

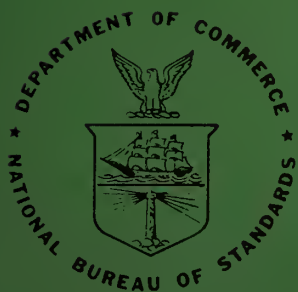


TECHNICAL NOTE

246

A Survey of Some Empirical and Semi-Empirical Interatomic and Intermolecular Potentials

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U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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ABSTRACT

Many empirical and semi-empirical potential functions have been proposed or developed to represent the pairwise interaction of atoms and molecules. The simple pair potentials proposed usually contain parameters to be adjusted to fit certain properties, for example, when chemical combination does not occur, virial coefficients and similar quantities for the gaseous state, or compressibility and heat of sublimation for the crystalline state. In the present survey a number of potentials proposed recently are examined to indicate the variety of concepts employed and the suitability of the potential functions.

Key Words: Atoms, compressibility, heat of sublimation, molecules, potential functions - empirical and semi-empirical, transport properties, virial coefficients

A SURVEY OF SOME EMPIRICAL AND SEMI-EMPIRICAL INTERATOMIC
AND INTERMOLECULAR POTENTIALS

Benjamin M. Axilrod*

1. Introduction

Many empirical and semi-empirical potential functions have been proposed or developed to represent the pairwise interaction of atoms and molecules.¹ These functions usually contain parameters to be adjusted to fit certain properties, for example, when chemical combination does not occur, virial coefficients and similar quantities for the gaseous state, or compressibility and heat of sublimation for the crystalline state. It should be emphasized that our interest is principally in pairs or systems that do not react chemically.

A proposed potential is judged a good approximation to the true interaction if the proposed function is successful in predicting experimental properties other than those used for obtaining the potential parameters. If a number of properties are predicted in agreement with experiment, we obviously have more confidence in the potential.

Usually, potentials of simple functional form are sought in order to facilitate the calculation of the various properties. The latter influence has sometimes led to the use of potential forms or of atomic models that are obviously incorrect, such as the rigid sphere atom model. Nevertheless, such incorrect potentials have often proved useful for indicating the sensitivity of different properties to the shape of the potential and for deriving approximations to various properties.

Some approaches are strictly empirical, others employ some classical or quantum theory concepts. In the following sections, a number of recent papers are examined to indicate the variety of concepts employed and the suitability of the potential functions.

Potentials given in earlier works and their application to equilibrium and transport properties in gases are described in the treatise of Hirschfelder, Curtiss and Bird [1]². Recent surveys of empirical potential functions for bound states of diatomic molecules, for which case spectroscopic information is the principal source of experimental data, have been made by Steele, Lippincott and Vanderslice [2] and by Varshni [3].

Since we are interested in methods that can apply or have been applied to the repulsive interaction, the papers discussed here were selected with this viewpoint. Some, however, which describe methods for bound states were included either because of possible application to repulsive interaction or because of the novelty of the method.

2. Repulsive Potential for Atoms in S States -- Buckingham

Buckingham [4] proposed a semi-empirical function to fit the repulsive interaction of a pair of atoms in S states for the internuclear separation R ranging from zero to the point where the potential is zero. He emphasized "the aim is to fit the correct repulsive potential so far as it is known, not merely an incomplete theoretical approximation, e. g., first-order perturbation energy" [4]. The function proposed was

$$V(R) = (Z_1 Z_2 / R) p(R) \exp(-aR) \quad (1)$$

¹Theory predicts that the interaction of a pair of particles (atoms, etc.) is influenced by the presence of neighboring particles. Since this complicates the problem, as a first approximation it is usual to disregard this effect. Intuitively, this approximation is better in gases (except at high density) than in solids or liquids.

²Numbers in brackets indicate literature references at the end of this paper.

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where Z_1 and Z_2 are the nuclear charges of the two atoms and $p(R)$ is a polynomial

$$p(R) = 1 + p_1 R + \dots + p_j R^j$$

usually of the fourth degree. The suitability of eq. (1) was indicated by noting it was consistent with the following facts: for extremely small separations, the interaction potential must be dominated by the Coulomb repulsion of the nuclei, and for larger separations theoretical calculations of the repulsion of two hydrogen or two helium atoms were found³ well represented by the product of a polynomial and an exponential, a property that might be expected to apply for other simple atomic pairs.

The arbitrariness in the choice of the constants \underline{a} and the p_i was reduced by examining the behavior of $V(R)$ for very small \underline{R} . For the latter condition, first-order perturbation calculation indicated that V_e , the electronic energy of the system,

$$V_e = V(R) - Z_1 Z_2 / R, \quad (2)$$

was approximately

$$V_e(R) \cong E_0 + E_2 R^2 + \dots \quad (2a)$$

where E_0 is the energy of the "united atom" of nuclear charge $Z_1 + Z_2$. Eq. (2a) together with eq. (1) yields the relations between \underline{p} 's and \underline{E} 's

$$p_1 = a + E_0 / (Z_1 Z_2); \quad p_2 = \frac{1}{2} a^2 + E_0 a / (Z_1 Z_2)$$

$$p_3 = \frac{1}{6} a^3 + [E_2 + \frac{1}{2} E_0 a^2] / (Z_1 Z_2).$$

Thus, if E_0 is known -- the electron configurations of the interacting atoms must be correlated with the proper united atom electronic state -- this information, together with data on the repulsive potential at various separations can be used to determine the constants in eq. (1).

The preceding ideas were applied [4] to the interactions $H + H(^3\Sigma)$, $H + He$, and $He + He$ and the results are summarized in the following paragraphs.

2.1 The $H + H(^3\Sigma_\mu \text{ State})$ Interaction

The excited state $(1s, 2p)^3P$ of He was taken as the appropriate united atom state. Insufficient experimental evidence existed for this case so the constants \underline{a} and p_1 were obtained by fitting (a) the experimental united atom energy⁴ and (b) for the range 1.5 to $6a_0$, theoretical calculations of James, Coolidge and Present [5] (for close distances) and of Hirschfelder and Linnett [6] (for larger separations). The potential derived to fit the above data for internuclear distances less than $6a_0$ was, in atomic units (e^2/a_0 , with R in units of a_0):

$$V(R) = (1/R)(1 + 1.167R + 0.039R^2 + 0.518R^3 + 0.864R^4) \exp(-2.3R). \quad (3)$$

³Buckingham examined the Heitler-London-Sugiura results and the Griffing-Wehner [J. Chem. Phys. 23, 1024 (1955)] data for hydrogen and helium, respectively.

⁴Measured relative to the separated atoms as the zero of energy. Thus: the energy of the $1S_0$ ground state of He is -2.903 atomic units, the energy of the $(1s, 2p)^3P$ state is 0.770 above the former; and the relative electronic energy of the united atom E_0 is

$$E_0 = E(\text{He: } 1s2p^3P) - 2E(\text{H: } 1s^1S) = -2.903 + .770 + 1.000 = -1.133.$$

In the various examples, Buckingham used electronic energies from C. M. Moore, Atomic Energy Levels, Vol. I. (Nat. Bur. of Standards, 1949).

Buckingham also gave an equation [eq. (3a), below] of the type of eq. (3), except with a fifth power polynomial, to fit the united atom energy and to approximate the James-Coolidge-Present data and a potential $V_{DL}(R)$ derived with second-order perturbation theory by Dalgarno and Lynn [7]. The potential V_{DL} was somewhat lower than that of Hirschfelder and Linnett and vanished between 5 and $6a_0$ and had a minimum about $7a_0$.

$$V(R) = (1/R)(1 + .967R - .174R^2 + .830R^3 + .54R^4 - .12R^5) \exp(-2.1R). \quad (3a)$$

Numerical values given by eqs. (3) and (3a) are listed in Table I.

TABLE I

Repulsive Potentials for H + He Interactions (in atomic units)

$R(a_0)$	H + H($^3\Sigma_u$) (From Table 1, reference 4)			H + He (From Table 2, reference 4)		
	Eq. (3)	JCP & HL ^a	Eq. (3a)	Eq. (5)	Scattering ^b	$V_{M.R.S.}$ (Eq. (4))
0.8	0.512	<u>JCP</u>	0.529	----	----	----
1.0	.360	----	.373	0.204	----	----
1.5	.190	0.190	.189	.120	----	----
1.87	.125	.125	.121	----	----	----
2.0	----	<u>HL</u>	----	.0750	0.0716	0.0904 ^d
2.629	.0495	.0486	----	----	----	----
3.0	----	----	.0241	.0191	.0188	.0194 ^d
3.077	.0268	.0261	----	----	----	----
4.0	----	----	.00397	.00329	----	.00332
4.018	.00639	.00686	----	----	----	----
5.0	----	----	.00037	.000422	----	.000506
5.012	.00119	.00145	----	----	----	----
6.0	----	----	-.00030	3.57 ^{-5c}	----	5.65 ⁻⁵
6.011	.00021	.00025	----	----	----	----

^aReferences 5 and 6, respectively.

^bReference 8.

^cA notation here and elsewhere such as 3.57⁻⁵ means 3.57 x 10⁻⁵.

^dCalculated from equation (4).

2.2 The H + He Interaction

The united atom ($Li(1s)^2(2s)^2S$) energy is available and also a potential derived from atom-atom scattering data [8] for separations of 2.2 to 3.2 a_0 . In addition it appears [4] that $V(R)$ was required to be zero for a value of R near 6.8 a_0 , the zero of an "exp-six" potential obtained by Mason, Ross and Schatz [9] for separations greater than 2 a_0 . The latter authors, to represent the repulsive energies they calculated for the range 2 to 5 a_0 by a variational method and to represent also the attractive dispersion energy which is important for larger separations, fitted their results with the equation

$$V(R) = 4.606 \exp(-1.76R) - 2.94/R^6. \quad (4)$$

The constant $C_{\text{H-He}} = 2.94$ was not fitted but was obtained [9] by applying combining rules to theoretically derived values of the dispersion force constants $C_{\text{H-H}}$ and $C_{\text{He-He}}$ for the interaction of the like pairs.

The repulsive potential obtained by Buckingham was

$$V(R) = (2/R) (1 + 0.113R - 2.069R^2 + 2.089R^3 - 0.259R^4) \exp(-2.15R) \quad (5)$$

The potential from scattering [8] and the theoretical calculations [9] are close near $3a_0$ separation so in this region equations (4) and (5) are in good agreement. The scattering potential near $2a_0$ is appreciably below the theoretical potential [9] so that as R decreases below $3a_0$ equation (5) yields lower values than (4). Between 5.5 and $6.5a_0$ where $V(R)$ is much reduced, (less than 2×10^{-4} compared to greater than 0.003 below $4a_0$) equation (5) yields values about two-thirds those of equation (4). Numerical values from equations (4) and (5) are shown in Table I.

2.3 The He + He Interaction

The interacting atoms are in $(1s)^2 \ ^1S_0$ states and it is assumed that the united atom state is $(1s)^2 (2s)^2$ as in Be (1S_0). The potential of equation (1) was fitted entirely to experimental data namely V_e for the united atom, potentials from scattering results (for distances of 1 to $2a_0^{10}$ and 2.5^e to $3a_0^{11}$) and the zero of $V(R)$ to R_0 , the zero of empirical potentials⁵ based on analysis of equilibrium and transport properties of helium gas.

The derived potential was

$$V(R) = (4/R) (1 + 0.265R - 2.419R^2 + 2.616R^3 - 0.436R^4) \exp(-2.48R) \quad (6)$$

Since as R decreases from 3 to $1a_0$ the atom-atom scattering potential [10, 11] differed increasingly from some contemporary quantum theoretical calculations [12, 13] of the interaction (from near agreement to four times smaller) equation (6) does likewise in this range. Potential values obtained from equation (6) and from the scattering data used are shown in Table II, and in Figures 1 and 2.

Subsequently Buckingham and Duparc [14] made a quite accurate quantum mechanical calculation of the He + He interaction for the range zero to $0.8a_0$. The electronic energy V_e was in good agreement with a value at 0.4 \AA calculated with different wave functions by Ransill [15]. A semi-empirical potential, equation (6a), to improve on equation (6) was derived by fitting: the experimental united atom energy; a theoretical value by Bingel's [16] method⁶ (and with BD wave functions) of E_2 , the coefficient of R^2 in equation (2a) for V_e ; recent atom-atom scattering data [17] for separations⁷ of 1.8 to $2.8a_0$;

⁵In reference 4 use is made of the Lennard-Jones (12-6) potential of de Boer and Lunbeck [R. J. Lunbeck, Thesis, Amsterdam (1951)], and an (exp-6, 8) potential [R. A. Buckingham and R. A. Scriven, Proc. Phys. Soc. A65, 376 (1952)] which had zeros at 4.84 and $4.94a_0$, respectively.

⁶Reference 16 gives explicit expressions for E_2 and for E_3 , the coefficient of R^3 if equation (2a) is extended, in terms of the electron charge densities of the united atom.

TABLE II

Repulsive Potentials for He + He Interaction (in atomic units)

R(a ₀)	Buckingham (1958)		Buckingham and Duparc (1962)			Recent Scattering (S) and Theoretical (T) Values, ^d
	Equation (6)	Scattering	Equation (6a)	Scattering ^c	Lowest B. D. Theo. Value	
0.8	0.567		0.939		1.516	
1.0	.344	.331 ^a	.621			0.918T
1.04						.537S
1.4	.189	.181 ^a	.309			.406T
						.233S
1.89						.129S
2.0	.0814	.0958 ^a	.0958	.0959		.120T
2.8			.0148	.0176		
3.0	.0120	.0111 ^b	.00879			
4.0	.942 ⁻³		.454 ⁻³			

^a Reference 10.^b Reference 11.^c Reference 17.^d S. from reference 18; ^T from reference 19, computed from $V(R) = 7.036 \exp[-3.846R(\text{\AA})]$ a. u., an equation in reference 19 for range 0.5 to 1.0A^o.

and the zero of $V(R)$ in equation (1) which was adjusted to be at $4.90a_0$, "roughly in accord with other empirical evidence". The equation obtained was

$$V(R) = (4/R) [1 + .611R - 2.268R^2 + 4.033R^3 - .736R^4] \exp(-2.826R) \quad (6a)$$

The above semi-empirical potential was lower than the best BD theoretically derived potential over the entire range from zero to $0.8a_0$ (the difference increasing from about 1% to 17% in $V_e(R)$ and being about 40% in $V(R)$ at $0.8a_0$).

Equation (6a) was noted [4] as being appreciably higher than the potential from the 1949 scattering data [10] for the range 1 to $2a_0$. Very recent scattering experiments [18] for this range yield a higher potential particularly at $1a_0$, and are in better agreement with equation (6a). Some of these points are apparent from the data in Table II which includes potential values derived from equation (6a), the scattering data used as a guide in obtaining the latter equation, and also the most recent scattering data [18] for small separations and some of the results of Phillipson's elaborate theoretical potential calculation [19]. The last two sets of data indicate a sizeable disagreement still existing between atom-atom scattering and quantum theory calculations near $1a_0$ separation so that in fitting a semi-empirical function of equation (1) type a choice must be made between fitting the theoretical or experimental data or a composite of the two.

3. SEMI-EMPIRICAL FUNCTIONS -- Frost and Associates

Frost and Associates [20, 21, 22] proposed semi-empirical potential energy functions for diatomic molecules and for the repulsion of inert gas atoms. The plan [20] was to cover the range from the united atom to the separated atoms and to use the known properties of these two cases as a guide in the choice of functions.

Initially [20] calculations were made for H_2^+ and H_2 in bound ground states, first with the simple two parameter potential

$$V(R) = (e^2/R - b) \exp(-aR), \quad (e \text{ is the electronic charge}) \quad (7)$$

and next with a more complicated one-parameter potential having the form of the energy for the H_2^+ ion as obtained in a simple quantum mechanical calculation. Equation (7) was selected to fit some theoretical considerations including:

a. V , the potential for nuclear motion is the sum of the nuclear repulsion and of V_e , the electronic energy.

b. The electronic energy $V_e = V - e^2/R$ must remain finite as R vanishes, and should vary as $-e^2/R$ for large R .

c. V must be capable, with appropriate constants, of having a minimum.

With equation (7) two of the three spectroscopic constants, equilibrium separation, R_e , the dissociation energy, D_e , and the force constant, k_e , were used in various combinations to calculate the third constant as well as other spectroscopic or related constants, i.e., higher derivatives of the potential.

Subsequently equation (7) was modified [21] to apply to general diatomic molecules by replacing e^2 with c where c was taken as $Z_1 Z_2 e^2$, the product of "effective" nuclear charges:

$$V(R) = (c/R - b) \exp(-aR) \quad (8)$$

The parameters a , b and c were derived in terms of the spectroscopic constants D_e , R_e and k_e from the values at the minimum of the potential, its first derivative and its second derivative (equal to k_e). The relations for the parameters are:

$$a = p/R_e, \quad b = D_e (1+p) \exp(p), \quad c = D_e R_e p \exp(p) \quad (9)$$

$$\text{where } p = (1 + k_e R_e^2 / D_e)^{1/2} - 1.$$

These potential parameters were obtained for nine hydrides and ten homonuclear diatomic molecules; in five instances the same element was common to the hydride and the homonuclear molecule. The third and fourth derivatives of the potential of equation (8) were calculated and were compared with values obtained from the experimental spectroscopic quantities, α_e and $\omega_e x_e$, the vibration-rotation coupling and the anharmonicity constants, respectively. The calculated results [21] were of the right order of magnitude but were not better than those obtained with the Morse or some other semi-empirical functions.

