0 determines the steepness of the potential. The expression (2.11) has been found appropriate in many instances.[62–67] At large separations, where the attractive forces are appreciable, the Born-Mayer potential will, of course, overestimate the total interaction energy.

A similar revision of (2.9), but more complete with the inclusion of an attractive term, is the modified Buckingham (exp-6) potential[10]

$$\begin{aligned} U(R)&=\frac{\epsilon}{1-(6/\alpha)}\left\{\frac{6}{\alpha}\exp\left[\alpha\left(1-\frac{R}{R_e}\right)\right]-\left(\frac{R_e}{R}\right)^6\right\}, && R\geq R_{\max},\\ &=\infty, && R<R_{\max}, \quad (2.12)\end{aligned}$$

where ϵ has the same meaning as in (2.10); α is a measure of the steepness of the repulsive term; R_e is the equilibrium separation and is related to σ in (2.10) by $\sigma/R_e=0.8909$; $R_{\max}$ is that value of R for which the (exp-6) potential goes through a spurious maximum. For values of $R<R_{\max}$, the upper expression in (2.12) tends to $-\infty$ and hence is not usable in this range. The value of $R_{\max}$ itself generally occurs in the neighborhood of $\sim 0.25R_e$. Subject to this restriction, the modified Buckingham potential, too, has been found

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[52] See the discussion leading up to Eq. (2.11) and references 58, 59, 61, 65, and 66, below.

[53] For a very comprehensive review and discussion of empirical potentials, see reference 10. A briefer but more recent review by R. A. Buckingham can be found in J. Planetary Space Sci. **3**, 205 (1961).

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[67] K. P. Srivastava, J. Chem. Phys. **28**, 543 (1958). See also references 4, 6, 9, 10, 13, 17, and 39.

TABLE I. Approximate lower limits $R_{\min}$ of ranges of separations S_{emp} over which potentials (2.10) to (2.13) were fitted empirically.

System	$R_{\min}$ (a_0)	Reference
He-He	3.5	10
Ne-Ne	4.5	68
Ar-Ar	5.5	63
Ar-Ar	6	68
Kr-Kr	6	82
Xe-Xe	7	72
Rn-Rn	7	85

to be consistent with various mutually independent experimental results.[68,69]

Another form, somewhat similar to the preceding two, is the well-known Morse[70] potential

$$U(R)=\epsilon[e^{-2b(R-R_e)}-2e^{-b(R-R_e)}], \tag{2.13}$$

where b is a steepness parameter, and all other symbols have the same meaning as previously. Although the Morse function is generally employed in the description of diatomic molecules,[71] Konowalow and Hirschfelder[72] have recently applied it to the pairwise interaction of rare-gas atoms and have found it to reproduce independent experimental data (different from those utilized to evaluate its parameters), with good accuracy.

The preceding four empirical potentials (2.10) to (2.13) are, of course, most reliable only in S_{emp}, the intervals of separations $R_{\min}\leq R\leq R_{\max}$ associated with the specific experiments from which the appropriate potential parameters were determined (see Table I for values of $R_{\min}$). In the absence of further data for support, extrapolations of these potentials to separations R progressively further and further outside S_{emp} must, therefore, be viewed with due caution. This was mentioned already above, in particular, with respect to the Lennard-Jones (12–6) potential. Now, unfortunately, the major portions of the ranges of separations S_{theo} considered in the present work ($0.01\ a_0\leq R\leq 6$–$8\ a_0$) generally lie considerably below S_{emp}, so that overlap between these two ranges occurs only near the upper (lower) limits of $S_{\mathrm{theo}}(S_{\mathrm{emp}})$. Strictly speaking, therefore, it is only within and very near these overlap regions that a comparison of our theoretical result (2.8) with the empirical potentials (2.10) to (2.13) can be reliably employed to test the validity of Eq. (2.8). In this respect, therefore, relations (2.10) to (2.13) are evidently of only restricted usefulness. Indeed, recourse to these was taken, mainly, for one compelling reason: The great dearth of more suitable experimental data, save for the relatively few measurements, in limited ranges, obtained by Amdur *et al.*, and by Berry, which are discussed below.

On the other hand, from a merely *phenomenological* point of view, it may conceivably be of interest to follow the behavior of these empirical potentials also when extrapolated to values of $R\ll R_{\min}$. In particular, such observations might provide an answer, e.g., to the question whether Amdur's cited remark[25] concerning the Lennard-Jones potential for the Ar–Ar interaction applies to other binary rare-gas systems as well. Furthermore, Buckingham (reference 78) notes that in the (exp-6) potential bearing his name, "the R^{-6} term has little real significance inside the zero of the potential and its retention there tends to obscure the nature of the rise in the potential at smaller distances. For this reason, some empirical potentials in use effectively eliminate this negative term for small R." In the light of these observations it may, therefore, be of interest to examine the behavior at small R both of the total and of the repulsive part of the (exp-6) potential separately. Hence, some attention is given in Sec. III also to *extrapolated* portions, specifically, of the (12–6) and (exp-6) potentials, and to the repulsive part of the latter separately.

In the atomic-beam technique employed by Amdur[25] and colleagues, and by Berry,[73] the interaction potentials are determined from measurements of the total scattering cross section $S(E,\Theta)$ in atom-atom collisions, where E is the energy of the beam particles, and Θ is the effective average angular aperture of the beam-and-detector system. Classical scattering theory is then used to calculate $U(R)$ from the observed variation of S with E. Either an inverse power or a Born-Mayer potential can be fitted to the data. This method has been characterized by Buckingham[53] as "one of the most fruitful sources of information about the short-range repulsions between atoms." Its results concerning the systems under consideration are presented and discussed in detail in Sec. III.

At small separations, an independent test of our potential (2.8) is the following.[74] By definition, the theoretical interaction potential consists of the internuclear Coulomb repulsion $Z_1Z_2e^2/R$, plus the total electron energy H of the interacting atoms, and diminished by the ground-state energies $H(Z_1)$, $H(Z_2)$ of the individual atoms when these are infinitely far apart, i.e.,

$$U(R)=[(Z_1Z_2e^2/R)+H]-[H(Z_1)+H(Z_2)]. \tag{2.14}$$

If we now consider the limit as R tends to zero, then the electron energy H of the interacting pair of atoms should clearly tend to that of the "united atom," i.e., an atom of atomic number Z_1+Z_2. Hence, upon transposing the

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[68] S. C. Saxena, J. G. Kelley, and W. W. Watson, Phys. Fluids 4, 1216 (1961).

[69] F. Van Der Valk and A. E. De Vries, J. Chem. Phys. 34, 345 (1961).

[70] P. M. Morse, Phys. Rev. 34, 57 (1929).

[71] G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), Chaps. 4, 6–8.

[72] D. D. Konowalow and J. O. Hirschfelder, Phys. Fluids 4, 629 (1961).

[73] H. W. Berry, Phys. Rev. **75**, 913 (1949); **99**, 553 (1955).

[74] R. A. Buckingham, J. Planetary Space Sci. **3**, 205 (1961).