The constant c was studied, first to see if the same value of Z was obtained for the hydride of an element and its diatomic molecule; then a comparison was made with the effective nuclear charge for the valence electrons as given by Slater's rules. For the latter comparison there was correlation but for the heavier nuclei the correlation was poor.

In later work [22] semi-empirical potentials were proposed by Frost and Woodson for inert gas atoms and for diatomic molecules to include the $1/R^6$ dispersion forces, and for the diatomic ionic interaction if present. The inert gas potential suggested was

$$V_{ig} = (c/R) \exp(-aR) + b \exp(-aR) - d [1/R^6 - F(aR)] \quad (10)$$

where $F(aR)$ is a function such that the bracketed term remains finite as R goes to zero. For diatomic molecules including the case of ionic interaction the first term in equation (10) was replaced by

$$c'/R + [(c-c')/R] \exp(-aR) \quad (10a)$$

where c' is the product of the ionic charges and c is as previously defined. It was then suggested that the interatomic potential in an alkali halide molecule could be represented as the sum of the interaction of the isoelectronic inert gas atom pair, i.e., for $K^+ + Br^-$ the pair $Ar + Kr$, plus the Coulombic interaction of unit positive and negative point charges at the internuclear distance R . For convenience the simple exponential-six potential

$$V(R) = A \exp(-BR) - C/R^6$$

of Whalley and Schneider^[23] including their parameters was adopted by Frost and Woodson to represent the "inert gas portion" of the alkali halide potential. Surprisingly close agreement with experimental dissociation energies and equilibrium separations, usually within a few percent, was obtained for (Table III) a series of molecules from KCl (isoelectronic to $Ar-Ar$) through CsI (isoelectronic to $Xe-Xe$). For mixed inert gas atom pairs the combining rules of Mason^[24] were used. Probably a cancellation of neglected effects was responsible for the close agreement between calculated and experimental data.

4. POTENTIAL FOR INERT GASES - Woolley

Woolley^[25] considered the behavior of the modified Buckingham exp-six potential which had been used for a number of gases to fit second virial coefficient, transport and crystal data. This potential is a modification of the following:

$$V(R) = [\epsilon/(1-6/\alpha)] \{ (6/\alpha) \exp[\alpha(1-R/R_m)] - (R_m/R)^6 \}, \quad (11)$$

TABLE III (from Reference 22)

Comparison of Calculations with Observed Data for
Some Alkali Halide Gas Molecules

Diatom	R_e (calcd.)	R (obsd.) ^a	D_e (calcd.)	D_e - (obsd.) ^b
KCl	5.075	5.0392	0.1808	0.1814
KBr		5.3304		.1735
RbCl	5.300	5.2664	.1739	.1763
KI		5.7596		.1622
CsCl	5.555	5.4920	.1633	.1683
RbI		6.0035		.1568
CsBr	5.846	5.8053	.1556	.1616
CsI	6.354	6.2645	.1402	.1561
RbBr	5.531	5.5649	.1672	.1681

$$\left(\frac{dV}{dR}\right)_R = R_e = 0; D_e = -V(R_e)$$

^aSee A. Honig, M. Mandel, M. L. Stitch and C. H. Townes, Phys. Rev. 96, 629 (1954).

^bCalculated from E. S. Rittner, J. Chem. Phys., 19, 1030 (1951).

where the potential has a minimum at R_m , $-\epsilon$ is $V(R_m)$ and α determines the steepness of the repulsive part of the potential. The potential of equation (11) has a spurious maximum at a small separation, R_{max} . This has been corrected by arbitrarily defining the potential of equation (11) as infinite for R less than R_{max} . With the latter adjustment one has the modified Buckingham exp-six potential;

$$V(R) \text{ as in equation (11), } R \geq R_{max}$$

$$V(R) = \infty, \quad R < R_{max} \quad \{11a\}$$

Woolley desired a more realistic potential in order to extend calculations to higher temperatures. He sought an analytic function for the potential of inert gases that would extend to very small separations and would include a term giving essentially an inverse sixth power attraction near the potential minimum and beyond. At extremely close approach of a pair of inert gas atoms the interaction should be the Coulombic nuclear repulsion and with increasing separation, screening of the nuclei by the electrons would cause a decay in repulsion more rapid than as $1/R$. A very general type of function was proposed. An example of this function for which some calculations were made is (equation 10 of reference 25):

$$V/\epsilon = \frac{1+\gamma}{\gamma-5+\mu} \left\{ \frac{6-\mu}{1+\gamma} (R_m/R) \exp[\gamma(1-R/R_m)] - (R_m/R)^6 \left(\frac{1-\exp(-\gamma R/R_m)}{1-\exp(-\gamma)} \right)^8 \right\} \quad (12)$$

where $\mu = 8\gamma/[\exp(\gamma) - 1]$ and R_m is the equilibrium separation.

The above is a scaled equation and the parameter γ together with R_m introduce the influence of screening of the nuclear charges by the electron shells. In reference 25, γ was related to the α of the modified Buckingham equation, equation (11a), in several ways such as equating second, or third derivatives at the minimum for equation (11a) and for equation (12) with the factor $(-)^8$ omitted.

The eighth power correction factor defined $f(R)/f(R_m) = (-)^8$ which multiplies the van der Waals attraction type potential $(R_m/R)^6$ in the second term in eq. 12 was made plausible as follows: The attractive term is proportional to the product of the effective polarizabilities of the interacting atoms; the effective polarizability when two atoms overlap is taken as that part contributed by the non-intersecting spherical electron cloud centered on each nucleus. From the estimate of the effective polarizability a correction factor we define as F , corresponding to $f(R)/f(R_m)$ and more complicated than the latter, was obtained. The factor F was found to vary with the eighth power of the distance R for very small separations; the factor $f(R)/f(R_m)$ has the same R dependence at small separations and in general similar behavior to F .

The function equation (12) was graphed [25] for integral values of γ from 11 to 15 for R/R_m from about 0.1 to 1.4 and with the convenient linear ordinate $\log_{10} [(V/\epsilon) + 2]$ to give coincidence of curves at the minimum.

The curves (Figure 4) were compared with plots of repulsive potentials derived from inert gas scattering data by Amdur and associates [26] (for the gases He through Xe) and Berry⁷ (for Ne and Ar).

The helium, neon and argon scattering data of Amdur and associates were fitted by γ values of about 11, 13, and 11, respectively; Berry's data for argon fitted the curve for γ equal to 12. For krypton and xenon the potential from scattering deviated more from parallelism to the family of curves of equation (12) than the scattering potentials for the other gases.

The behavior of the potential of equation (12) as the separation approached zero was examined [25] to see if it approached the Coulombic nuclear repulsion when the parameters γ etc., chosen as above to fit the experimental data, were inserted. With the latter parameters the coefficient [defined $(Z_1 Z_2)_{calc}$] of the $1/R$ term of equation (12) for R approaching zero was within an order of magnitude of $Z_1 Z_2$ for the inert gases. The values of $(Z_1 Z_2)_{calc}$ and $Z_1 Z_2$ for He, Ne, Ar, Kr and Xe pairs were roughly, respectively: 10, 4; 310, 100; 800, 320; 250, 1300; and 730, 2900.

5. EMPIRICAL POTENTIALS FITTED TO GAS OR GAS AND CRYSTAL DATA

5.1 Mason and Rice

Mason and Rice [28], following a procedure of Corner [29], used experimental data from both the crystalline and gaseous states to obtain parameters for the modified Buckingham exp-six potential (equation 11a) for a series of non-polar molecules.⁸ In their work [30] on hydrogen and helium which was based on experimental gas data only, they found that this exp-six potential was an improvement over the Lennard-Jones (12-6) potential for reproducing second virial and viscosity coefficients.

⁷To reduce the scattering data to units of V/ϵ and R/R_m , the values of ϵ and R_m determined by Mason and Rice (reference 28) were used.

⁸This work (reference 28) is referred to in reference 1, page 181, where the derived potential parameters are tabulated. We include a summary of reference 28, as the procedure for obtaining the parameters is of interest in discussing other researches.

In a subsequent paper [28], in which calculations were made on spherical (Ne, Ar, Kr, Xe, CH₄) and non-spherical (N₂, CO, CO₂) molecules, a different approach was taken. The procedure for obtaining the potential parameters was very briefly as follows. Crystal data, namely, the nearest neighbor distance or crystal lattice spacing r_0 and the heat of sublimation at absolute zero $\Delta H(0^\circ)$ were used to obtain the values of the parameters R_m and ϵ corresponding to each one of a series of selected a values. With one of the latter pairs of values of R_m and ϵ , the experimental second virial and viscosity coefficients as functions of temperature were fitted to theoretical expressions¹⁰ for these coefficients to obtain a new value of a . If the a for the crystal and gas properties agreed, all three parameters (a , R_m , ϵ) were accepted as representative for the substance; otherwise the process was repeated for another pair of values of R_m and ϵ .

The best values of the a 's were in the range 12 to 14 for the spherical molecules.

For the spherical molecules the gas properties, second virial coefficient, viscosity, self and thermal diffusion coefficients were calculated for the Lennard-Jones (12-6) potential with the parameters R_m and ϵ/k derived by the Corner method from crystal or crystal and second virial data. The values obtained as a function of temperature were compared with corresponding exp-six potential values and experimental data. No overall superiority was indicated for one type of empirical potential relative to the other.

It was noted [28] that for gases composed of non-spherical molecules the two parameter Lennard-Jones (12-6) potential

$$V(R) = \epsilon \left[\left(\frac{R_m}{R} \right)^{12} - 2 \left(\frac{R_m}{R} \right)^6 \right]$$

has not been too successful in fitting different properties with a single set of parameters, and that the exp-six potential with three parameters might be more successful. However, from the analysis for this type molecule¹¹ it was found necessary with the exp-six potential [eq. 11a] to choose different parameters to reproduce different properties. This behavior was considered an indication that the assumptions of central intermolecular forces and elastic collisions are not adequate to describe the behavior of most real gases.

5.2 Whalley and Schneider

A slightly different approach from that of Mason and Rice was taken by Whalley and Schneider [23]. The latter used their second virial coefficient measurements [31, 32] (for the range about 300 to 900°K) on argon, krypton and xenon to obtain the best parameters for the Lennard-Jones (12-6) and (9-6) potentials and the modified Buckingham exp-six potential of equation (11a); these potentials were then used to derive crystal data.

⁹ See Appendix for more detailed outline of Corner's procedure.

¹⁰ The theoretical expressions (see reference 1, Chapters 3 and 8) for particular intermolecular potentials are usually developed in terms of the reduced temperature, $T^* = kT/\epsilon$. For example, the second virial coefficient in "reduced form" is $B(T) = b_0 B^*(\beta, T^*)$ where β is a parameter characteristic of the potential (β is the a of the exp-six potential). $b_0 = (2/3) \pi s^3$ where s may be R_0 or R_m depending on the potential form. For each type of potential B^* is calculated as a function of T^* for a set of β values. For the modified Buckingham potential of equation (11a) B^* was tabulated by Mason and Rice [J. Chem. Phys. 22, 522 (1954)].

¹¹ Actually, calculated results were given for CO and N₂ which crystallize in their lowest temperature phases in the cubic close-packed lattice, the case for which the Corner relations had been obtained at the time of the work done in reference 28. CO₂ and O₂, for which the lowest temperature form was stated²⁸ as not cubic, were only examined in regard to fitting the second virial and gas viscosity data with an exp-six potential and it was found that different parameters were needed for the two properties.

As far as fitting the second virial coefficients, the "goodness of fit", based upon the standard deviation of the difference of the experimental and calculated second virial coefficient, was about the same for all three potentials. In the case of krypton and xenon the exp-six potential gave equally good fits for α in the range 12 to 15; for argon, a good fit was obtained only with α of 15.

TABLE IV

Potential Parameters and Crystal Data for Argon, Krypton and Xenon^[23]

	Potential	ϵ/k	R_m	r_0	$\Delta H(O^\circ K)$
		$^\circ K$	\AA	\AA	kcal/mole
Argon	L.J. (9-6)	89.6	4.08	3.93	1.718 ± 5^a
	L.J. (12-6)	119.5	3.83	3.76	2.033 ± 6
	Exp-6, $\alpha=15$	131.5	3.73	3.74	2.128 ± 7
Experimental				3.81	1.998 ± 40
Krypton	L.J. (9-6)	125.1	3.94	3.78	2.400 ± 6
	L.J. (12-6)	166.7	4.13	4.04	2.848 ± 8
	Exp-6, $\alpha=12$	144.9	4.35	4.21	2.536 ± 10
	$\alpha=15$	183.6	3.96	3.90	2.574 ± 8
Experimental				3.93	2.733 ± 50
Xenon	L.J. (9-6)	168.4	4.89	4.68	3.236 ± 23
	L.J. (12-6)	225.3	4.57	4.45	3.850 ± 10
	Exp-6, $\alpha=12$	196.1	4.80	4.64	3.397 ± 18
	$\alpha=14$	233.3	4.58	4.48	3.861 ± 16
	$\alpha=15$	248.9	4.50	4.41	4.043 ± 16
Experimental				4.30	3.936

Note a: Value \pm std. error. Std. errors for the other quantities are reported in reference 23.

Some of the results including the crystal data; namely, nearest-neighbor distance, r_0 , and heat of sublimation ΔH ($O^\circ K$) (obtained using Corner's [29] equations) are shown in Table IV. It should be noted (Table IV) that the potential parameters R_m and ϵ varied considerably for the different potentials.

It was concluded [23] that the crystal properties were moderately well predicted using any of the potentials derived from the second virial data and that one potential could be chosen which would fit either r_0 or ΔH quite well but not both together; the potentials were considered too simple to fit all three properties exactly [23].

It is of interest to compare the potential parameters of the present and previous sections. For Ar, Kr, and Xe, respectively, the LJ (12-6) parameters of Whalley and Schneider and of Mason and Rice [28] (shown in parentheses) are: for R_m in \AA , 3.83 (3.87), 4.13 (4.04), 4.57 (4.46), i.e., about 1 to 2 percent different; for ϵ/k in $^\circ K$, 119.5 (119.3), 166.7 (159), 225.3 (231.2), or

about zero to 3 percent different. The exp-six data is not so readily compared as the α 's were usually different and as is evident from Table I the other parameters are sensitive to α .

5.3 Schamp and Associates

Experimental and theoretical work similar to that of Whalley and Schneider [23] (WS) was carried out on methane, an approximately spherical molecule, by Schamp et al.³³ The experimental temperature range, 273° to 473°K was rather limited. Following the determination of the second and third virial coefficients, the WS procedure was used on the second virial data to obtain parameters for the Lennard-Jones 12-6 and 9-6 potentials and the modified Buckingham exp-six potential (with α 's from 12 to 15).

With the standard deviation of the difference between calculated and experiment second virial values as a criterion, and with due regard for experimental uncertainty, it was concluded that no potential was superior to the others for representing the temperature dependence of the second virial. Similarly to the previous case (Table IV), the potential parameters varied considerably between potentials.

The various sets of potential parameters were used to obtain (from Corner's equations) the crystal data, namely the heat of sublimation, $\Delta H(O^\circ K)$, and r_o , the nearest-neighbor distance (measured between molecular centers). The results are:

Potential	r_o , in \AA	$\Delta H(O^\circ K)$, kcal/mole
L.J. (9-6)	4.41	2.12
L.J. (12-6)	4.22	2.51
Exp-6, $\alpha=12$	4.39	2.23
$\alpha=13$	4.31	2.38
$\alpha=14$	4.24	2.52
$\alpha=15$	4.18	2.64
Experimental	4.16	2.51

The agreement between calculated and experimental values is best for the L.J. (12-6) potential and the exp-six potential with α equal to 14 or 15.

The viscosity of methane was calculated for the various potentials listed above (except L.J. (9-6), for temperatures from 90 to 772°K. From the average and the maximum deviations relative to measured data, it was noted there was little difference between the potentials although the exp-six with α equal to 12 or 13 gave the poorest fits. For all potentials and at all temperatures the calculated values were lower than those measured by an average of at least 3 percent.

5.4 Konowalow and Hirschfelder

An analysis following Corner's procedure was made for the nonpolar gases Ne, Ar, Kr, Xe, CH_4 and N_2 by Konowalow and Hirschfelder [34] who assumed a Morse intermolecular potential:

$$V(R) = \epsilon (x^2 - 2x) \quad (13)$$

where

$$x = \exp [-(c/R_o) (R - R_m)]$$

As before, R_o is the separation at which $V(R)$ is zero, ϵ is the depth of the potential well and R_m is the separation at the minimum. As a preliminary, calculations for the above potential were made of the theoretical second virial coefficient [35]; lattice sums needed for using crystal data to obtain potential parameters were also determined [34]. The experimental crystal data r_o and ΔH were used for a series of c values to obtain pairs of values of ϵ and R_m . With the

latter parameter values, theoretical second virials were computed and the c selected which yielded the best fit to the experimental virial coefficient at or near room temperature.

The parameters for the Morse potential were:

Ne	5.1	2.775	3.152	43.99
Ar	5.0	3.386	3.855	144.8
Kr	4.5	3.510	4.038	182.7
Xe	4.9	3.872	4.420	274.7
CH ₄	4.9	3.683	4.204	177.5
N ₂	5.5	3.579	4.030	134.4

The parameters R_m and ϵ/k were compared [34] to similar parameters obtained by Mason and Rice²⁸ for the equation (11) exp-six and the Lennard-Jones (12-6) potentials. The separation at the minimum, R_m , agreed to within a percent for all three potentials.¹² Except for neon, ϵ/k was 15 ± 2 percent greater than for the exp-six potential, for which in turn ϵ/k was very slightly greater* (by about one to three percent) than for the L. J. (12-6) potential.