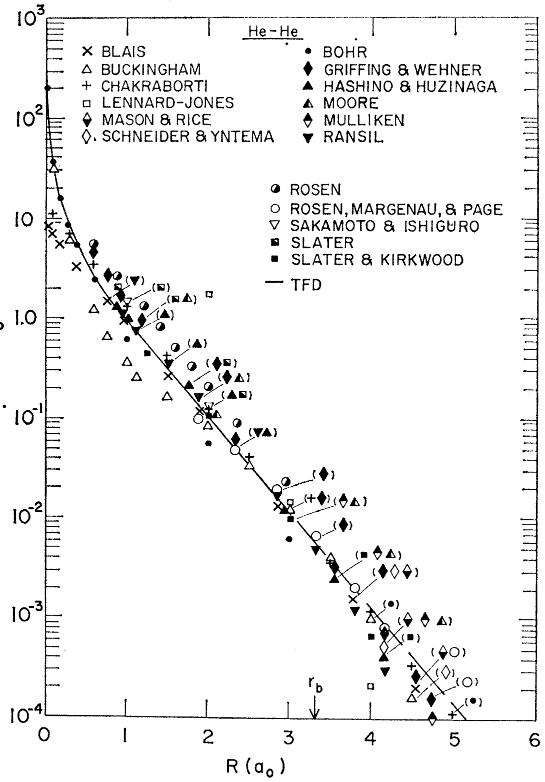

FIG. 3. Repulsive interaction potentials for the He-He system. The first group of six references relate to experimental work; the remainder to calculated results. (Data for Mason and Rice, and for Schneider and Yntema, from reference 21.)

internuclear repulsion term to the left-hand side of (2.14) and calling the left-hand side of the resulting relation the "theoretical difference" or Δ_{theo}, and the right-hand side the "experimental difference" or Δ_{exp}, then in the limit as $R \to 0$, Δ_{theo} should approach Δ_{exp}. That is,

$$\Delta_{\text{theo}} \equiv \lim_{R\to 0}\{U(R)-(Z_1Z_2e^2/R)\} \to \{H(Z_1+Z_2)-[H(Z_1)+H(Z_2)]\} \equiv \Delta_{\text{exp}}, \quad (2.15)$$

which, for homonuclear systems, simplifies to

$$\Delta_{\text{theo}} = \lim_{R\to 0}\{U(R)-(Z^2e^2/R)\} \to \{H(2Z)-2H(Z)\} \equiv \Delta_{\text{exp}}. \quad (2.16)$$

This relation can, therefore, be used as an independent test of the reliability of $U(R)$ for small R, provided the experimental data required for the evaluation of Δ_{exp} are available. The latter, unfortunately, is the case for only a relatively small number of elements,[75] and hence the united-atom test (2.16) can be applied to only two (He-He and Ar-Ar) of the six systems treated in the following section.

III. RARE-GAS POTENTIALS[76]

(A) Helium

Of all pairs of interacting ground-state atoms, none appears to have received as much attention as has the He-He system.[21,22,30–38] Yet, despite this intensive effort and the relative simplicity of this system, substantial disagreement between theory and experiment over a certain interval of separations still remains unresolved. This is illustrated in Figs. 3 and 4, with the exceptionally high density of plotted points (in Fig. 3) reflecting the very large number of studies made of this system, and the unresolved discrepancy between theory and experiment quite conspicuous (in Fig. 4) in the approximate interval $0.75a_0 \lesssim R \lesssim 1.75a_0$.

Deferring a more detailed consideration of this discrepancy until later and confining our attention for the present to Fig. 3 alone, we see that for $R \lesssim 3.75a_0$, our TFD curve [Eq. (2.8)] and its extrapolation are generally well supported by both other theory and by experiment. Near the uppermost end of the energy scale, the points given by Blais *et al.*[62] and by Chakraborti[63] do lie considerably below the TFD curve. This deviation, however, is spurious and due to the unrealistic tendency of the Born-Mayer potential [Eq. (2.11)] to tend to some constant A as $R \to 0$. Again, when observing the points calculated by Rosen[34] in the range $0.5a_0 \lesssim R \lesssim 1.9a_0$, one must recall that these refer only

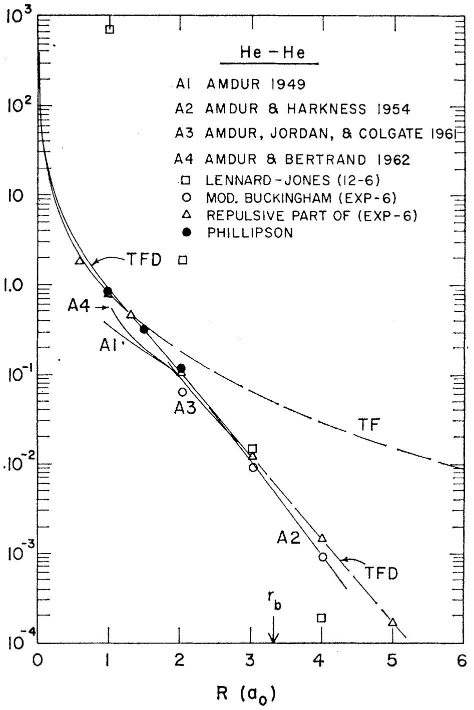

FIG. 4. Repulsive interaction potentials for the He-He system (concluded).

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[75] C. E. Moore, *Atomic Energy Levels,* National Bureau of Standards, Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

[76] To conserve space and maintain continuity, the numerical data supporting our curves in Figs. 3–13 are collected in Table II in the Appendix.

to the repulsive part of the potential. The expression for the total interaction potential, due to Rosen, Margenau, and Page[10] (RMP), goes through a spurious maximum for $R \lesssim 1.89a_0$, a feature that is discernible in Fig. 3 and which also accounts for the absence of RMP points at separations $R \lesssim 1.89a_0$. In the range $1.89a_0 \lesssim R \lesssim 4.0a_0$, on the other hand, our TFD potential is clearly seen to be in good agreement with the RMP quantum-mechanical calculation. Remarks exactly analogous to those made concerning the Rosen and RMP potentials, respectively, apply also to the Slater[37] and the Slater and Kirkwood (SK) potentials.[38] The former, again, being merely the repulsive part of the potential, is seen to lie somewhat higher than our corresponding TFD values in the region $0.89a_0-2.0a_0$. The complete SK potential, on the other hand, is seen to be in close agreement with our TFD potential from $R \simeq 1.23a_0$ to $\sim 3.5a_0$, (with a spurious maximum in the SK curve occurring near the lower limit). In approximately the same interval of separations, the calculations by Hashino and Huzinaga,[31] by Ransil,[21] and most recently by Phillipson,[22] are likewise found to agree very closely with our TFD curve. For $R \lesssim 0.6a_0$, the Bohr potential, too, is seen practically to coincide with the TFD curve, but is evidently too small for $1a_0 \lesssim R \lesssim 3a_0$. In this latter interval, we also note the linearity of the TFD curve (already mentioned in Sec. II) and the good agreement that is obtained between its extrapolation and the results of other investigations, up to ~ 3.5 or $4a_0$. The linearity property is, thus, shown to permit an extension of the calculated range of $U(R)_{\mathrm{TFD}}$ by about 25%. Beyond this point, our (extrapolated) potential is evidently too large.

Turning next to Fig. 4, we immediately note that the TF potential closely follows our TFD curve up to $R \simeq 1.5a_0$ but, as expected on the basis of the discussion in Sec. II, falls off much too slowly at greater internuclear distances. With regard to the curves $A1$ to $A4$ obtained by Amdur[77] *et al.* from the analysis of gas-scattering experiments, agreement of our theoretical potential with $A3$ is close, but that with $A2$ deteriorates for $R \gtrsim 3a_0$, as expected on the basis of the value[51] $r_b \simeq 3.32a_0$ and the weakness of our model there (see Sec. II). The pair of curves $A1$, $A4$, is of especial interest for two reasons. Firstly, they show that, with the more modern apparatus used, a large portion of the curve obtained many years previously has become displaced towards significantly higher values. This manifestly improves the accord with our theoretical curve substantially, (a feature that recurs even more strikingly in the case of the Ar-Ar interaction, Fig. 7, below). On the other hand, this pair of curves emphasizes the current disagreement between theory and experiment at $1a_0 \lesssim R \lesssim 1.5a_0$. Much of the impetus for this recent work by Amdur and Bertrand, indeed, stemmed from an awareness of the earlier discrepancy and the subsequent attempt to determine whether this was attributable to possible inadequacies of the older, much less sophisticated molecular-beam apparatus.[77] The result, curve $A4$, suggests that part of the discrepancy, apparently, was due to such inadequacy. Nevertheless, the theoretical values are still about 1.5 times higher than these latest gas-scattering measurements. Also aware of this disagreement, and reasonably confident in the reliability of their theoretical calculations, several workers[21,22] have favored a reinvestigation of the gas-scattering analysis. Amdur,[77] however, has indicated that if his results were to undergo any further modification at all, this would most likely be in the downward direction, and thus increase rather than diminish the discrepancy. At present, no resolution of this impasse appears in sight.

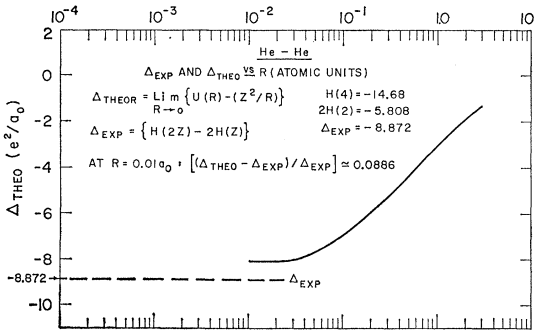

FIG. 5. United-atom test for the He-He potential.

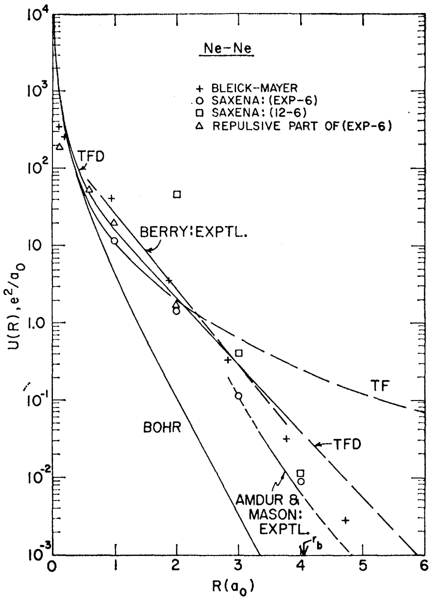

FIG. 6. Repulsive interaction potentials for the Ne-Ne system.

Directing our attention next to the Lennard-Jones (12–6) potential, U_{LJ},[10] we note that with decreasing

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[77] I. Amdur, J. Chem. Phys. **17**, 844 (1949); I. Amdur and A. L. Harkness, *ibid.* **22**, 664 (1954); I. Amdur, J. E. Jordan, and S. O. Colgate, *ibid.* **34**, 1525 (1961); I. Amdur and R. Bertrand, *ibid.* **36**, 1078 (1962). (The results of the last work were kindly communicated by Professor Amdur to the author in 1961.)

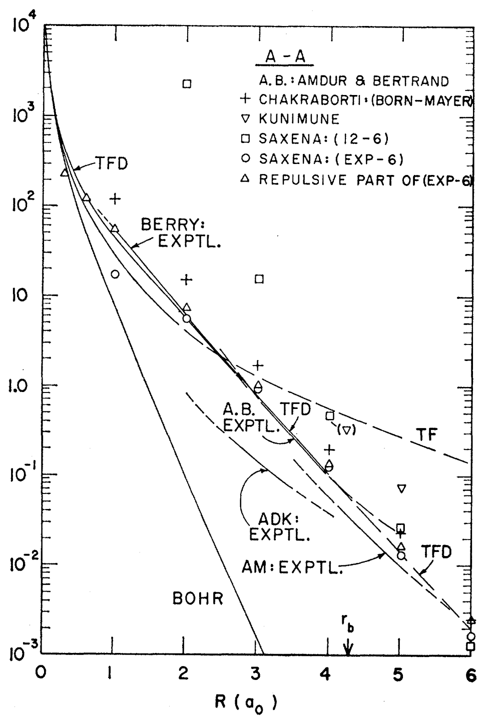

FIG. 7. Repulsive interaction potentials for the Ar-Ar system.

R, U_{LJ} very rapidly rises to values exceeding the experimental (and theoretical) ones by $\sim 300\%$ at $R=1a_0$, in qualitative agreement with Amdur's corresponding observation for the case of argon.[25] Anticipating here that the He-He and Ar-Ar cases turn out to be fairly typical in this respect, it follows that (inward) extrapolations of U_{LJ}, indeed, are exceedingly unrealistic and thus not usable for testing the reliability of U_{TFD} at separations appreciably less than $R_{\min}$.

In marked contrast to this behavior of U_{LJ}, the extrapolated (exp-6) or modified Buckingham potential, U_{MB},[10] is seen to remain quite close to the experimental curves down to $R\sim 2a_0$; its repulsive part, U_{rep}, in fact, follows the theoretical curves (TFD and others) down to $R\sim 1a_0$, even though $R_{\min}\sim 3.5a_0$ (Table I). More specifically, near $R=4a_0$, U_{MB} agrees almost exactly with Amdur's experimental curve; U_{rep}, with the extrapolated TFD curve. At $R=3a_0$, both U_{MB} and U_{rep} are about equidistant from the experimental curve. At $R=2a_0$, the total U_{MB} is noticeably bending over towards its spurious maximum and lies $\sim 35\%$ lower than the corresponding experimental value; U_{rep}, on the other hand, agrees fairly well with both theory and experiment. Indeed, even for $1a_0 \leq R \leq 2a_0$, U_{rep} is still seen to follow the theoretical values (TFD and others) quite closely.

In view of the remarks made concerning the empirical potentials in Sec. II and the fact that $R_{\min}$ here $\sim 3.5a_0$, the approximate accords noted above between the extrapolated U_{MB} (total or repulsive) and other curves are, of course, *not* to be construed as reliable experimental support of the latter. Indeed, because of the extrapolations involved, one cannot at this point rule out the possibility that these accords are, in fact, fortuitous. On the other hand, however, there also appears to be no evidence compelling one to conclude that this agreement *must* be accidental and hence, the rather surprising fact that such accords as have been noted actually do exist seemed too striking, and possibly useful, to be completely ignored. (See also Sec. IIID). In particular, if not fortuitous, the agreement noted would tend to confirm Buckingham's suggestion[78] (quoted in Sec. II) concerning the inappropriateness of the R^{-6} term in U_{MB} at separations R inside the zero of the potential. These points will be considered again in conjunction with the remaining two-center systems discussed below.

Returning very briefly to a consideration of Fig. 3, we note that the Buckingham[78] potential there agrees rather accurately with our TFD curve from $R=0.1a_0$ to $R\simeq 3.5a_0$, except in the interval associated with the discrepancy discussed in the preceding paragraph. This exception is, of course, a direct consequence of the fact that the semiempirical Buckingham potential was itself fitted to Amdur's gas-scattering results.