A test of the derived Morse potential was made by calculating the second virial coefficient for temperature higher than room temperature (to about 800°K) and also for Ne, Ar and N₂ to lower than room temperature. The derived virial coefficients together with values obtained for the exp-six and the L. J. (12-6) potential, both sets based on the potential parameters of Mason and Rice²⁸, were all compared with experiment. Figure 5 shows these results for argon. Except for krypton the agreement was considered good with the concordance of the first two slightly better than for the (12-6) potential. For krypton¹³ none of the three potentials fitted the experimental data closely over the temperature range.¹⁴ A good fit for krypton, however, was obtained by using two sets of Morse parameters ($\epsilon_h, c_h; \epsilon_t, c_t$) one for $R < R_0$ the other for $R > R_0$; the potential, but not the first derivative, was required to be continuous at R_0 .

5.5 Extrapolations

In concluding this section of fitting empirical potentials to gas and crystal data, we refer briefly to other work which suggests limitations of the method such as extrapolation of the potential to pair separations outside the range for which the parameters were fitted and also application to other properties than those used for fitting. (Some evidence on the latter was mentioned for the data on Ar, Kr and Xe by Whalley and Schneider).

¹²Except for N₂ and the L. J. (12-6) data for which the comparison values were from Table I-a² of reference 1.

¹³In reference 28 the graph for krypton extends to less than 600°K this partly explains the difference in conclusions in references 34 and 28; in the latter, it was noted that the L. J. (12-6) potential did not give a good fit for krypton although the exp-six did so.

¹⁴It should be noted that our manuscript, which was completed in the summer of 1963, contained literature references only up to April 1963. Information that came to my attention (Dec. 1963) work by Saxena and Gambhir [S. C. Saxena and R. S. Gambhir, 6 (6), 577 (1963)] indicates that the low temperature second virial coefficient data for argon, krypton and methane are fitted much better particularly at low temperatures by a Morse potential as compared to the Lennard-Jones (12-6) or the modified Buckingham (exp-six) potential [m. B. (exp-six)] suggested combining rules for computing the potential parameters for the Morse potential parameters for the Morse potential between two unlike molecules from the known corresponding parameters of the like molecules. They find for the atom pairs, Ne-Ar, Kr-Ar and Ar-CH₄ the overall agreement is reasonable and also somewhat better than that obtained with the L. J. (12-6) and m. B. (exp-six) potentials.

As to the first point, Abrahamson [36] made theoretical calculations by the Thomas-Fermi-Dirac statistical method of the repulsive interaction for like pairs of the inert gases, helium through radon. A comparison of his results to semi-empirical, experimental and other theoretical calculations was made (see Figures 6-12). He stressed the superiority of the modified Buckingham exp-six potential over the Lennard-Jones (12-6) potential for representing repulsive interactions at very small separations, which we estimate as roughly $1/2 R_m$ to $1/4 R_m$.

Guggenheim and McGlashan [37] made an extensive study of the properties of argon, mostly for the crystalline state, for a semi-empirical potential that they devised. This (GM) potential had the following features; near the minimum, $R = R_m$, it was an anharmonic oscillator type with cubic and quartic terms,

$$V = -E + Ks^2 - As^3 + Bs^4 \text{ where } s = (R - R_m)/R_m;$$

for distances $R > 1.4 R_m$ (i.e., greater than the nearest-neighbor distance r_0 in the crystal, as r_0 is roughly equal to R_m) a simple attractive term c_1/R^6 was used with c_1 taken from theoretical calculation; between the first and second regions a graphical interpolation was introduced; for small distances $R \leq d$ a hard sphere potential was employed; a graphical interpolation connected the point $V(R=d)=0$ with the first region - d was adjusted to fit both high temperature second virial coefficient (gas) data and an average of the effective diameter obtained by inserting high temperature experimental viscosities into theoretical expressions for the viscosity of a gas of hard spheres. The (GM) potential for argon atoms is shown in Figure 15.

The vibrational energy of the lattice was approximated by using the Einstein assumption of a single characteristic frequency ν and first disregarding anharmonicity in the vibrations of the atoms about equilibrium. With this approximation and the above potential as a basis, expressions for the face-centered cubic lattice were obtained for a) ν , b) the partition function, c) the molar free energy, d) the total energy, e) the entropy and f) the equation of state -- a), c), d) and f) all in terms of r_0 and R_m and the other pair potential parameters. (Use was later made of the fact that a) and f) do not depend on the parameter $E \equiv -V(R_m)$. To obtain a measure of the importance of the quartic term calculations were made with $B = 0$ and $B = A$.

The procedure for getting the potential constants was roughly as follows. Values of ν were obtained as a function of temperature from experimental entropy data by using equation (e). The equation (a) and equation (f) ($p\nu/RT = \dots$) for zero pressure yield two equations, linear in \underline{K} and \underline{A} and whose coefficients, the F's and G's, are simple functions of R_m and r_0 :

$$\text{from (a); } \nu^2 R_m^2 = KF_1 + AF_2 + C_1 F_3$$

$$\text{from (f); } 0 = KG_1 + AG_2 + C_1 G_3 - (1/\nu R_m^2) \coth(h\nu/kT)$$

$$[KG_4 + AG_5 + C_1 G_6]$$

where \underline{T} is the temperature and h and k are the Planck and Boltzmann constants, respectively. For a chosen temperature, $T = T_t$ (triple-point = 838°K), the pair of equations was solved repeatedly for series of trial values of R_m . The solutions for \underline{K} and \underline{A} were plotted as functions of R_m . The process was repeated for another suitable temperature,¹⁵ chosen as $1/2 T_t$. The intersection of the two \underline{K} curves yielded a value of \underline{K} and of R_m ; similarly the \underline{A} curves yielded a value of \underline{A} and of R_m . The values of R_m at the two intersection points needed to be the same. This was found true when C_1 was varied over a modest range of its theoretical value.

With R_m , \underline{K} and \underline{A} known, the parameter \underline{E} was then found by assuming the experimental enthalpy, H_m^{exp} , to be equal to the total energy (reasonable at low pressure) and inserting H_m^{exp} in expression (d) for the total energy and solving for \underline{E} .

¹⁵The two temperatures should differ widely and also the lesser must not be so low that the uncertainty in the experimental entropy would be large and that the Einstein approximation would be a poor one.

Calculated values [37] of the temperature dependence (from 25° to T_t) of the entropy, enthalpy and molar volume, and the pressure dependence of the molar volume for the crystalline state, and also the second virial coefficient for the gas was obtained for the (GM) potential and compared both with experiment and with similar data for a Lennard-Jones (12-6) pair potential. The constants of the latter potential were fitted to crystal properties (lattice constant and heat of sublimation at 0°K).¹⁶

For the second virial coefficient the two potentials were equally suitable for reproducing experimental values. For the temperature dependence of entropy¹⁷, total energy (enthalpy) and molar volume (proportional to r_0^3) Guggenheim and McGlashan found their potential superior to the L.J. (12-6) potential while for the pressure dependence of the molar volume the reverse was true. Since Zucker¹⁸ actually obtained the parameters for L.J. (m-6) potentials with m varied between 10 and 14 and then chose that m value namely 12 which yielded the best fit to the experimental data for pressure dependence of molar volume, this superiority of the L.J. (12-6) is not unexpected.

The influence of anharmonicity in the vibrational motion of the atoms on the various calculated crystal properties for the (GM) potential (with $B = A$) was slight in contrast to the similar effect of anharmonicity for the L.J. (12-6) potential. From an examination of the equations (e) and (f) it was observed that the effect of anharmonicity was much greater on the pv product than on entropy. However, it was found for the former quantity that, using accepted values of E , K , A and C , the sign of the effect of anharmonicity depended on the magnitude of B . The authors believed [37] that they could not expect a reduction in their ignorance of B by improvement in theory or experiment and concluded it was best to ignore the influence of anharmonicity of the vibrations.

The lesser flexibility of the L.J. (12-6) compared to the (GM) potential was emphasized by Guggenheim and McGlashan who observed that the former potential is equivalent in the (GM) potential to fixing the constants K , A , B and C , all in terms of E . Nevertheless the L.J. (12-6) potential predicted all the crystal properties except entropy to within a few percent.

6. Delta Function Models

As a step in the direction of calculating the intermolecular potential by detailed quantum theoretical methods, very approximate calculations have been made for simplified atomic and molecular models. An example is the use of models in which delta function potentials [38, 39, 40] are substituted for Coulomb potentials to represent the electron-nucleus interaction, together with other simplifying assumptions. Normally the problem is treated as one-dimensional. Usually the case of the one electron hydrogenlike atom or two electron molecule is first solved and generalization to many-electron molecules made by some semi-empirical process based on physical intuition.

¹⁶The L.J. (12-6) parameters of Domb and Zucker [C. Domb and I. J. Zucker, Nature (London) 178, 484 (1956) and I. J. Zucker, J. Chem. Phys. 25, 915 (1956) were used.

¹⁷Since experimental entropy data were fitted to v , an exact fit would be expected³⁷ for this property.

¹⁸See previous footnote on page 14.

6.1 Frost

Frost [38] solved the Schroedinger equation for the problem of a hydrogenlike atom with the delta function potential taken as the limiting form of a square well potential of width \underline{w} and depth \underline{V} as the well became indefinitely narrower and deeper while the "strength" $\underline{g} = \underline{w} \underline{V}$ remained constant. The correct atomic energy levels were obtained if the delta potential strength \underline{g} was set equal to Ze^2/n ($-e$ is the electronic charge, Z the nuclear charge and n the principal quantum number). This accurate result was attributed [38] to a cancellation of error from the use of the delta function potential with a one-dimensional model.

For the molecule-ion H_2^+ the solution [38] of a Schroedinger equation with a delta potential centered at each nucleus was obtained. The results were less satisfactory; the ground state electronic energy being (over a range of nuclear separations) nearly half that for accurate calculations; also when the internuclear repulsion was added to the electronic energy to obtain a potential energy curve for internuclear motion, unsatisfactory values for the equilibrium separation R_m and dissociation energy D_e , occurred.

6.2 Lippincott

Similarly to Frost, Lippincott [39] represented the interacting atoms by a one-dimensional model in which atomic delta potentials, each a limiting form of a square well potential, are combined on bond formation to form a molecular delta potential; interelectronic repulsion was ignored. To overcome the difficulty encountered on bond formation by Frost who used delta functions centered at the nuclei, Lippincott allowed the delta potentials to shift or float¹⁹ symmetrically from the nuclei. The arbitrary assumptions were made: "a) Bond formation can result from the coalescing of two shifted atomic delta functions of the correct separated atom energy into a molecular delta function in which the delta functions are located back on the nuclear positions when the internuclear distance is equal to the equilibrium bond length. b) The interatomic attraction and internuclear repulsion may be implicitly allowed for by the shifts of the delta functions from the nuclear positions, with the result that the total energy of the system may be identified with that obtained by solution of the Schroedinger equation for the model". Treating the molecule-ion H_2^+ first, Lippincott found, on solving the Schroedinger equation with square potential wells and then passing to the limit (delta potentials), a total energy

$$E = - (me^4/2 \chi^2) [1 + \exp(-ca)]^2, \quad (14a)$$

where the variable \underline{c} , roughly proportional to the delta potential strength, is given by

$$c = (me^2/\chi^2) [1 + \exp(-ca)]. \quad (14b)$$

\underline{a} is the separation of atomic delta potentials, \underline{m} , \underline{e} and χ are the usual atomic constants. Equation (14b) is solved for \underline{c} by trial, but first a suitable relation between \underline{a} and nuclear separation \underline{R} is required. A simple equation to fit assumption (b) and to yield a potential minimum was assumed, namely

$$a = R[1 - R_m/R + (R_m/R)^2] \quad (15)$$

where R_m is the nuclear separation at the energy minimum. From equation (15) we see that for stretched bonds \underline{a} is less than \underline{R} and for compressed bonds \underline{a} is greater than \underline{R} ; furthermore \underline{a} is always greater than R_m except at equilibrium.

If the separated atom energy, $E(R = \infty) = -me^4/2 \chi^2$ (here the energy of one hydrogen atom), is subtracted from the total energy in equation (14a), one obtains the interaction potential $V(R)$.

¹⁹Floating wave functions, derived for Coulomb rather than delta potentials, were first used by Gurnee and Magee [E. F. Gurnee and J. L. Magee, J. Chem. Phys. 18, 142 (1950)] for two bonding hydrogen atoms. Hurley [A. C. Hurley, Proc. Roy. Soc. A226, 179 (1954)] also studied the behavior of floating wave functions prior to Lippincott's work.

For nuclear separations of interest the term $\exp(-2ca)$ in equation (14a) was small relative to $\exp(-ca)$ and was neglected.²⁰

Bond properties such as \underline{c} , \underline{R}_m , dissociation energy \underline{D} and force constant $k_e = (d^2E/dR^2)$ were calculated³⁹ for H_2^+ and the results agreed well with experiment. The experimental value of \underline{c} is defined in terms of other experimental bond properties as $c = (1/2) k_e R_m / D_e$.

The solution of the hydrogen molecule problem was considered similarly to the H_2^+ example and with the same one-dimensional potential. Spin and electron-electron repulsion were neglected and the Schrodinger equation was separable for the two electrons. Thus equations like (14a) and (14b) were obtained for each electron; equation (15) was again used to relate \underline{a} to \underline{R} . Expressions for energy \underline{E} and \underline{c} for this same problem treated as an equivalent one-electron problem followed from the two-electron equations by introducing

$$c(H_2) = (2)^{1/2} c(H_2^+) \quad (16)$$

The bond properties obtained for H_2 from the equivalent one-electron equations agreed with experiment but not as well as for H_2^+ .

The equations for \underline{c} and \underline{E} for the one-electron equivalent of the H_2 molecule were generalized to the homonuclear diatomic molecule M_2 containing a total of \underline{s} electrons:

$$E = -s(me^4/2\hbar^2) [1 + \exp(-ca)]^2 \quad (17a)$$

with

$$c = s^{1/2} (me^2/\hbar^2) [1 + \exp(-ca)] \quad (17b)$$

and with equation (15) applied as before.

When equations (17) were applied to obtain \underline{c} values for diatomic molecules of the elements in the second row of the periodic table, Li through F, the agreement was not considered [39] satisfactory for Li and F.

Further semi-empirical modifications were made^[39] to improve the agreement between predicted and experimental bonding properties for a broad range of diatomic molecules.²¹ For example, noting that equation (17b) implicitly assumes the \underline{c} value is proportional to the ionization potential of the hydrogen atom and that \underline{c} is proportional to the delta potential strength, Lippincott modified equation (17b) for the diatomic molecule M_2 by multiplying the right hand side by the factor I_M/I_H . I_M and I_H are the ionization potentials, respectively, of the element under consideration and of the hydrogen atom.

²⁰This was also done in the energy equation for other results we quote later from reference 39.

²¹It is interesting to observe that originally several workers [41, 42] using regular quantum mechanical methods (Coulombic potentials, the three dimensional Schrodinger equation, etc.) found that simple floating atomic orbitals of $1s$ hydrogenic type yielded considerably improved binding energies for the molecular systems H_2^+ and H_2 as compared to results for similar fixed orbitals. Then this problem was subsequently reexamined, [43, 44, 45] in some cases with a mixture of fixed and floating orbitals. The conclusions of the later authors are that the improvement is not as large as originally found and that to introduce polarization the addition of 2 p orbitals to the $1s$ type, both types fixed at the nuclei, effects as good or better improvement than floating wave functions [44, 45] and with simpler calculations -- with the floating orbitals 3- and 4-center molecular integrals occur. It should be noted also that, in contrast to the delta potential model, in the more rigorous treatment [41-45] the wave functions were not centered on the nucleus at the equilibrium separation. Instead the displacement of the electron orbitals from the nuclei and also the orbital exponent, which governs the spread of the orbital, were varied to minimize the total energy of the system at each of a series of internuclear separations.

Mason and Vanderslice [40] employed a delta model of an atom to explain the repulsive interaction, first of a pair of hydrogen atoms then of a pair of inert gas atoms.

Upon considering Frost's work with such a model and the lack of quantitative agreement when his results were applied to molecules, the former authors suggested reasons such as: a) neglect of interelectronic repulsion, b) uncertain basis for internuclear repulsion, and c) underestimation of overlap of each atomic orbital (AO) with the potential well of the other nucleus. The elimination individually of the sources of error was presumed difficult and also would not preserve a simple model.