We conclude the analysis of the reliability of the TFD potential for the He-He interaction by applying the independent "united-atom" test described in Sec. II above. The resulting plot and relevant numerical data[2,75] are shown in Fig. 5. The quantity Δ_{theo}, directly dependent on U_{TFD}, will be observed to come fairly close to approaching the corresponding experimental quantity Δ_{exp}. In fact, as also shown in the figure, the test (2.16) is satisfied to within an error of less than 9%, or much less than the over-all accuracy of $\sim 20\%$ generally ascribed[47] to the statistical model *per se*. Our TFD potential (2.8) for the He-He interaction thus appears to be reliable in the interval $0.01a_0 \leq R \leq 3.5a_0$.[79]

(B) Neon

In Fig. 6, we compare the TFD potential for neon, first with an experimental curve obtained from gas-scattering analysis by Berry.[73] We note that the agreement is reasonable. At larger separations, the accord of our TFD potential with Amdur and Mason's[80] (AM) experimental curve is not as good as one might wish. It

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[78] R. A. Buckingham, Trans. Faraday Soc. 54, 453 (1958).

[79] Considering the paucity of electrons in the helium atom, the accuracy of our expression based on the *statistical* model (which latter is often held to require the presence of a *large* number of electrons) may seem surprising. It is a fact, however, that also for the H-H interaction even Firsov's TF expression agrees very closely up to $R\simeq 1.5a_0$ with other theoretical and experimental values. (For the latter, see reference 10.) One is, therefore, led to consider that even a single atomic electron (and *a fortiori*, a pair) may be amenable to statistical considerations, possibly because of its wave-mechanical or probabilistic properties. The latter, as is well known, endow it of course with characteristics quite different from those of the classical "one-particle" model. Alternatively, even on a classical approach, it is perhaps the rapidity of the electronic motion that makes the statistical treatment meaningful. See also reference 2(a), p. 174.

[80] I. Amdur and E. A. Mason, J. Chem. Phys. 23, 415 (1955).

is still considerably closer, however, than that attained by either the Bohr potential or by that due to Firsov.

Now, the theoretical Bleick-Mayer[39] calculation, too, would seem to favor higher values, lying roughly midway between the AM curve and the (extrapolated) TFD potential. Furthermore, in the light of Amdur's[77] most recent experiments on the He-He and, especially, the Ar-Ar systems (see Fig. 7 and its discussion below), it would appear reasonable for one to inquire whether also the 1955 Ne-Ne measurement, if repeated with the present updated apparatus, would likewise yield a curve displaced substantially upward from the position shown here, thereby tending to reduce the present disagreement. As the AM segment in Fig. 6 was obtained with apparatus equivalent in refinement to that which yielded the recent revisional He-He and Ar-Ar data,[81] however, no upward revision analogous to that undergone by curves $A1$ (Fig. 4) and ADK (Fig. 7) for helium and argon, respectively, can be expected to arise for the AM neon curve by the present techniques. One wonders, therefore, whether this discrepancy between theory and experiment at $3a_0 \leq R \leq 4a_0$ here is possibly similar to that encountered in the He-He interaction at $R \leq 2a_0$ above. If so, this might provide further impetus towards seeking a common solution for both.

As was the case in the He-He interaction above, the LJ (12-6) potential is again observed to rise much too steeply with decreasing R, thereby causing U_{LJ} also here to exceed the experimental values near $R = 1a_0$ by $\sim 300\%$. (U_{LJ} at $R = 1a_0$ lies outside the limits of the graph and is, therefore, not shown in Fig. 6.) This again confirms the relevant statements concerning U_{LJ} deduced previously.

Similar confirmation is obtained from Fig. 6 also for the behavior, noted earlier, of the extrapolations of U_{MB} and U_{rep}. For here, even though $R_{\mathrm{min}} \sim 4.5a_0$, U_{MB} with parameters given recently by Saxena[68] remains, with decreasing R, relatively close to both the experimental as well as the theoretical curves; while U_{rep} stays even closer to these down to $R \sim 0.5a_0$, again in good agreement with Buckingham's relevant remark.[78] At the same time it should be reemphasized, however, that because of the great extrapolations involved, this behavior of U_{MB} and U_{rep} should not be looked upon as reliable experimental evidence for the validity of U_{TFD}. Instead, we here merely note the *existence* of this approximate agreement, possibly fortuitous, between U_{rep} and other experimental and theoretical curves, including U_{TFD}, even at $R \ll R_{\mathrm{min}}$.

At separations smaller than $\sim 0.3a_0$, the Bohr, TF, and TFD potential all give very nearly the same values for $U(R)$. For larger values of R, however, Bohr's screened Coulomb potential falls off much too steeply and Firsov's TF potential, as before, much too slowly.

We conclude that our TFD potential (2.8) agrees with experiment more closely throughout the region tested than do either the Bohr or TF potentials.

(C) Argon

Figure 7 for the argon interaction again compares our TFD potential (2.8) with experimental curves due to Berry,[73] and with several others due to Amdur and his co-workers.[81] The agreement with Berry's curve is seen to be quite close, and that with Amdur and Bertrand's most recent measurements, almost complete. This latter near-coincidence between the experimental and theoretical curves, it will be observed, is brought about by the substantial upward revision of an earlier measurement by Amdur, Davenport, and Kells[81] (ADK). This upward shift is qualitatively similar to that already encountered in conjunction with the He-He interaction (Fig. 4), but differs from it quantitatively by being approximately five times greater in magnitude. We note that here as well as in the He-He case, the magnitude of the shift increases with increasing energies $U(R)$. An analogous upward displacement and steeper slope imparted to the AM experimental segment in Fig. 7 would clearly tend to improve not only its agreement with the extrapolated TFD curve, but also the self-consistency and continuity between the AM segment and the 1961 A.B. measurement. Again, no such revision is experimentally to be expected in the present case, however, because, unlike ADK, the 1954 AM curve was obtained with an apparatus equivalent in sophistication to that used in the 1961 remeasurements on the He-He and Ar-Ar systems.[81] Thus, as in the preceding two cases, a discrepancy between theory and experiment also here remains presently unresolved.

Since $R_{\mathrm{min}} \sim 6a_0$ in the present case (Table I), U_{MB}, with Saxena's[68] parameters, here *can* be used to test the validity of U_{TFD} at these large values of R. We note that near the upper extremum of separations considered in Fig. 7, the extrapolated TFD curve lies not far from U_{MB}.

A phenomenologically interesting feature, *not* adduced as experimental support of U_{TFD}, is the nearly uniform

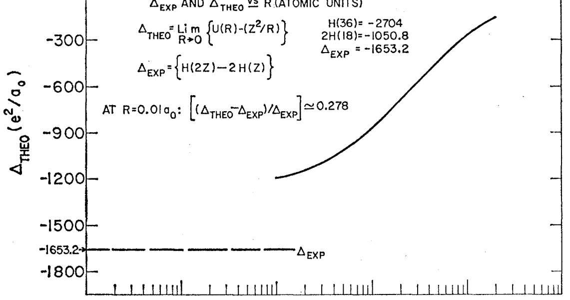

FIG. 8. United-atom test for the Ar-Ar potential.

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[81] I. Amdur, D. E. Davenport, and M. C. Kells, J. Chem. Phys. **18**, 525 (1950); I. Amdur and E. A. Mason, *ibid.* **22**, 670 (1954); I. Amdur and R. Bertrand (unpublished, private communication).

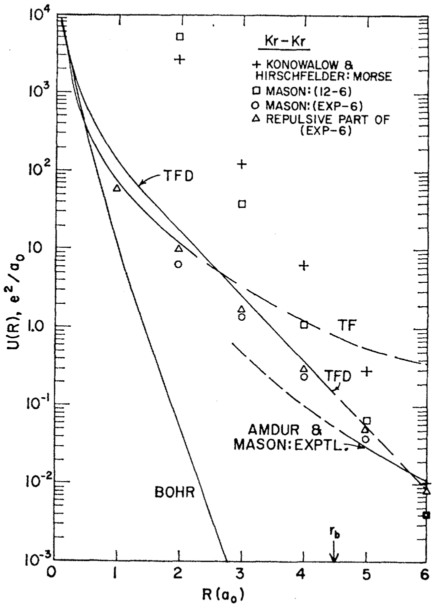

FIG. 9. Repulsive interaction potentials for the Kr-Kr system.

proximity of U_{MB} and U_{rep} to most of the experimental and TFD curves from $\sim 5a_0$ down to below $\sim 1a_0$. (Below $R\sim 2a_0$, U_{MB} evidently begins to arc over towards its spurious maximum.) If this accord is not accidental, it would again tend to support Buckingham's[78] remarks (Sec. II) concerning U_{rep}. Also of phenomenological interest, perhaps, is the continuous near-linearity of U_{rep}, U_{MB}, and the curves A. B., Berry, and TFD.

In contrast with this behavior of U_{MB} and U_{rep}, one again notes the rapid rise of U_{LJ} for $R<6a_0$, such that even at $R=2a_0$, U_{LJ} already exceeds the experimental value by nearly 300%. On the other hand, at $R=6a_0$, where U_{LJ} *is* valid, (Table I), the TFD curve is seen to lie not very far from U_{LJ}.[68]

The fact that Chakraborti's[63] empirical potential remains consistently somewhat above the other experimental curves is probably attributable, at least in part, to our extrapolation of his expression to values of R much smaller than those at which the parameters A and R_0 [in Eq. (2.11)] were fitted empirically.

As noted in the Ne-Ne case, the three theoretical potentials (Bohr, TF, TFD), all coalesce for very small R (here $\lesssim 0.2a_0$), but for separations R greater than $\sim 1a_0$ and $3a_0$, respectively, the Bohr potential is again seen to fall off far too steeply, and the TF potential much too slowly.

As the empirical values for the total electron energies $H(Z)$ with $Z=18$ and $Z=36$ required for testing $U(R)$ by relation (2.16) are known,[2] we have applied the test here and show the results in Fig. 8. At first sight, the error of nearly 28% to within which $U(R)$ satisfies relation (2.16) at $R=0.01a_0$, may seem disappointingly high. It must be remembered, however, that the test is to hold, strictly speaking, only for $R\to 0$. An estimated extrapolation of the curve shown in Fig. 8 to $R=0.001a_0$ would give $\Delta_{\mathrm{theo}}\sim -1320e^2/a_0$ and, hence, would reduce the error to $\sim 20\%$, or just about the accuracy usually associated with the statistical model.[47]

In summary, we conclude that, judging by the currently available experimental data, our TFD potential (2.8) for the Ar-Ar interaction reproduces these data quite closely over practically the entire range of R up to $\sim 6a_0$.

(D) Krypton

For the case of the Kr-Kr interaction, $R_{\mathrm{min}}\sim 6a_0$ (Table I), so that here, using Mason's[82] parameters, U_{MB} and U_{LJ} *are* usable for testing the reliability of our TFD potential (2.8). At $R=6a_0$, it can be seen from Fig. 9 that both the TFD and the experimental AM[83] curves exceed U_{LJ} and U_{MB} roughly by a factor of two. The considerably closer agreement of U_{rep} (rather than U_{MB}) with U_{AM} would again appear to support Buckingham's[78] observations concerning U_{rep} as compared to U_{MB} (Sec. II).

$U_{\mathrm{TFD}}\sim U_{\mathrm{AM}}$ near $R=5.7a_0$; but agreement between these two curves diminishes with decreasing R until, near $R=4.6a_0$, one finds $U_{\mathrm{TFD}}\sim 2U_{\mathrm{AM}}$. This discrepancy is somewhat similar to that encountered also in the preceding cases at "large" separations. Whether this is attributable to the crudeness of our extrapolation procedure, to the intrinsic weakness of our model near $R=r_b$ (Sec. I), or possibly to other causes, is not clear. The accord with experiment in the region $4.5a_0\gtrsim R\gtrsim 6a_0$, however, *is* markedly closer than that attained by either

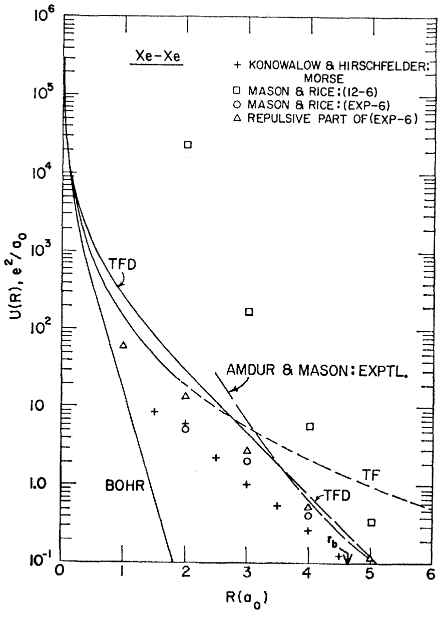

FIG. 10. Repulsive interaction potentials for the Xe-Xe system.

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[82] E. A. Mason, J. Chem. Phys. 32, 1832 (1960).

[83] I. Amdur and E. A. Mason, J. Chem. Phys. 23, 2268 (1955).

the Bohr or TF potentials. Except at very small separations, both of the latter curves again run too low and too high, respectively, generally by orders of magnitude.

The empirically fitted Lennard-Jones[82] and Morse[72] potentials, respectively, are again shown, mainly, to indicate that while these are much too high at small separations ($\lesssim 3a_0$), both curves approximately do approach our TFD potential as R increases towards those sufficiently large values where the Morse and (12-6) potentials *are* applicable. At the same time, the relative positions of these two empirical curves, together with those of the (exp-6) values, afford a rough measure of the uncertainty of each near $R=6a_0$.

As in the previous interactions, the extrapolated total (exp-6) curve, U_{MB}, is again seen to arc over towards its typical spurious maximum (and thence to $-\infty$) with decreasing R, whereas the purely repulsive part, U_{rep}, follows the TFD curve more closely down to $R\sim 1a_0$. Because of the large extrapolations involved, however, this approximate agreement can, of course, *not* be construed as empirically supporting U_{TFD} (see, however, below).

In view of the apparently complete lack of available experimental data on $U(R)$ for Kr-Kr (and also for Xe-Xe and Rn-Rn) at $R<4.5a_0$, experiments designed to explore this region of separations would seem to hold considerable interest. With the aid of such data for Kr-Kr and, hopefully, for all of the remaining rare gases (and others), it would then obviously be possible to assess the reliability of theoretical potentials (including TFD) more completely. Moreover, such data may possibly shed some light on the question whether or not the relation U_{rep} (extrapolated)$\sim U$(experimental) for $1a_0\lesssim R\lesssim 4a_0$, observed to hold within order of magnitude or closer in the preceding three systems (A) to (C), recurs regularly. In the affirmative event, this empirical relation would then further corroborate not only Buckingham's[78] assertion regarding U_{rep} (Sec. II), but might conceivably also prove useful as a crude order-of-magnitude guide to estimates of $U(R)$ for interactions of comparable systems and separations for which *reliable* values for $U(R)$ are as yet unknown.