From consideration of a) Berlin's interpretation of the Hellman-Feynman electro static theorem²², namely attraction is caused by accumulation of electronic charge between nuclei and repulsion by removal of charge from this region, and b) Hurley's work [42,46] on the use of floating AO's to satisfy this theorem, Mason and Vanderslice proposed a delta function model in which the AO's "float" relative to the nuclei as the atoms approach. Since the delta potentials determine the location of the centers of the AO's, the delta potentials also need to shift relative to the nuclei. Thus this model is similar to Lippincott's; it was treated as one-dimensional.²³

The basic interaction calculated was that for two hydrogen atoms with parallel spins ($^3\Sigma$ state). If the procedure of Lippincott for a pair of bonding hydrogen atoms is followed, except that each one-electron wave function is made anti-symmetric (a node midway between the nuclei), the solution of the Schroedinger equation yields a total energy:

$$E = -1/2 g^2 [1 - \exp(-ca)]^2 \approx -1/2 g^2 [1 - 2 \exp(-ca)], \quad (18a)$$

in atomic units, and where

$$c = g [1 - \exp(-ca)], \quad (18b)$$

with \underline{a} the separation between delta potentials and \underline{g} the delta potential strength. The interaction energy, the difference between total energy at some finite nuclear separation and that at infinite separation is

$$V(\underline{a}) \approx g^2 \exp(-ca), \quad (19)$$

where as in equation (18a) the term in $\exp(-2ca)$ is discarded. \underline{g} is chosen to obtain the correct energy of two separated hydrogen atoms, that is (equation 18a) $E(\infty) = 1/2 g^2$ must be one in atomic units, so \underline{g} is $\sqrt{2}$ in atomic units.

To obtain the dependence of \underline{a} on \underline{R} it is assumed, following the Hellmann-Feynman theorem, that the interaction being repulsive \underline{a} is greater than \underline{R} but $\underline{a} \rightarrow \underline{R}$ as $\underline{R} \rightarrow \infty$. Further for the united atom the 1s atomic functions coalesce to a 2p function, an effect that is approximated by taking \underline{a} as $2\underline{a}_0$ for \underline{R} equal to 0. The relation adapted for \underline{a} , expressed in atomic units \underline{a}_0 is

$$a = R + 2 \exp(-R). \quad (20)$$

²²See reference 1

²³It is stated in reference 40 that for the examples reported a three-dimensional treatment gave identical final results to the one-dimensional method.

Mason and Vanderslice emphasize that in thermal collisions even at high temperature the shift of the delta functions from the nuclei is relatively small so the sensitivity of the results in this energy range to the particular dependence of \underline{a} on \underline{R} is not critical. We note in view of the nonlinear relation between \underline{a} and \underline{R} , that $V(R)$ through equation (19) is not strictly an exponential in \underline{R} .

The repulsive interaction of a pair of H atoms calculated from equations (18) - (20) for \underline{R} between \underline{a}_0 and $4\underline{a}_0$ was compared with a "most likely" curve²⁴ composed of James-Coolidge-Present [5] and Hirschfelder-Linnett [6] data. The agreement was excellent for separations of $4\underline{a}_0$ down to $2.4\underline{a}_0$; the delta potential data deviated by increasing amounts from the "most likely" value as \underline{R} was reduced below $2.4\underline{a}_0$, reaching a difference of 30 percent at $1.1\underline{a}_0$.

On considering the interaction of two inert gas atoms, it was assumed [40] that the total interaction energy is the sum of the average energies of each pair of electrons as for two hydrogen atoms. The interaction energy of two atoms each with n electrons is then from Equation (19)

$$V(a) = n g^2 \exp(-ca) \quad (21)$$

Parameter \underline{c} is again obtained from equation (18b). The parameters \underline{g} and \underline{a} need to be specified. Lippincott's assumption was adopted [40], namely the delta potential strength \underline{g} is proportional to the ionization potential of the atom and hence to obtain the \underline{g} value for the atom pair A-A the \underline{g} value for hydrogen should be multiplied by the ratio of ionization potentials of atoms A and H,

$$g_A = \sqrt{2} I_A / I_H \quad (22)$$

For \underline{a} , by analogy with equation (20) it is assumed that

$$a = R + 2 r \exp(-R/\bar{r}), \text{ in units of } a_0, \quad (23)$$

where \bar{r} is the radius of the outermost electronic orbit of the isolated atom.²⁵

In the final form of the equations there are no adjustable parameters, the interaction potential is fixed when the ionization potential, the atomic number and the radius of the outermost electronic orbit are introduced.

The interaction potentials were obtained for like atom pairs of the inert gases [40] and were compared (Figures 14-18) with experimental potentials derived from atom-atom scattering, or gas property and crystal data, and in a few cases with detailed quantum theoretical calculations. A few interaction potential values calculated from equations (18b) and (21)-(23) are shown in Table V together with the comparison values. It was noted [40] that the agreement of the delta function interaction potential values with experimentally derived values is as good or better than that of the detailed quantum theory calculations for helium, neon and argon, the only cases for which such calculations were available.

The delta function model was also applied to the interaction of unlike atom pairs. Plausible combining rules for this situation led to the following potential of interaction of an atom of type 1 with an atom of type 2:

$$V_{12} = (n_1 n_2)^{1/2} (g_1 g_2) \exp[-(c_1 a_1 + c_2 a_2)/2] \quad (24)$$

²⁴Reference 1, page 1062-63

²⁵Obtained either from self-consistent-field calculations, or less accurately using screening constants and equations derived for the average radius of hydrogen-like atomic orbitals. (see reference 1, page 951 ff)

where \underline{n}_1 , \underline{g}_1 and \underline{c}_1 have the same meaning as \underline{n} , \underline{g} , and \underline{c} in the preceding equations but refer to an atom of type $\underline{1}$. \underline{a}_1 is obtained from an equation like equation (23) with \underline{r}_1 in place of \underline{r} ; \underline{c}_1 is given by an equation like equation (18b) with \underline{c}_1 , \underline{g}_1 , and \underline{a}_1 in place \underline{c} , \underline{g} , \underline{a} . A similar procedure applies to \underline{a}_2 and \underline{c}_2 . Calculated values of $V_{12}(R)$ were obtained with equation (24) for H-He, He-Ar and Ne-Ar pairs and compared with potentials from atom-atom scattering data; agreement comparable to the homonuclear case resulted.

Mason and Vanderslice point out [40] that because of the great oversimplification of the delta function model, its extension to other systems or the calculation of other properties must be done with much caution.

7. A Semi-Classical Model of Atomic Interaction

An electrostatic model of the atom was proposed by Jefimenko [47] with features to permit its application to pairwise interaction of both

TABLE V
Interaction Potential of Inert Gas Atom Pairs^a

R	Delta Model	Detailed Theoretical Calculation	Scattering	Gas and Crystal Data
a_0	ev	ev	ev	ev
		<u>Helium</u>		
1.0	19.8	26.9 ^{b*} 25.0 ^d	9.0 ^c 16. ^e	
2.0	2.02	3.10 ^b 3.27 ^d	3.3 ^e	
2.5	0.58		0.90 ^f	
		<u>Neon</u>		
3.41	0.64	2.15 ^g	0.88 ^h	
4.36	0.077	0.218 ^g		0.075 ⁱ
		<u>Argon</u>		
3.0	6.69		3.90 ^j	
4.0		13.0 ^k		
5.0	0.336	2.05 ^k	0.257 ^l	
		<u>Krypton</u>		
4.5	2.21		1.45 ^m	
5.5	0.59		0.487 ^m	
		<u>Xenon</u>		
6.0	0.85		0.71 ⁿ	
6.8	0.346		0.262 ⁿ	

* Footnotes on following page

^aDelta potential from equations (18b), (21)-(23); other data from references below listed in reference 40 except values with notes d and e.

^bS. Huzinaga, Pro. Theo. Phys. (Kyoto) 17, 512 (1957); 18, 139 (1957).

(Continued on next page)

^cReference 10.

^dP. E. Phillipson, Phys. Rev. 125, 1981 (1962).

^eReference 18.

^fReference 11.

^gW. E. Bleick and J. E. Mayer, J. Chem. Phys. 2, 252 (1934).

^hI. Amdur and E. A. Mason, Ibid. 23, 415 (1955).

ⁱReference 28.

^jAmdur, Davenport and Kells, J. Chem. Phys. 18, 525 (1950).

^kM. Kunimune, Pro. Theo. Phys. (Kyoto) 5, 412 (1950).

^lI. Amdur and E. A. Mason, J. Chem. Phys. 22, 670 (1954).

^mI. Amdur and E. A. Mason, Ibid. 23, 2268 (1955).

ⁿI. Amdur and E. A. Mason, Ibid. 25, 624 (1956).

combining and non-combining atoms. The justification for an electrostatic view of the interatomic forces was based on the Hellmann-Feynman Theorem which states essentially: In a molecule the force on an individual nucleus is that exerted electrostatically by the other nuclei and by the electrons where the latter are represented as a charge cloud whose density is given by the probability density determined quantum mechanically (as by solving the Schroedinger equation). Jefimenko suggests it is plausible that approximate solutions to interatomic interactions can be obtained for electrostatic atom models that "are only partially compatible with the quantum mechanical requirements of the system under consideration".

The atom model is formed as follows: The electron charge cloud is a very thin spherical shell of radius a and total charge $-Ne$; the shell is centered about the nucleus which is a positive charge of Ne units (not the actual charge Ze). N is an effective charge factor; for hydrogen N is set equal to one, while for other elements (except inert gases) N is fixed by requiring that the ionization energy of the atom model with N electrons must equal the total experimental ionization energy of the valence electrons of the element considered.

The energy of a one electron atom (the negative of the ionization energy), the sum of the shell-nucleus attraction, $-e^2/a$, and the shell self-energy, $+(1/2)(e^2/a)$, was obtained.²⁶ If a is made equal to the Bohr radius, $a_0 = \hbar^2/me^2$, one obtains the correct energy, or negative of ionization energy, of the hydrogen atom:

$$W_H = -I_H = -e^4 m/2\hbar^2.$$

To obtain the ionization energy of an element X with effective charge factor N , e is replaced by Ne in the equation for I_H to yield

$$I_X = (Ne)^4 m/2\hbar^2 \quad (25)$$

The effective charge factor is then

$$Ne = (I_X/I_H)^{1/4} \quad (26)$$

A model of a homonuclear diatomic molecule is formed from two identical atomic models with inter-nuclear separation R . As the atoms interact each shell is assumed to retain its spherical shape and remain rigidly attached to its nucleus. The electrostatic energy of the interacting systems (shell₁-shell₂ plus shell₁-nucleus₂ plus shell₂-nucleus₁ plus nucleus₁-nucleus₂) was determined for the three cases (a) no shell interpenetration, (b) electron shells interpenetrate but nuclei remain outside opposite shells, and (c) shells interpenetrate enough to enclose both nuclei (Figure 21)

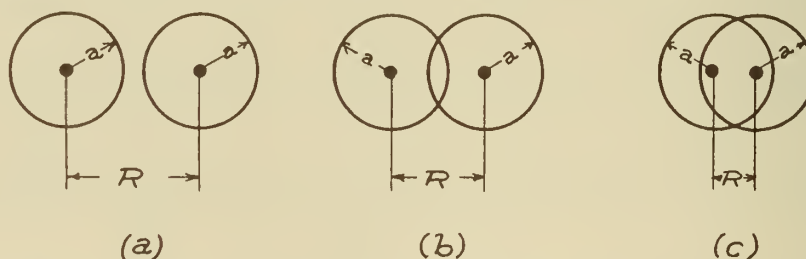


Figure 21 - Semi-classical model of a homonuclear diatomic molecule. (after Jefimenko).

²⁶ Obviously this atomic energy has no minimum as a is decreased.

The interaction energies obtained^[42] were

$$V(R) = 0, R > 2a \quad (27a)$$

$$V(R) = -[(Ne)^2/4a^2R] (2a-R)^2, a < R < 2a \quad (27b)$$

$$V(R) = [(Ne)^2/4a^2R] [8a^2 - (2a+R)^2], R < a \quad (27c)$$

These equations represent a potential having a well and with very approximately the character of a Morse potential except²⁷ that the bottom of the well is a cusp (at $R = a$) instead of a bowl. This deviation from reality can be removed by using an electron shell of finite thickness. The model thus indicates an equilibrium separation R_e equal to a . The well depth $V(R = a)$ equals the dissociation energy D_e . From equations (26) and (27b) the latter energy is

$$D_e = (e^2/4R_e) (I_X/I_H)^{1/2} \quad (28)$$

Values of D_e were calculated [42] from equation (28) for the homonuclear diatomic molecules of twenty elements by using experimental values of R_e and I_X . The substances included halogens; alkalis; H_2 ; C_2 ; O_2 and the similar (Group VIA) divalently-bonded S_2 , Se_2 , Te_2 ; N_2 and the similar (Group VA) trivalently-bonded P_2 , As_2 , Sb_2 , Bi_2 . For the alkalis (except Li_2) and H_2 and O_2 the agreement with measured dissociation energy values was better than 10 percent; for the halogens the calculated values were roughly 25 percent low; for many other substances it was noted [47] that the degree of agreement could not be judged because of uncertain experimental data. Considering the simplicity of the model the agreement with experiment is good.²⁸

The potential curves in reduced form ($V^*(R^*) = V/D_e$ with $R^* = R/R_e$) for I_2 and H_2 were calculated and compared with experiment. (Figures 22 and 23) For I_2 , except for the cusp shape at the bottom of the potential well and for too shallow a slope for R^* less than R_e^* the calculated and experimental curves were fairly close. In the case of H_2 the agreement was much poorer, the experimental curve having a much wider potential well and a more gradual slope for R^* greater than R_e^* . It was suggested [47] that for H_2 the agreement with experiment could be improved by incorporating into the model some of the effects of the mutual perturbation of the charge distributions of the two atoms.

To obtain purely repulsive interactions between two atoms, such as two H atoms with parallel spins, which quantum mechanically are related to spin orientation and the Pauli exclusion principle, it is necessary in the present model to introduce some concept equivalent to the exclusion principle. This was done by postulating [47] a "penetrability" concept for electron shells: 1) two perfectly penetrable shells can interpenetrate with no other interaction than the usual electrostatic one, as assumed in the previous derivation, 2) two perfectly impenetrable shells cannot penetrate at all.

The interaction energy of two atoms for case 2) will depend on the resistance the shells offer to shifting relative to their respective nuclei. In one extreme, infinite resistance to shifting leads to the hard sphere model. The other extreme, no resistance to shifting, leads to an interatomic repulsion, in reduced form

$$V_r(R^*) = 2 [(2-R^*)^2/(2+R^*)R^*] \quad (29)$$

²⁷Other exceptions; equation (27) is not asymptotic to the R -axis as R increases and as $R \rightarrow 0$, $V(R)$ varies $1/R$.

²⁸As a matter of interest we calculated N for equation (26) to see how closely N compares with the actual number of valence electrons. The values of I_X/I_H were taken from reference 47. The calculated values of N are 0.94 to 1.06 for the halogens, 0.73 to 0.79 for the alkalis, 1.2 to 1.4 for the divalent oxygen-like elements, and 1.4 to 1.6 for the trivalent series $N_2 \dots Bi_2$.

The true potential may be expected to lie between the above and the hard-sphere potential. \underline{V}_T was calculated [47] from equation (29) for H_2 ($^3\Sigma$ state) and exhibited similar characteristics (Figure 20) to a more accurate quantum mechanical curve²⁹ but was lower and vanished at $\underline{R} = 2a_0$ while the accurate calculation vanishes at about $7.5 a_0$.

As a further test of the model the reduced attractive potential, [equation (27) in reduced form] was used to calculate the reduced second virial coefficient. For low temperature, $T^* < 1.5$, the model potential results agreed with second virial values for the Lennard-Jones (12-6) potential; for higher temperatures the agreement was poorer: $(B^*)_{\text{model}}$, always negative approached zero at about $T^* = 10$; $B^*_{L,J}$ became positive at $T^* \sim 3.5$ and remained positive for increasing temperature. By arbitrarily making the model potential become that of a hard sphere at the small separation corresponding to the zero of the equation (27) potential on the repulsive part of the curve, it was possible to reproduce the Lennard-Jones (12-6) B^* vs T^* curve fairly well. From experimental second virial data (for $T^* < 1.5$) for the inert gases \overline{He} through \overline{Xe} , values were determined [47] of the effective charge factor \underline{N} . They were relatively small as may be expected in view of the weak interaction of the inert gases, and they ranged from 0.023 for He to 0.16 for Xe.

While this model deviates greatly from the exact situation it does predict some features of atomic interactions.

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APPENDIX

Corner's method. The pair potential of equation (11a) is expressed as $V = \epsilon V^*(R^*)$ that is a function of the reduced separation, $R^* = R/R_m$. By performing a lattice sum the potential $V_M(d, R^*, \epsilon, a)$ for one molecule in the crystal lattice displaced \underline{d} from equilibrium was obtained. From the latter potential the vibrational frequency $\underline{\nu}$ is found for the one molecule with the others at rest. As an approximation the average lattice vibrational frequency $\overline{\nu}$ is taken to be $\underline{\nu}$. The total energy of the lattice at $0^\circ K$, $U_M(R^*, \epsilon, a)$ is the sum of the potential energy $U_{pe} = 1/2 N V_M(0, R^* \dots)$, and the zero point energy $3/2 N h \nu$. The condition for equilibrium lattice spacing ($0^\circ K$) is that $x \equiv \partial U_M / \partial R^*$ be zero.

The experimental heat of sublimation, $\Delta H_{exp}(0^\circ K)$ is obtained by adding to the observed heat of sublimation the zero point energy, $(9/8) N k T_D$, where T_D is the experimental Debye temperature. The theoretical heat of sublimation at $0^\circ K$ is the potential energy U_{pe} of the crystal at equilibrium spacing r_0 . With ΔH_{exp} and r_0 known, a value of a is selected. Then after setting U_{pe} equal to ΔH_{exp} one obtains ϵ as a function of R^* . Inverse interpolation of \underline{X} shows the value of R^* for which \underline{X} vanishes and the corresponding ϵ and R_m (r_0 is known) are found.