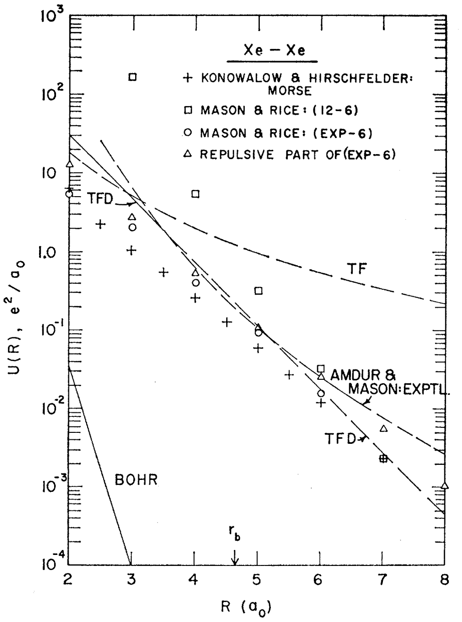

FIG. 11. Repulsive interaction potential for the Xe-Xe system (concluded).

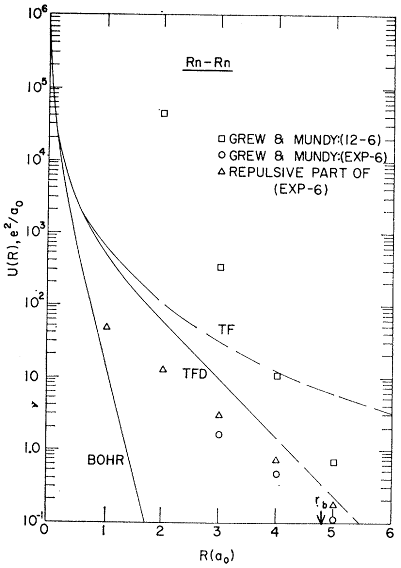

FIG. 12. Repulsive interaction potential for the Rn-Rn system.

(E) Xenon

In the Xe-Xe interaction, Figs. 10 and 11, the "inward" extrapolation of the experimental AM curve[84] for $3.5a_0\lesssim R\lesssim 5.5a_0$ is seen to agree quite well with our extrapolated TFD potential, but agreement with the AM curve itself is not as good. Contrary to the preceding four cases, (A) to (D), however, the AM curve here lies generally higher than the TFD potential and, in fact, all the other empirical potentials under consideration. [This holds, specifically, even with respect to the extrapolated $U_{\text{LJ}}(R_{\min}\sim 7a_0)$ which is now well known to rise too *rapidly* with decreasing R.] Whether all the latter, in the approximate interval $6a_0\lesssim R\lesssim 7a_0$ are too low, or whether the AM curve is too high, or possibly both, can perhaps be decided after a reconsideration of the inert-atom repulsive interactions recently suggested by Phillipson.[22]

For the Xe-Xe case, $R_{\min}\sim 7a_0$ (Table I), whence U_{MB}, U_{LJ}, and U_{Morse}[72] here *can* serve to test the reliability of our TFD potential (2.8). We note (Fig. 11) that near $R=7a_0$, U_{TFD} lies fairly close to the empirical potentials there.

Other comments concerning the Bohr, (exp-6), LJ, Morse, and TF potentials, contained in the preceding

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[84] I. Amdur and E. A. Mason, J. Chem. Phys. **25**, 624 (1956).

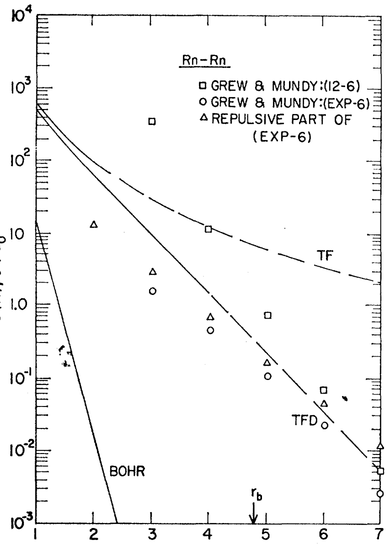

FIG. 13. Repulsive interaction potential for the Rn-Rn system (concluded).

subsections (A) to (D), apply essentially unchanged also here.

(F) Radon

Lastly, in Figs. 12 and 13, we show the Rn-Rn interaction. Unfortunately, experimental data for this case are exceedingly scant. Hence, comparison of our TFD potential is confined to but two cases, namely, U_{LJ} and U_{MB}, using the parameters recently obtained semiempirically by Grew and Mundy.[85] The results are quite similar to those found in the preceding cases: While the (12-6) potential is unrealistically high at small separations, it approaches our TFD curve (and its extrapolation) as R tends to those larger values ($R_{\min}\sim 7a_0$, Table I) at or near which the LJ curve does constitute an adequate description (see especially Fig. 13). As in the case of the Xe-Xe interaction, so also does this feature here, therefore, tend to support the extrapolation method applied to the TFD potential.

Agreement of U_{TFD} with U_{MB} or U_{rep}, though not very close near $R=7a_0$, is within order of magnitude. With respect to U_{rep}, this approximate accord persists, as in the preceding cases, even upon extrapolation down to $R\sim 1a_0$. In the absence, so far, of experimental data valid at these small separations, this very rough accord is *not* to be considered as reliable experimental confirmation of U_{TFD} (as stated already several times). Some interest may attach to this feature, however, in the sense described in part (D) above.

The coalescence of the three theoretical potentials at very small separations (here $\lesssim 0.1a_0$), and the very marked and opposing deviations of the Bohr and TF curves from the TFD values elsewhere are again seen to occur, as by now expected on the basis of the preceding five cases.

IV. SUMMARY AND CONCLUSIONS

Application of the theoretical interaction potential (2.8) to the six homonuclear pairs of rare-gas atoms studied here constitutes a first detailed test of its actual reliability and, concomitantly, provides new and detailed information concerning these rare-gas interactions[24] for internuclear spearations R ranging, approximately, from 0.01 to $8.0a_0$. Numerical values for $U(R)$ can generally be calculated up to $R\simeq r_b$, and can be obtained approximately by extrapolation for about $2a_0$ to $3a_0$ beyond r_b. More specifically, the results presented here show that our TFD curves (a) practically coincide with the Bohr potential at very small separations ($R\lesssim 0.1a_0-0.6a_0$), where the latter is generally held to be reliable[4,43]—and (b) are in close, or, at least, reasonable agreement with available empirical data at intermediate separations ($R\simeq 0.8a_0-7.0a_0$). This accord with experiment is both closer as well as more extensive than was previously estimated.[1,86] Comparison of the experimental data with Bohr's screened Coulomb potential (2.1), and with Firsov's TF potential (2.3), on the other hand, shows that for $R\gtrsim 1a_0$ the former falls off far too steeply with increasing R, whereas for $R\gtrsim 3a_0$ the latter decreases much too slowly.