²⁹Reference 1 page 1058; Hirschfelder-Linnett and James-Coolidge-Present data, loc. cit.

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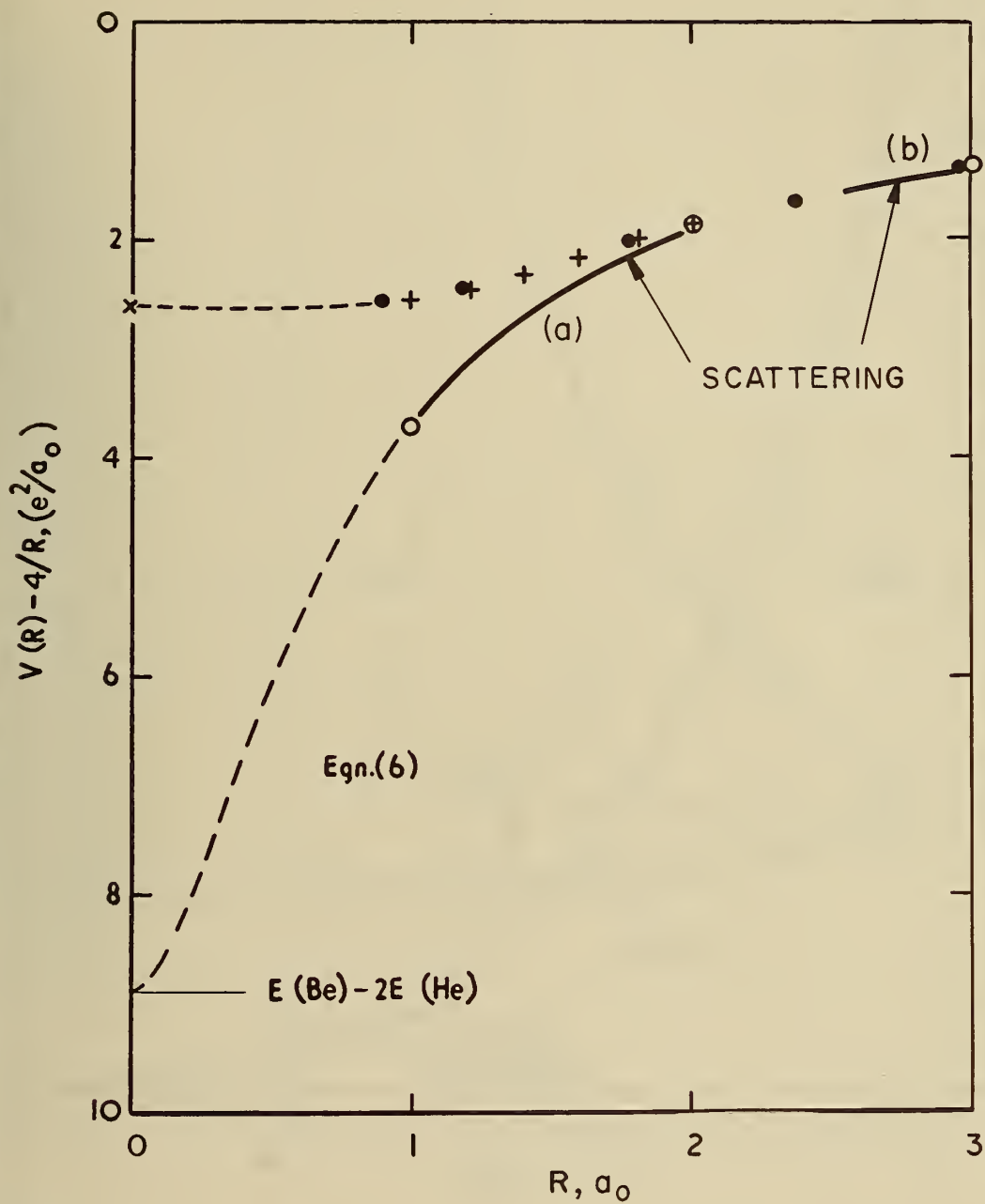


Figure 1 -
Variation of electronic interaction energy of two helium atoms with nuclear separation⁴ (after Buckingham Reference 4)

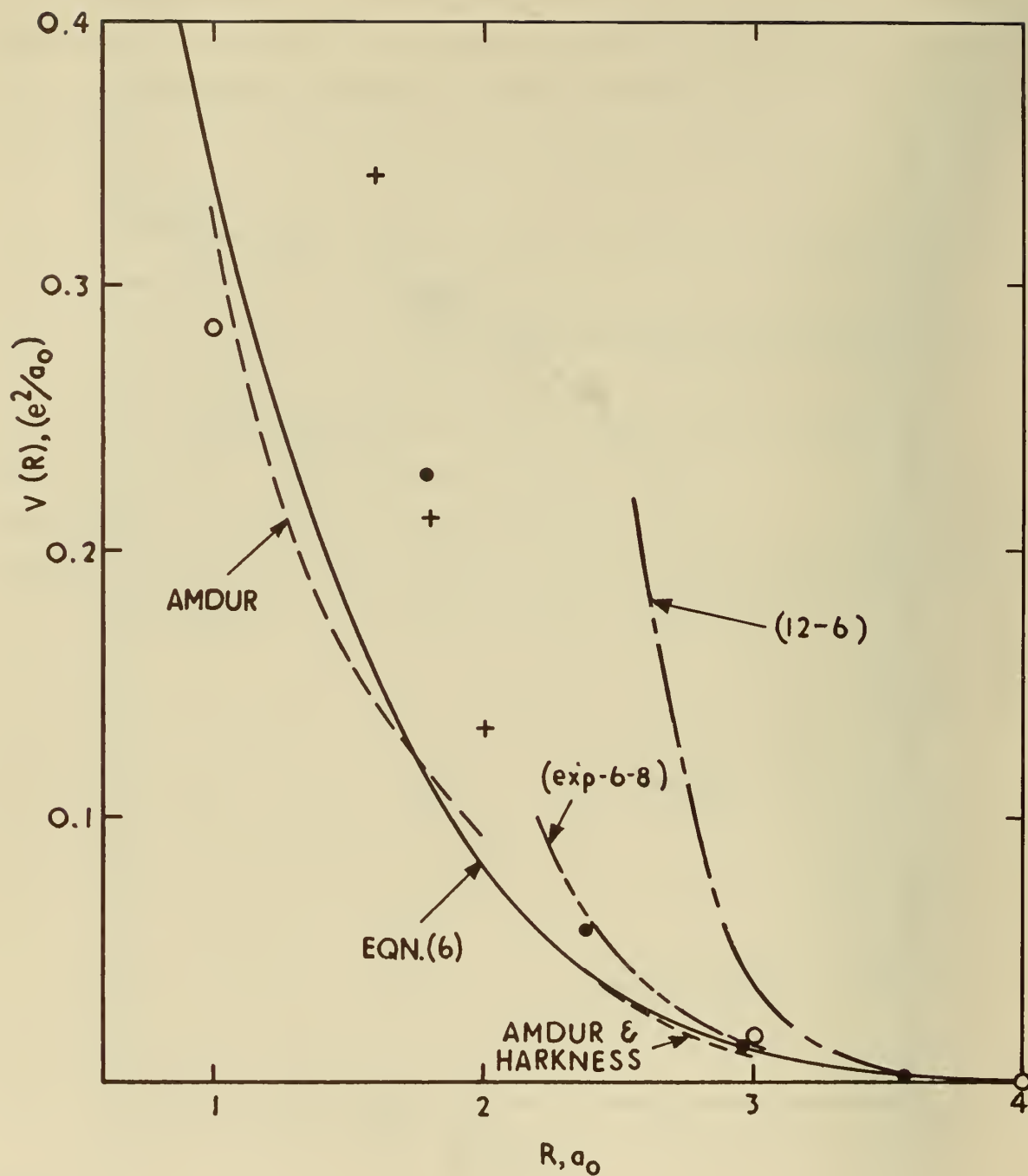


Figure 2 -

Variation of total interaction energy of two helium atoms with nuclear separation; theoretical points as in Figure 1 (after Buckingham Reference 4)

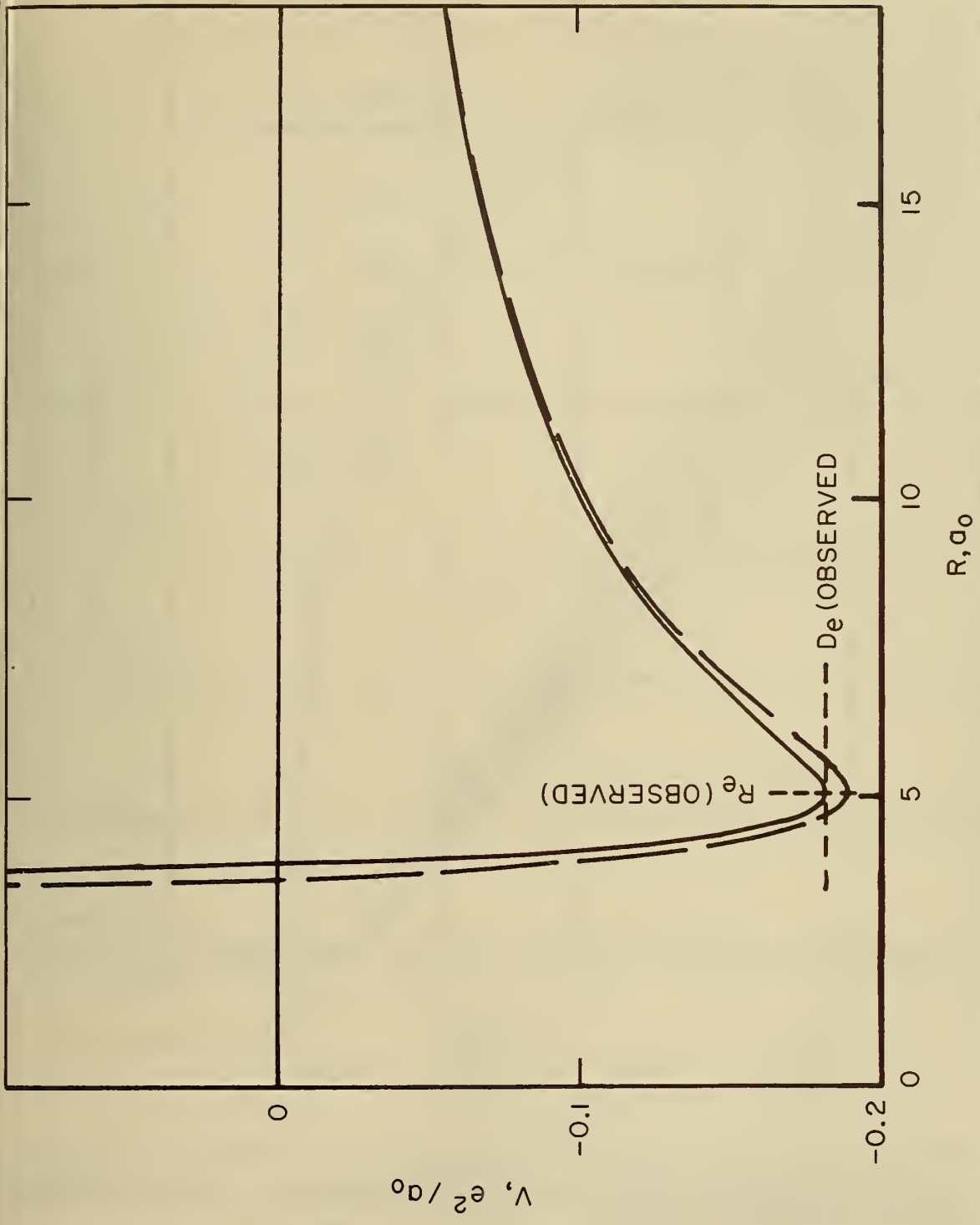


Figure 3 - Potential energy curve for KCl: \underline{V} and \underline{R} in atomic units Full curve, Frost and Woodson broken curve, Varshni. [Y. P. Varshni, Trans. Faraday Soc., 53, 132 (1958)]

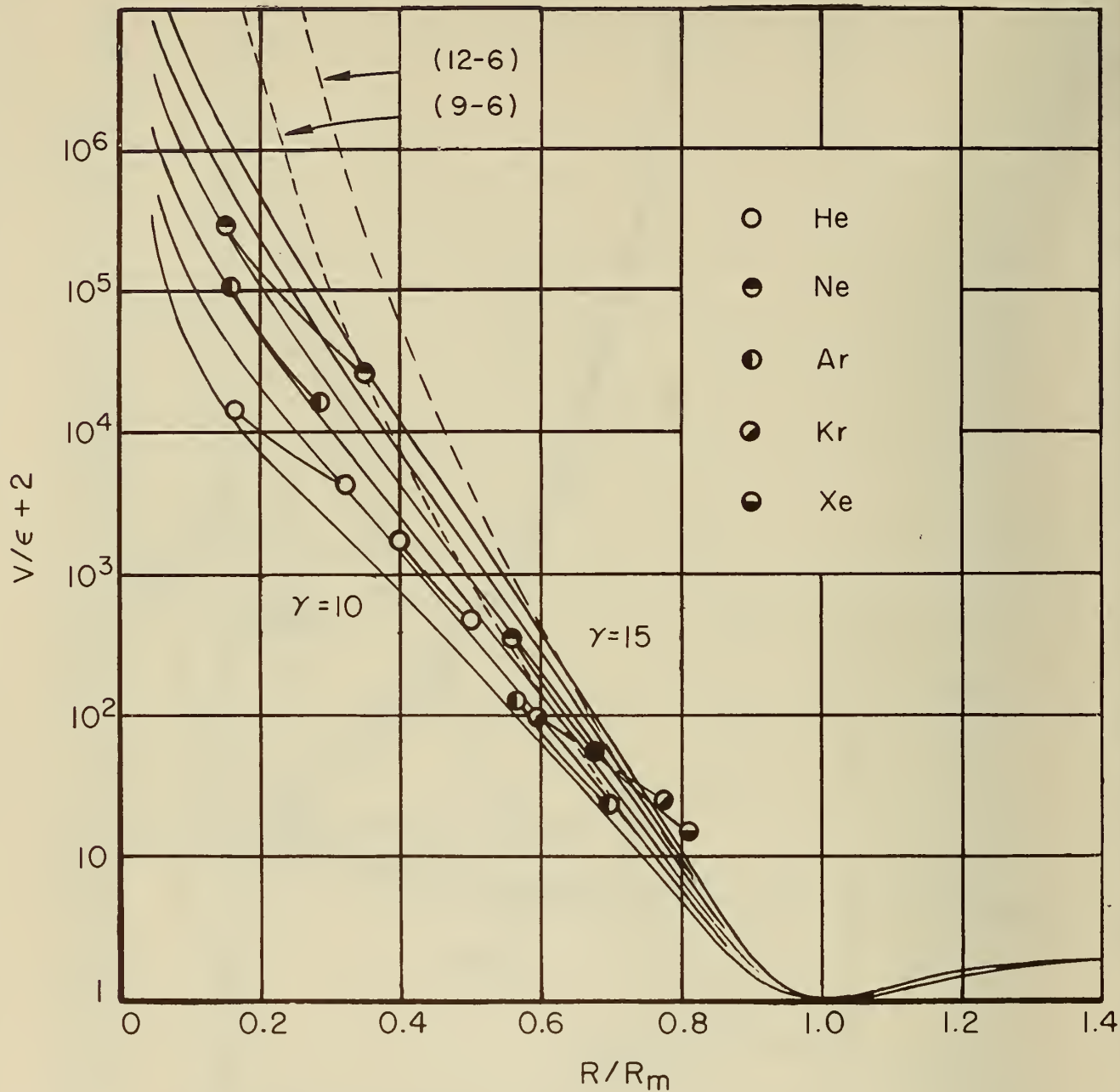


Figure 4 - The potential function given by Equation (12) with integer γ from 10 to 15. Lennard-Jone (6-12) and (6-9) potentials and inert gas scattering data are also shown (after Woolley).