One is thus led to conclude that, at very small and intermediate separations, our TFD potential (2.8), (including its suggested extrapolation), constitutes a reasonable representation of $U(R)$, and is generally much more accurate than the Bohr or Firsov potentials wherever these differ from our TFD curve.

At the same time it must be remembered, however, that our results and conclusions here are based upon the examination of a class of systems possessing two very special properties, namely, (i) homonuclearity ($Z_1=Z_2$) and (ii) closed-shell configurations of the interacting atoms. When either one or both of these conditions are relaxed, the conclusions drawn here may no longer be valid. This is so, because *hetero*nuclearity ($Z_1\neq Z_2$) alone will destroy much of the symmetry of our central result (2.8), in particular, by introducing two distinct values for the unrealistic bounding radii r_{b1}, r_{b2} of the interacting atoms. As the values of r_b range[51] from $3.32100a_0$ for helium to $4.79520a_0$ for radon, it is clear that the relative difference between r_{b1} and r_{b2}, (or the "sizes" of the interacting atoms), can be considerable. Physically, this disparity leads to additional and more involved configurations than those shown in Figs. 2 and 15 (while formally, this disparity manifests itself in rendering the evaluation of the two-center intgeral $\bar{\Lambda}$ more intricate. See Appendix B). Typical questions, arising because of these new and more complicated configurations when $Z_1\neq Z_2$ are the following: Will the calculation of $U(R)_{\mathrm{TFD}}$ still remain meaningful when

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[85] K. E. Grew and J. N. Mundy, Phys. Fluids 4, 1325 (1961).

[86] A. A. Abrahamson, R. D. Hatcher, and G. H. Vineyard, Bull. Am. Phys. Soc. 5, 231 (1960).

carried up to separations $R \simeq r_{b1}$ (assuming $r_{b1} < r_{b2}$)? Will the approximate linearity-property be preserved? If it is, how far beyond the cutoff value of R can the simple extrapolation method, described above, be extended? Can an empirical combination rule[10] be applied? To ascertain the effects of relaxing the homonuclearity condition (i) alone will, therefore, require a reexamination of our TFD potential. The results of this analysis will be described in detail in a forthcoming paper.[24]

On the other hand, relaxing condition (ii) alone, i.e., allowing one or both of the interacting atoms to have open-shell configuration, actually runs counter, in part, to the spirit of the statistical model of the atom for the following reasons. As the statistical electron density distribution $\rho(r)$ represents only an average of the actual distribution, even the gross shell-structure of the atomic electron cloud is obliterated in this approximation[2,87] (see Fig. 1). The behavior of individual electrons near the atom edge and outside closed shells, therefore, is even more poorly described by $\rho(r)$. Consequently, the effect of this relaxation, too, may lead to conclusions materially different from those stated above, and hence the applicability of U_{TFD} to such open-shell systems, too, should be examined anew. For the case of copper, this has been done, albeit in a somewhat indirect and incidental manner, by Vineyard[4] and by Sosin.[6] More detailed results for the noble metals as well as for certain other elements will be reported elsewhere.

When both conditions (i) and (ii) are relaxed simultaneously, the severest modification of our present conclusions may become necessary.[88]

Lastly and merely incidental to this study, the following is found at separations R smaller than those at which the corresponding potential parameters are empirically determined: (1) The Lennard-Jones (12–6) potential generally rises rapidly, with decreasing R, to values exceeding the experimental ones by several 100%. Such extrapolations are, therefore, quite unrealistic. (2) The modified Buckingham (exp-6) potential and particularly its repulsive part, on the contrary, are found to maintain order-of-magnitude and frequently closer agreement with experimental values, even when the former are extrapolated to separations near $1a_0$. Whether or not this is merely accidental is presently not clear.

ACKNOWLEDGMENTS

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Especial tribute is due also to the late Dr. John B. Gibson for his advice and assistance with the machine computations.

APPENDIX

A. Numerical Data

Some of the numerical results of the present calculation are collected in Table II. Extrapolated values of

TABLE II. Repulsive interaction energies $U(R)$ calculated from Eq. (2.8). R is the internuclear distance, r_b the bounding radius of the corresponding TFD atom. Atomic units are used throughout.

Z $R(a_0)$	2	10	18	36	54	86
0.01	391.91	9690.0	31206	123720	276620	697150
0.03	125.31	3039.3	9690.2	37908	83813	208450
0.06	59.155	1362.9	4407.9	16921.	37001	90535
0.1	33.073	747.48	2360.7	8881.1	19105	46067
0.3	7.9995	166.40	491.01	1714.1	3535.6	8001.8
0.6	2.5997	49.404	138.75	453.15	897.32	1922.8
1.0	0.90824	16.229	43.807	136.51	259.12	533.61
1.5	0.30389	5.4078	14.298	42.843	79.906	159.95
2.0	0.10711	2.0535	5.4115	16.081	29.594	58.428
2.5	0.035695	0.79962	2.1459	6.4522	11.863	23.438
3.0	0.011982	0.29711	0.83633	2.5829	4.8152	9.5162
3.5	(0.0039)[a]	0.10078	0.29879	0.97050	1.8505	3.7429
4.0	(0.0012)	0.040756	0.10195	0.32782	(0.76)	1.3257
4.5	(0.00042)	(0.015)	(0.038)	0.14192	(0.30)	(0.57)
5.0	(0.00014)	(0.0056)	(0.014)	(0.055)	(0.12)	(0.22)
5.5	···	(0.0021)	(0.0052)	(0.022)	(0.044)	(0.083)
6.0	···	···	(0.0019)	(0.0083)	(0.018)	(0.032)
8.0	···	···	···	···	(0.00044)	···
r_b	3.3210	4.0507	4.2818	4.5275	4.6577	4.7952

[a] Extrapolated values are enclosed in parentheses.

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[87] L. C. R. Alfred, Phys. Rev. **125**, 214 (1962).

[88] Two papers directly bearing on the present subject have appeared recently: (a) R. A. Buckingham and D. M. Duparc, in *Progress in International Research on Thermodynamic and Transport Properties* (Academic Press Inc., New York, 1962), p. 378 ff. (b) J. R. Townsend and G. S. Handler, J. Chem. Phys. **36**, 3325 (1962). Values of $U(R)$ calculated for the He-He interaction in (a) agree with the TFD values to within ~10%. Application (by the present author) of the result derived in (b) yields values for $U(R)$ which for all the inert gases agree quite closely with those obtainable from Firsov's expression (reference 47). Another paper, also related to the present work, is that by R. Gaspar, Acta Phys. Acad. Sci. Hung. **11**, 71 (1960).

U_{TFD}, enclosed in parentheses, were read off Figs. 3–13 and, hence, are given to two significant figures only. In all but the last three columns, the value of R associated with the entry immediately preceding the parenthesized one will be observed to lie always just a little within the corresponding value of r_b (tabulated in the last row for comparison), in close accord with the characteristic limitation of the TFD model described above.

B. Computation of Ψ and of $\bar{\Lambda}$

Two computational problems were encountered in the attempt to evaluate U_{TFD} numerically. The first of these was the previous nonexistence[2] of tables of the TFD screening functions $\Psi(Z,r)$ as well as of the TFD electron density distributions $\rho(Z,r)$ for arbitrary integral Z and Jensen's boundary conditions.[89] This prompted the writer to calculate $\Psi(Z,r)$ and also $\rho(Z,r)$ for the 104 elements corresponding to atomic numbers $Z=2$ to $Z=105$ at 117 values of the radial distance r from the atomic center in each case. The methods and results of this calculation are described in a previous paper[90] [hereafter referred to as (II)].