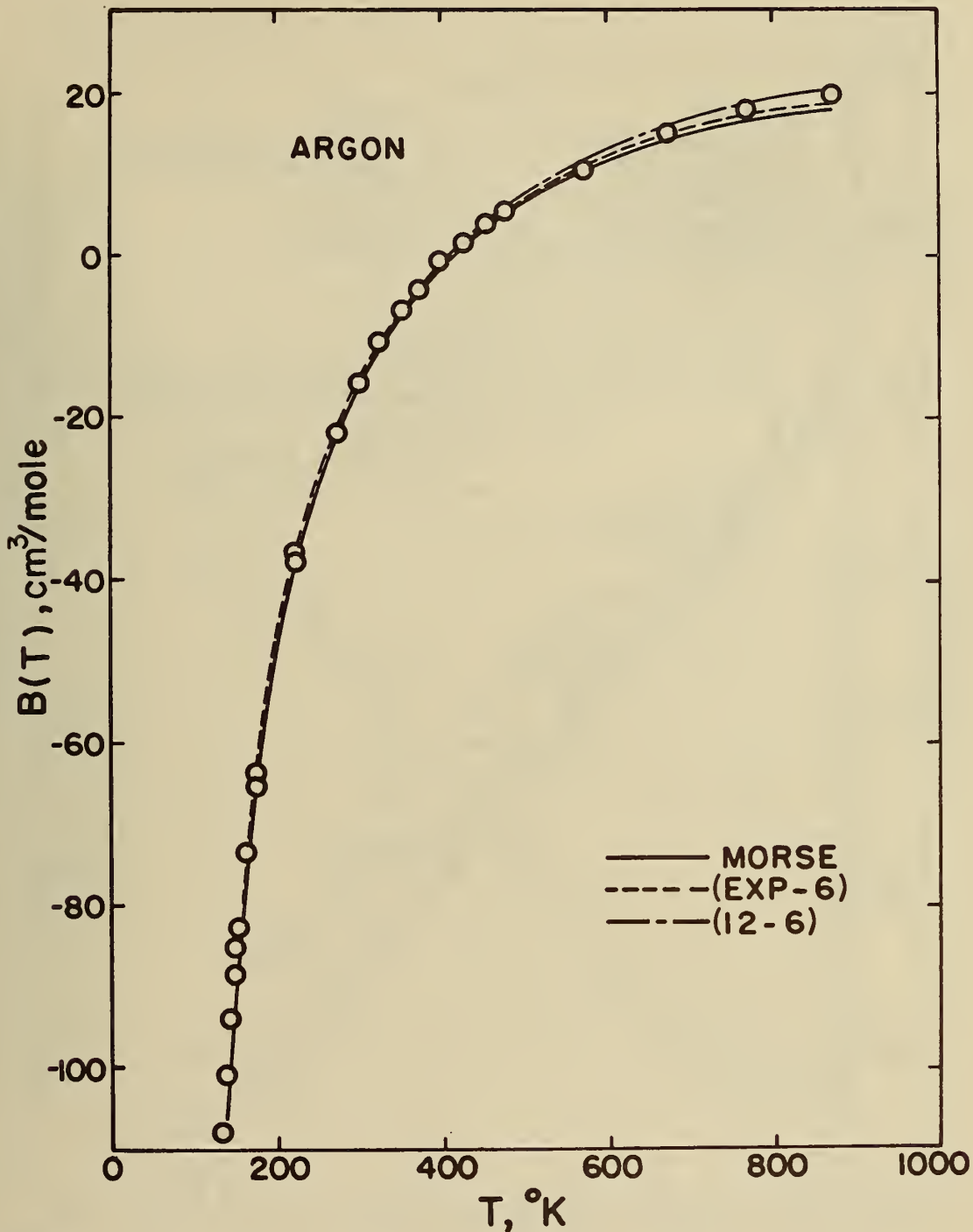


Figure 5 -

Comparison with experiment of the second coefficients for argon calculated for the Morse, Buckingham (exp 6), and the Lennard-Jones (12-6) potential models. The potential parameters have been determined at least in part from crystal data.

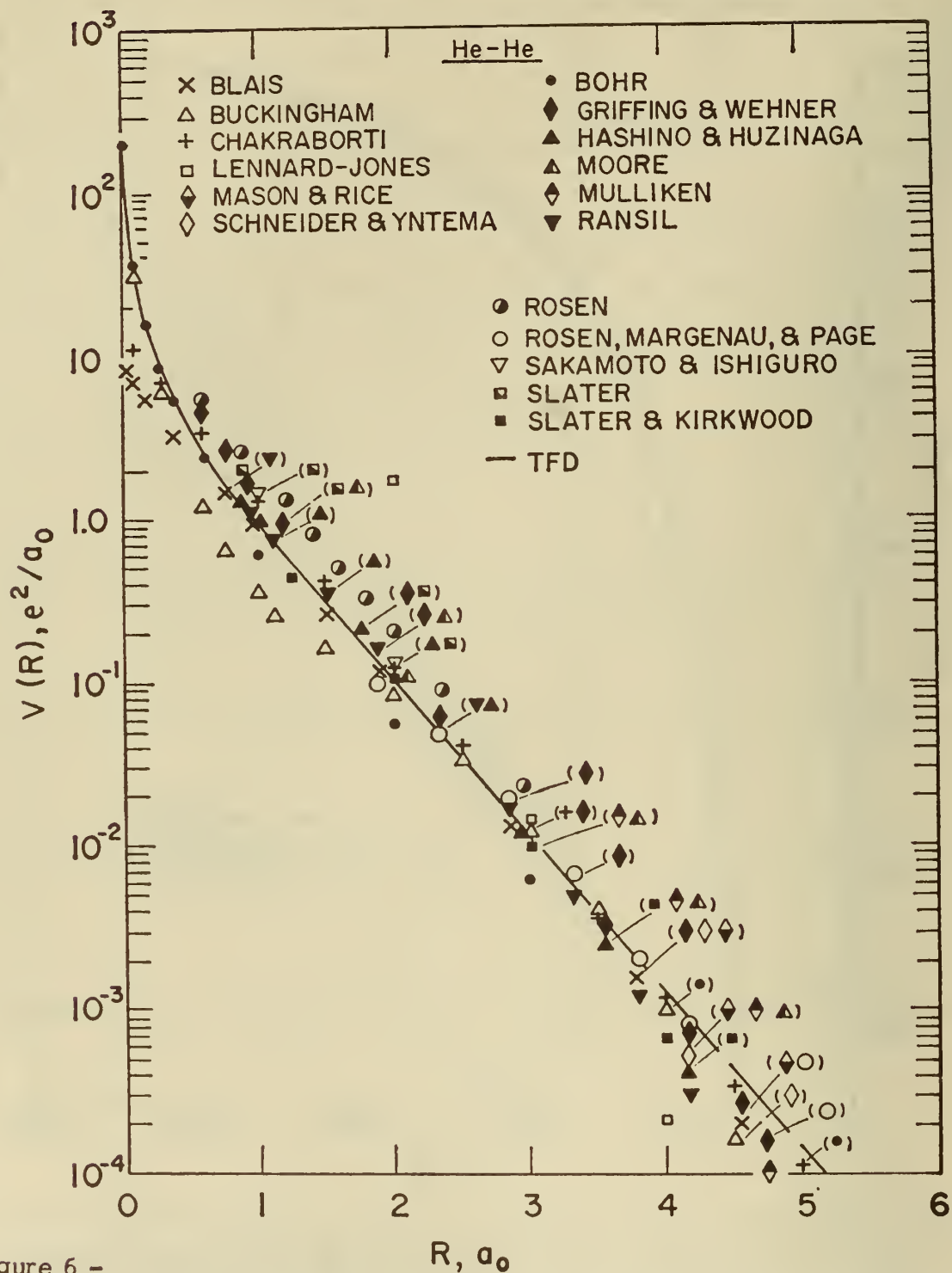


Figure 6 - Repulsive interaction potentials for the He-He system. The first group of six references relate to experimental work; the remainder to calculated results (after Abrahamson).

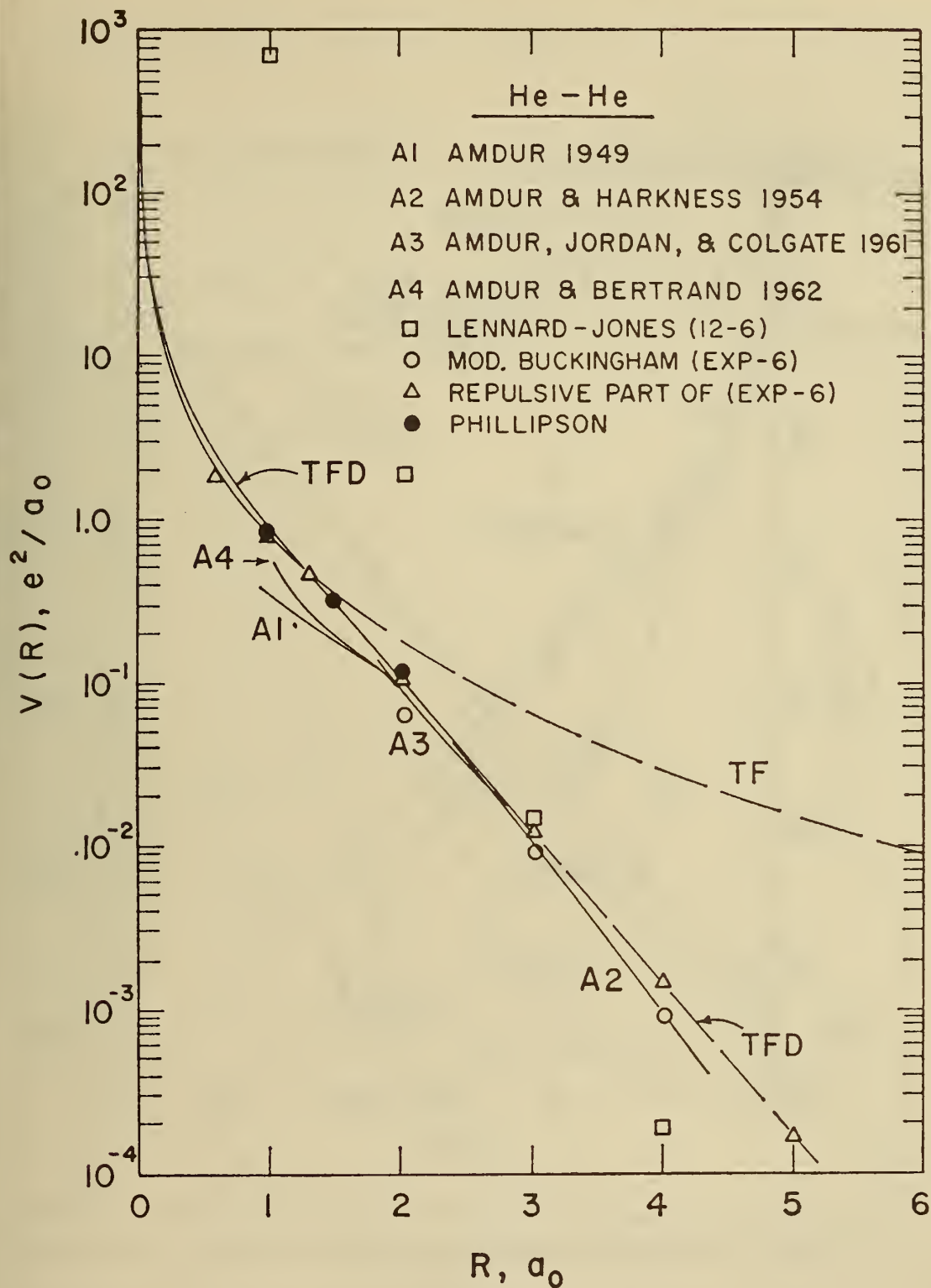


Figure 7 - Repulsive interaction potentials for the He-He system.

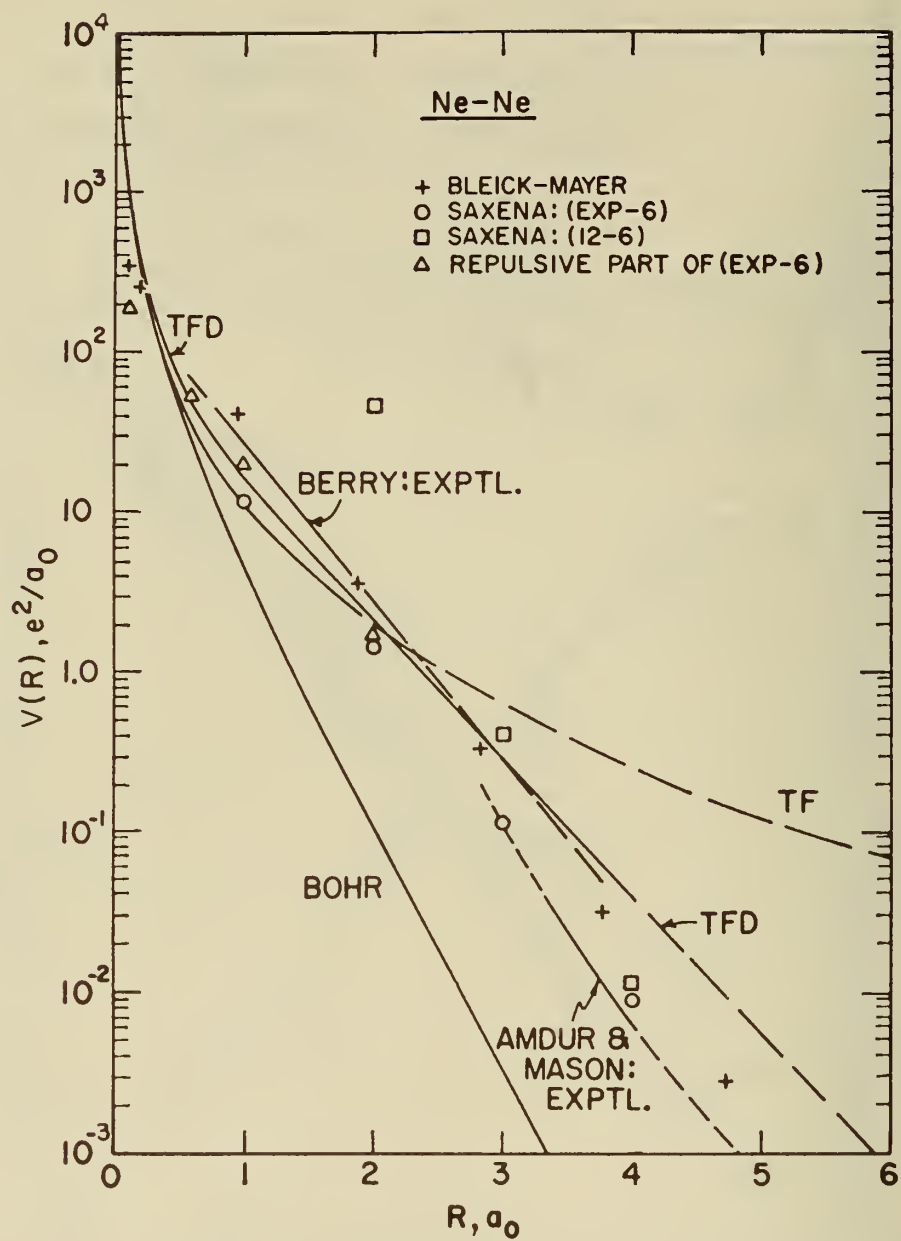


Figure 8 - Repulsive interaction potentials for the Ne-Ne system.

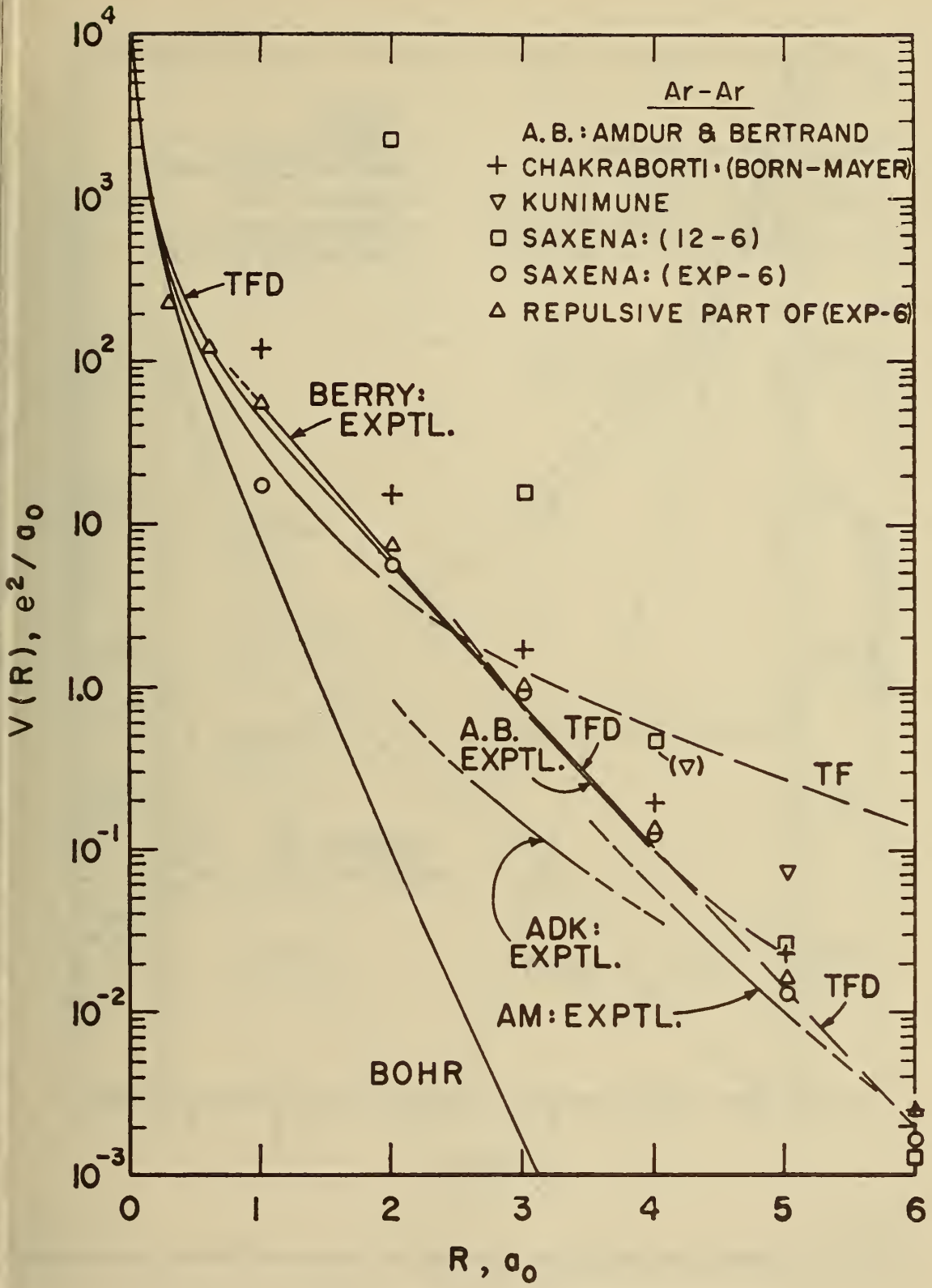


Figure 9 - Repulsive interaction potentials for the Ar-Ar system.

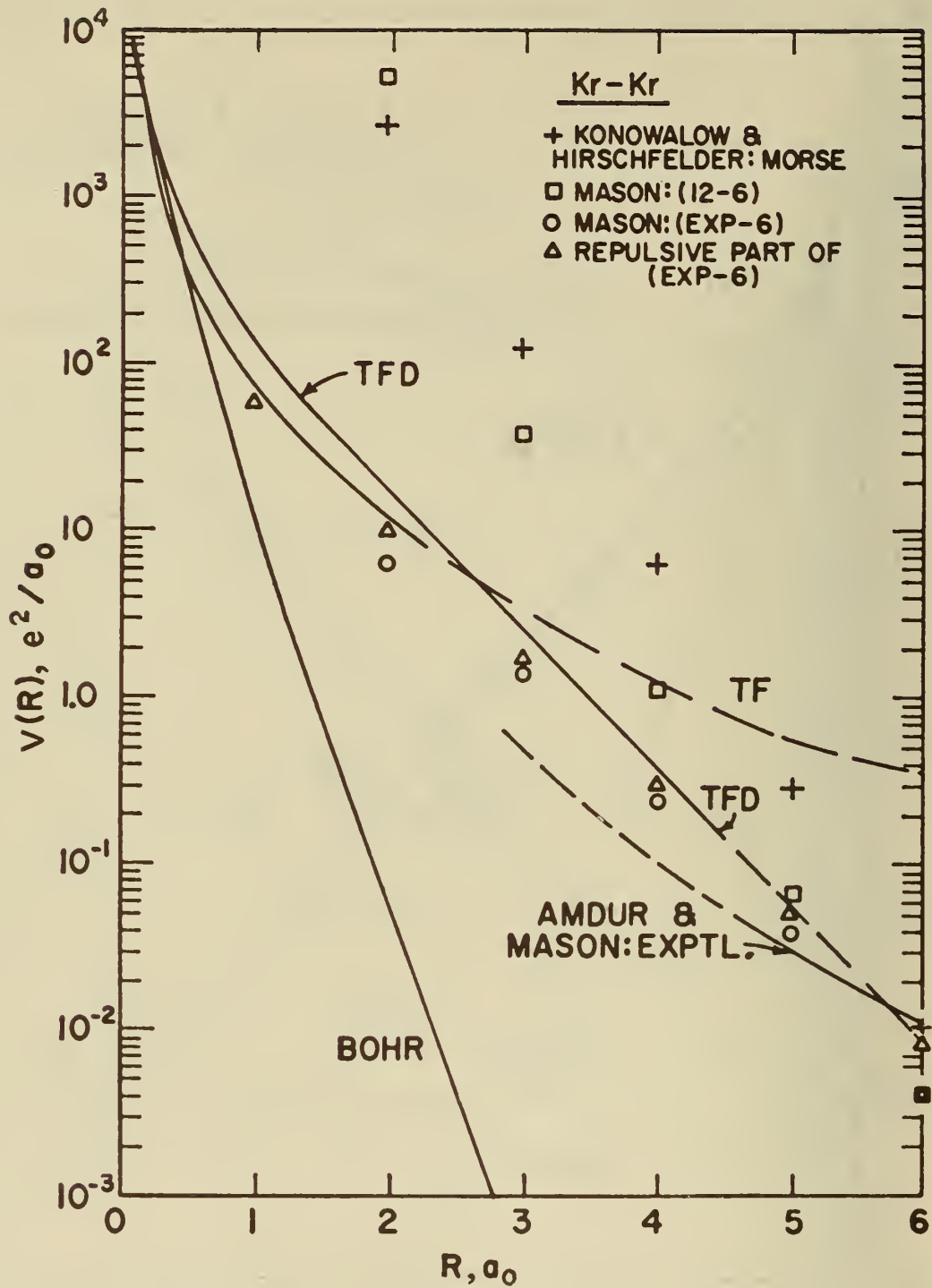


Figure 10 -

Repulsive interaction potentials for the Kr-Kr system (after Abrahamson).

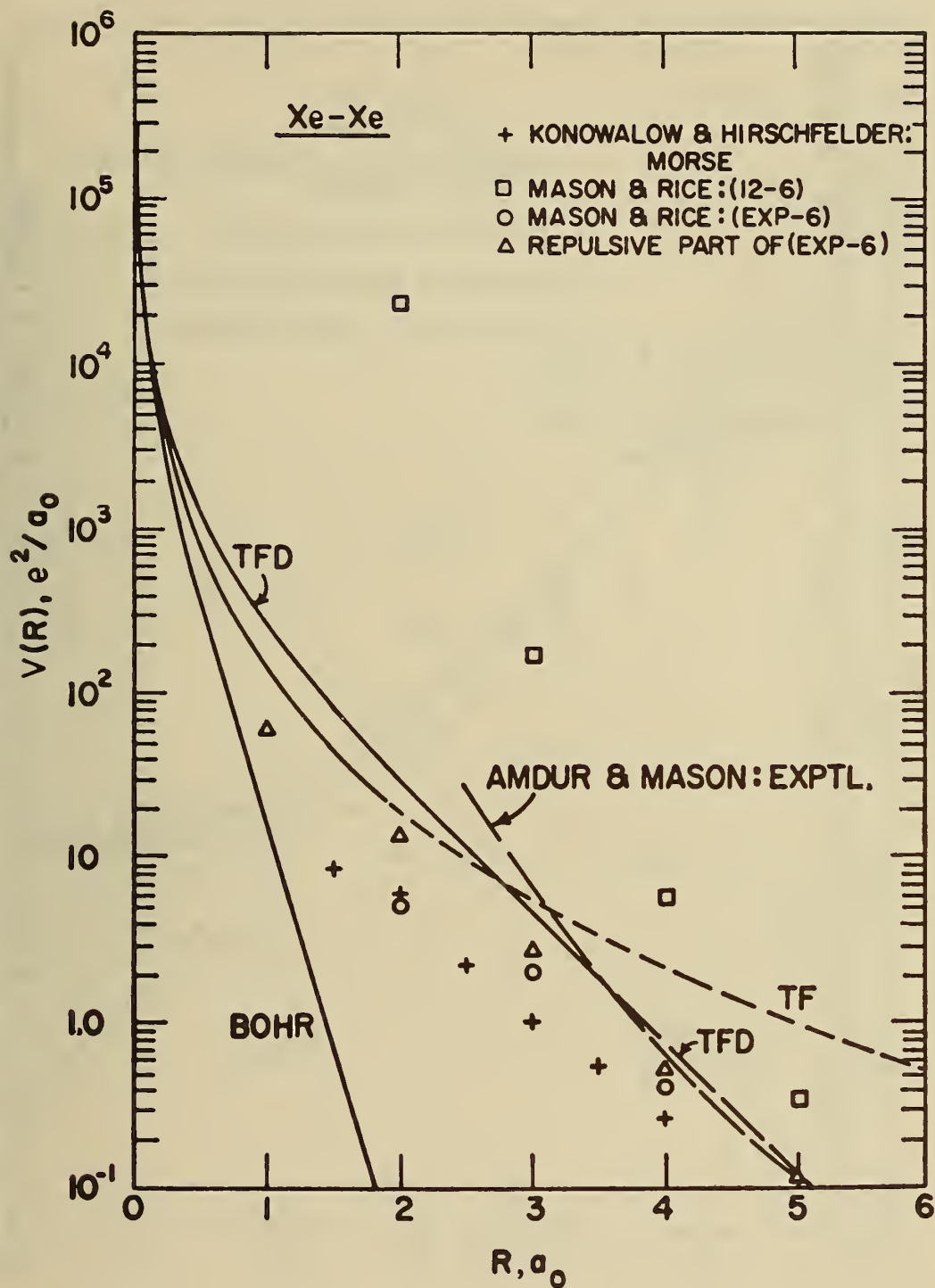


Figure 11 -
Repulsive interaction potentials for the Xe-Xe system (after Abrahamson Reference 36).

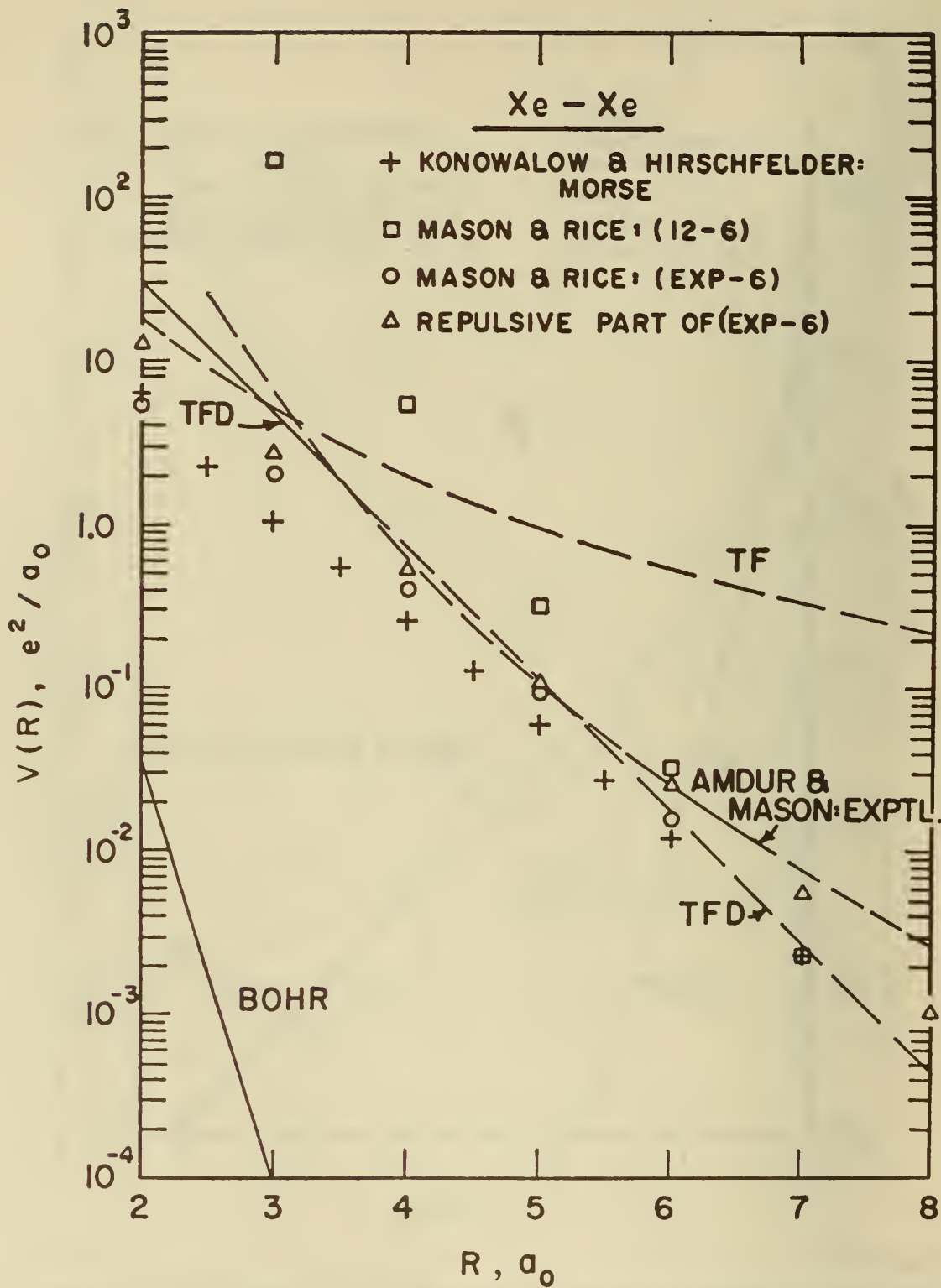


Figure 12 - Repulsive interaction potential for the Xe-Xe system.

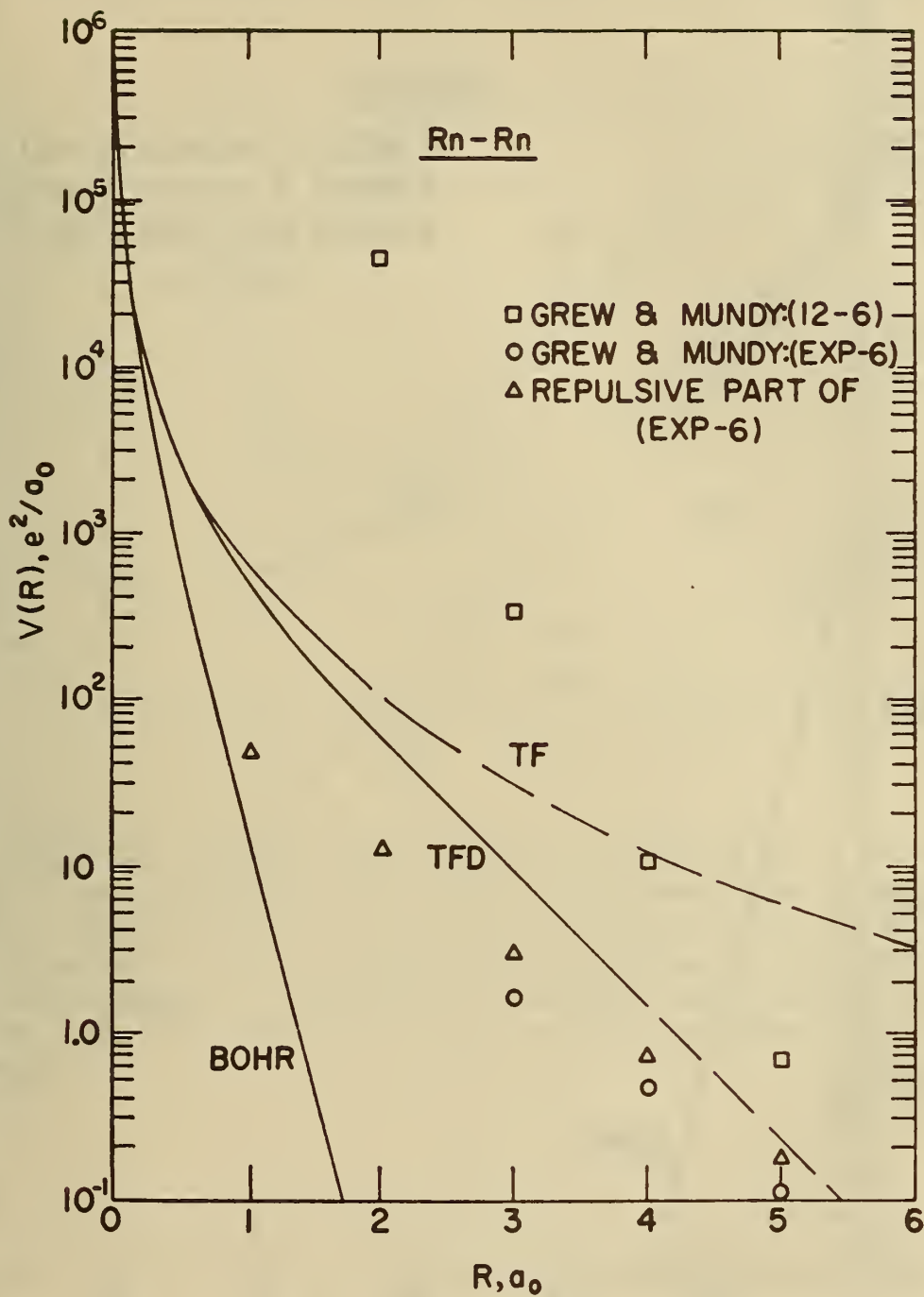


Figure 13 -
 Repulsive interaction potential for the Rn-Rn system (after Abrahamson).