The numerical evaluation of the two-center integral $\bar{\Lambda}$ given by (2.6) posed the second problem. For its solution, knowledge of the functions $\rho(Z,r)$, obtained in (II), was necessary but not sufficient. Recourse was had, therefore, to the following procedure due to Jensen[2]: Placing the nuclei of atoms 1 and 2, respectively, at the origin and at $z=R$ of a Cartesian coordinate system, and introducing r_1, r_2, θ, and φ as shown in Fig. 14, one can show by a tedious but straightforward calculation that the Jacobian of the transformation $(x,y,z) \rightarrow (r_1,r_2,\varphi)$ is

$$J \equiv \frac{\partial(x,y,z)}{\partial(r_1,r_2,\varphi)} = \frac{r_1 r_2}{R}, \tag{A1}$$

so that the volume element dv becomes

$$dv = (r_1 r_2/R)\, dr_1 dr_2 d\varphi. \tag{A2}$$

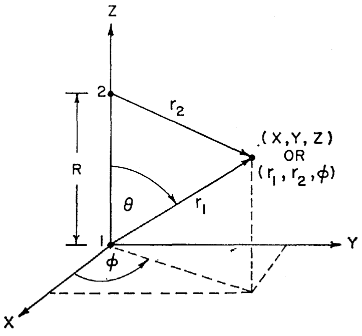

FIG. 14. Coordinate systems (x,y,z) and (r_1,r_2,φ) for two atoms, 1 and 2, with internuclear distance R.

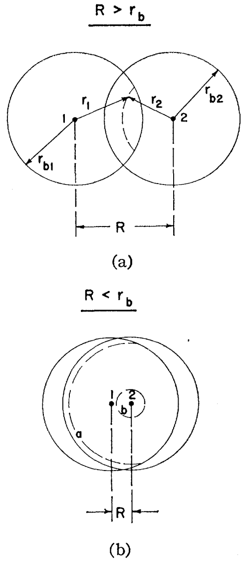

FIG. 15. Geometries, variables, and parameters used in the evaluation of the two-center integral $\bar{\Lambda}$ over the overlap region of a homonuclear pair of TFD atoms, having equal finite radii r_{b1} and r_{b2}, respectively, so that $r_{b1}=r_{b2}=r_b$. The dashed arcs indicate paths of integration for which r_2 is held constant, while r_1 alone varies.

By inspection of Fig. 14 as well as of the integrand $F(r_1,r_2)$ in $\bar{\Lambda}$, we see that our two-center system possesses axial symmetry and hence, after integration over φ, Eq. (2.6) becomes

$$\bar{\Lambda} = \frac{\pi}{3R} \int_{|R-r_2|}^{\min(r_{b1},R+r_2)} dr_1 \int_{\max(R-r_{b1},0)}^{r_{b2}} dr_2\, r_1 r_2 F(r_1,r_2). \tag{A3}$$

Here the limits of integration, deliberately expressed in forms suitable for use in machine computation (see below), are obtained as follows: We recall that the domain of integration is just the overlap region D_{12}, and that for a homonuclear pair of TFD atoms the finite bounding radii r_{bi} $(i=1,2)$ are equal, i.e.,

$$r_{b1} = r_{b2} \equiv r_b. \tag{A4}$$

Also, we assume throughout that

$$0 \leq R \leq r_{b1} + r_{b2} = 2r_b, \tag{A5}$$

because, for values of R larger than the maximum allowed by (A5), the atoms no longer overlap at all and hence,

$$\bar{\Lambda} = 0 \quad \text{when} \quad R > r_{b1} + r_{b2}. \tag{A6}$$

With this understanding, the problem naturally separates into the two parts (a) and (b) shown in Fig. 15.

For the case $R > r_b$, it is evident from Fig. 15(a) that as r_2 successively assumes its values allowed in D_{12} and defined by

$$R - r_{b1} \leq r_2 \leq r_{b2}, \tag{A7}$$

the variable r_1 takes on the values defined by

$$R - r_2 \leq r_1 \leq r_{b1}. \tag{A8}$$

The alternative case $R < r_b$ is a bit more complicated. Throughout the overlap region in Fig. 15(b), we have

$$0 \leq r_2 \leq r_{b2}, \tag{A9}$$

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[89] H. Jensen, Z. Physik **93**, 232 (1935).

[90] A. A. Abrahamson, Phys. Rev. **123**, 538 (1961).

but the extrema of r_1 vary, depending upon which of the "paths" a,b is being considered. Thus, by inspection of Fig. 15(b), we find that

$$r_2-R\leq r_1\leq r_{b1} \quad \text{for } r_2>R, \quad \text{or path (a);} \tag{A10a}$$

$$R-r_2\leq r_1\leq R+r_2 \quad \text{for } r_2<r_b-R, \quad \text{or path (b).} \tag{A10b}$$

Upon a little reflection, and noting that all the differences appearing in the left-hand members of the inequalities (A7) to (A10) are non-negative, one further finds that (A7) and (A9) may be combined by writing

$$\max(R-r_{b1},0)\leq r_2\leq r_{b2}, \tag{A11}$$

and similarly, that (A8) and (A10) may be combined into

$$|R-r_2|\leq r_1\leq \min(r_{b1},R+r_2), \tag{A12}$$

where $\min(x_1,x_2)$ means "the smaller of the two arguments x_1 and x_2," and similarly, $\max(x_1,x_2)$ selects the larger member of the pair. Relations (A11) and (A12) give the limits shown in (A3).

Even for but a single value of the internuclear separation parameter R, however, a hand calculation of the simplified form (A3) for $\bar{\Lambda}$ still involves a prohibitive amount of labor. For this reason, the ultimate evaluation of $\bar{\Lambda}(Z,R)$ for appropriate values of Z and at separations R ranging from $0.01a_0$ to $8.0a_0$, was performed on a high-speed electronic computer.

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Polarization of 9.4-MeV Protons Elastically Scattered from Copper*

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The polarization of 9.4-MeV protons elastically scattered from copper has been measured at 5° intervals from 20° to 150° (c.m.) using a helium polarimeter with counter telescopes. In this experiment an accuracy comparable to the accuracy of some of the best differential cross-section measurements has been obtained. Optical model calculations have been made for the polarization distribution, starting with the potential used by Easlea to fit the proton differential and reaction cross-section data. By varying the strength of the spin-orbit potential it was possible to obtain a good fit to the polarization distribution. The real part of the spin orbit potential was found to be (6±1) MeV and the imaginary part of the spin-orbit potential was less than 1 MeV.

INTRODUCTION

In recent years there have been many studies of proton elastic scattering at intermediate bombarding energies. Analyses of the experimental results have shown that an optical-model potential representing the interaction between the incoming proton and the target nucleus can be used to predict the general features of the scattering data, provided that the bombarding energy is sufficiently high that compound nucleus scattering can be neglected. The parameters of this optical model potential can be found if complete elastic scattering data is available including measurements of differential cross section, total reaction cross section and polarization.

The purpose of the present experiment was to investigate in detail a scattering process in which the nuclear scattering is expected to be predominantly shape elastic, and, therefore, describable by an optical model potential. Copper was chosen for this investigation because: The compound-elastic scattering is small, the (p,n) thresholds being well below the incident proton energy; the copper nucleus is not deformed so that one is justified in using spherical potentials in analyzing the results; the Coulomb barrier is sufficiently low that the

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