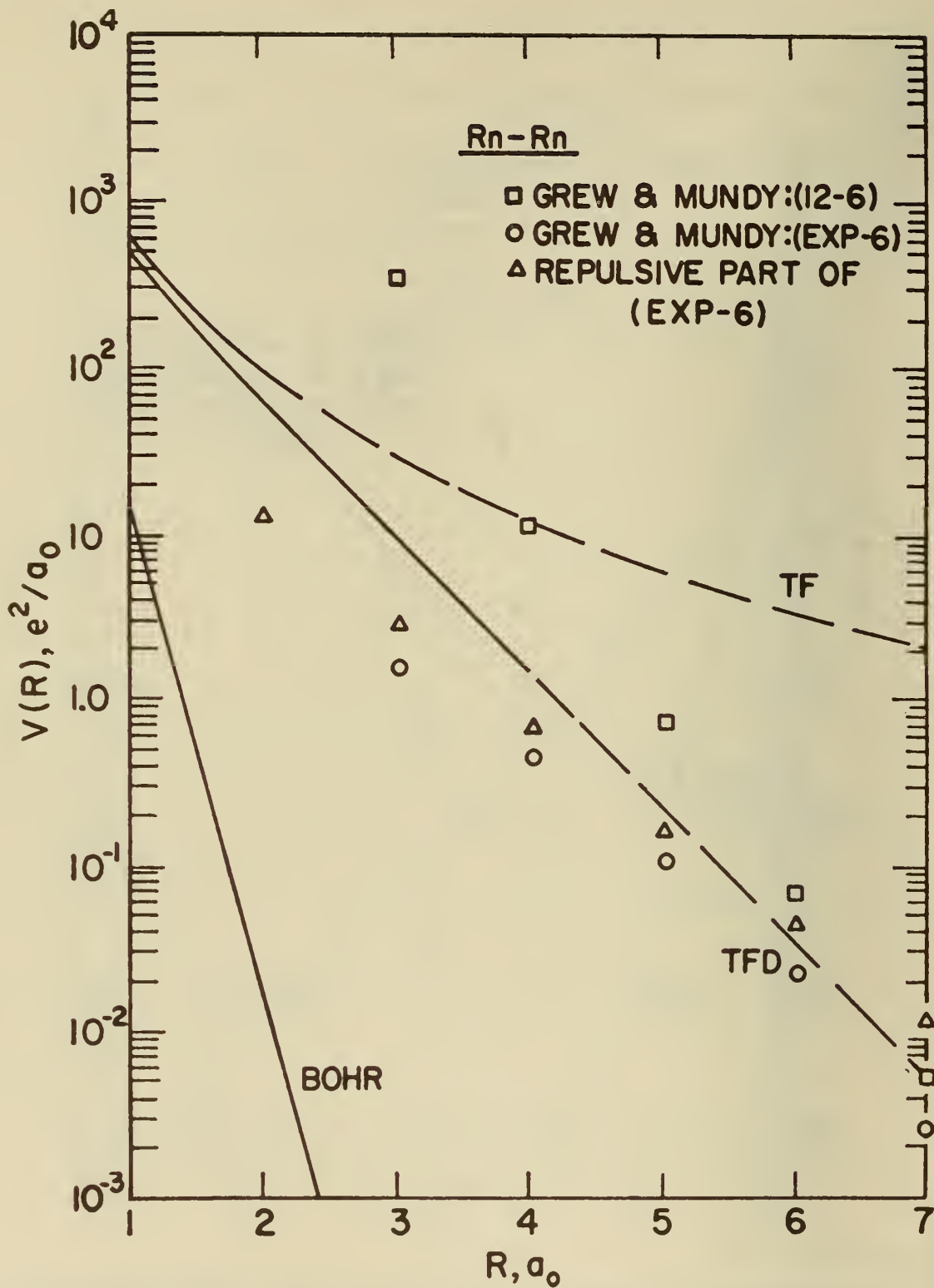


Figure 14 -
Repulsive interaction potentials for the Rn-Rn system (after Abrahamson).

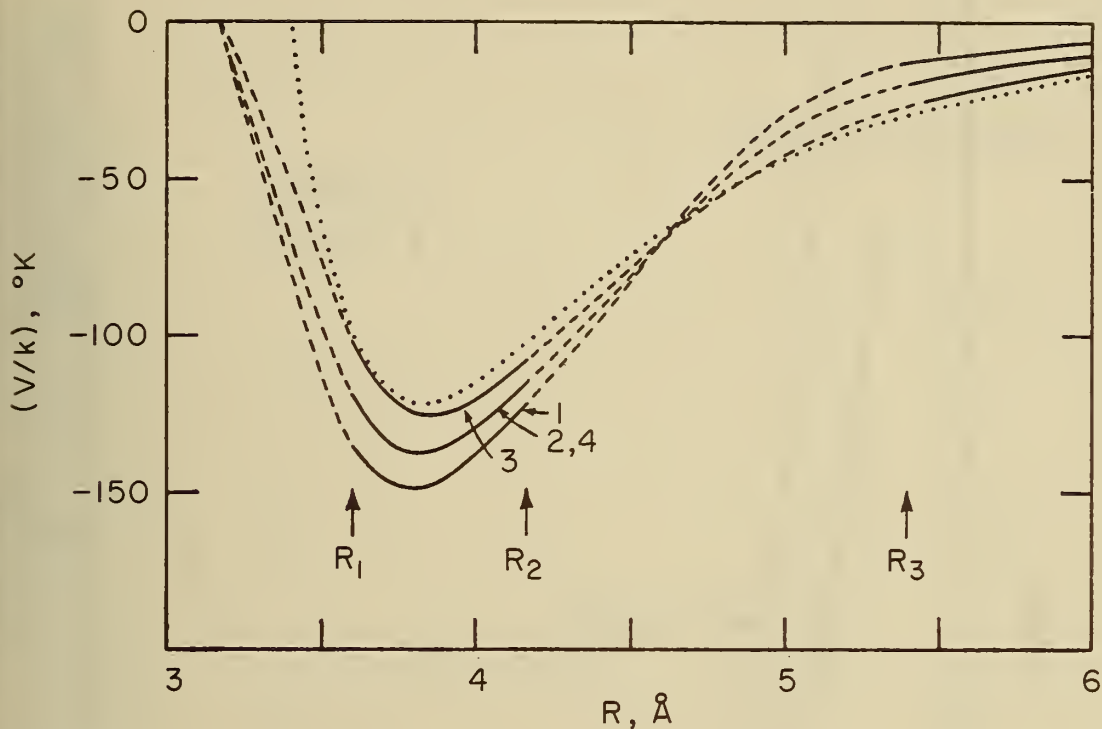


Figure 15 -

The interaction energy \underline{V} plotted against the separation \underline{R} of a pair of argon atoms for each of the sets 1, 2, 3 and 4 of parameters given in Table 2. The parts of each curve, calculated from formula (2-1) for $R_1 < R < R_2$, and from formula (2-2) for $R > R_3$, are shown as full lines, and the parts drawn free-hand are shown as broken lines. The dotted curve shown for comparison is the (6-12) interaction energy with the parameters of set 5 in Table 2.

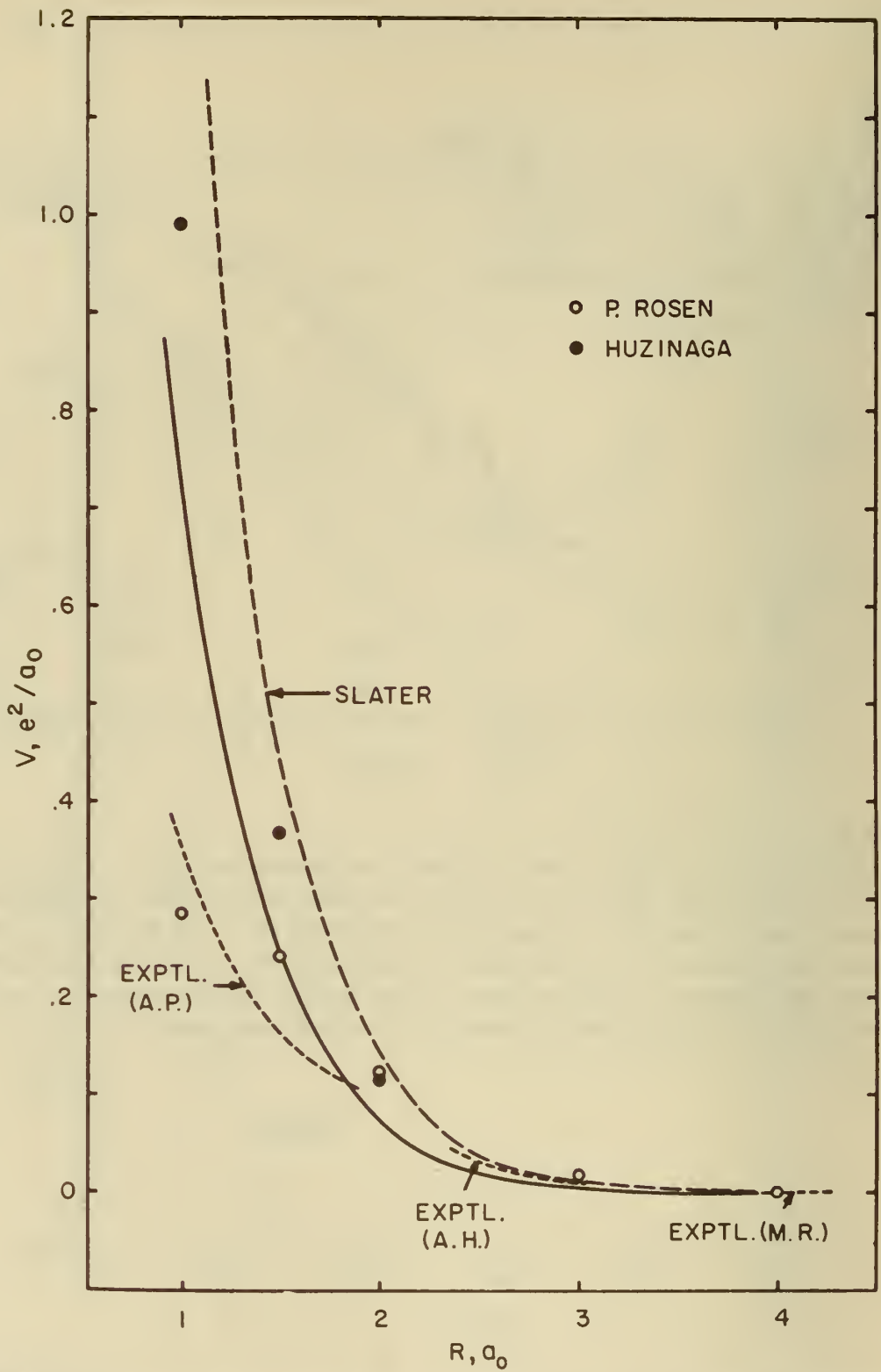


Figure 16 -
 Energy of interaction of two helium atoms. The solid curve is calculated from the delta-function model.

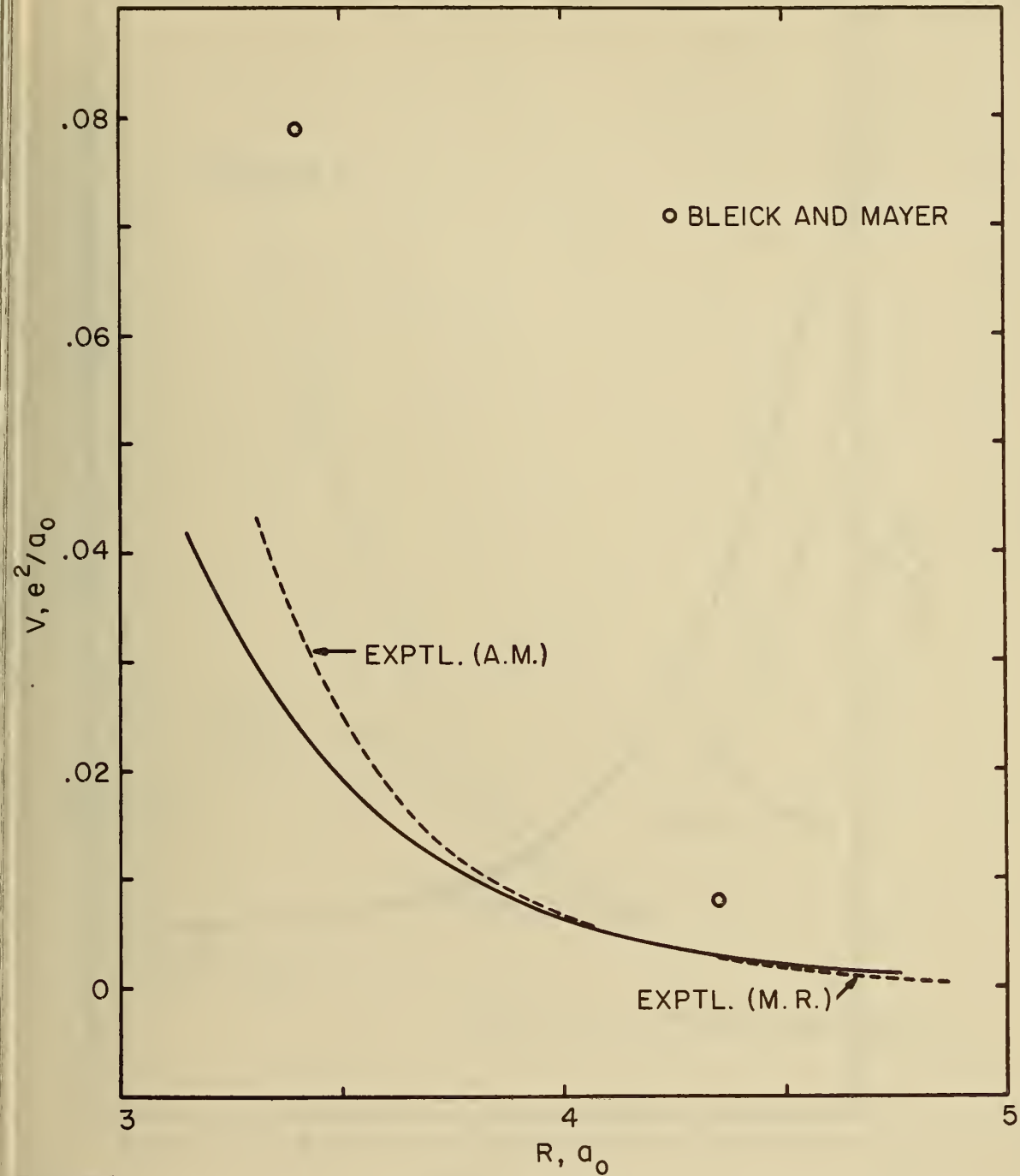


Figure 17 - Energy of interaction of two neon atoms. The solid curve is calculated from the delta-function model.

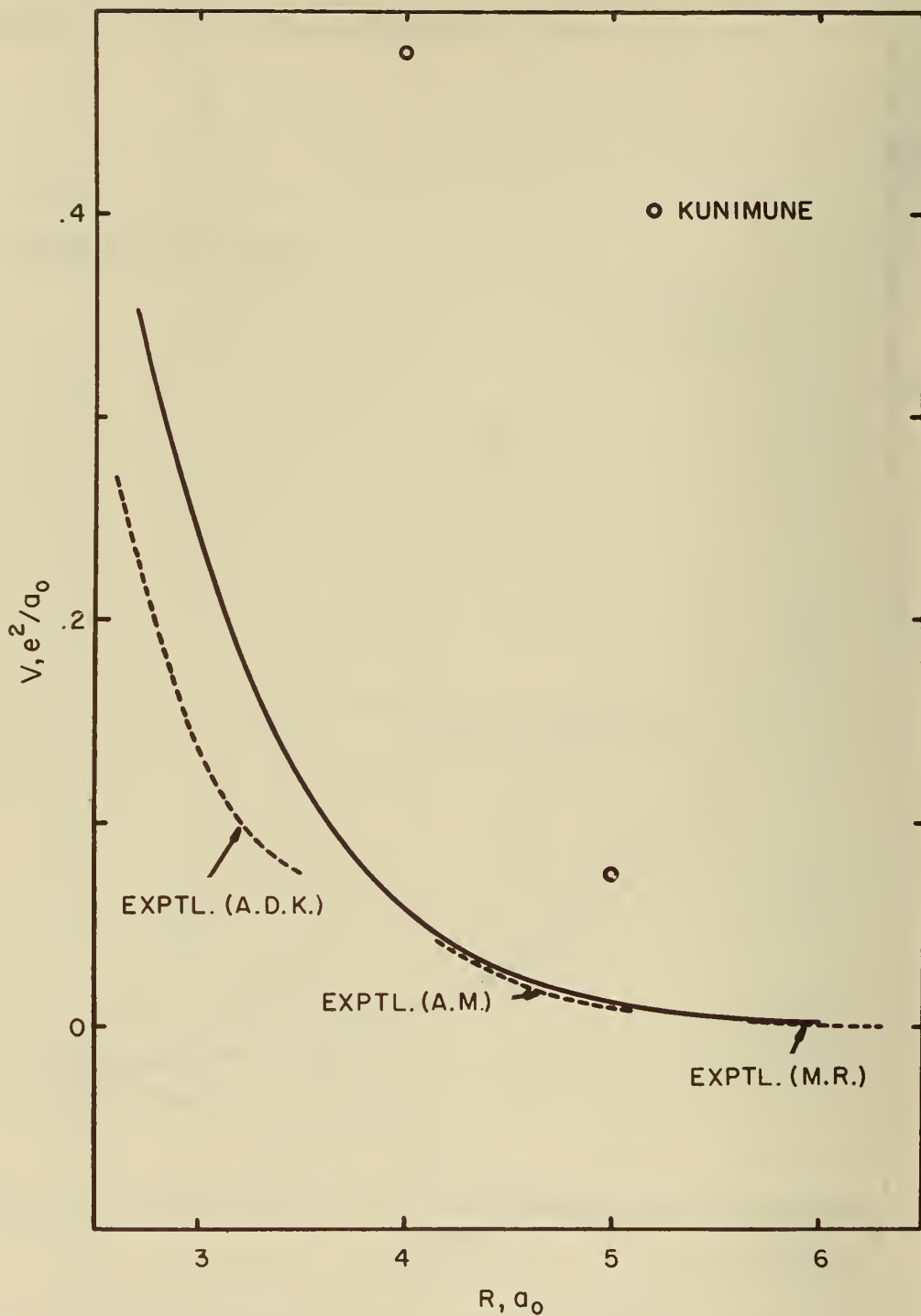


Figure 18 -

Energy of interaction of two argon atoms. The solid curve is calculated from the delta-function model.

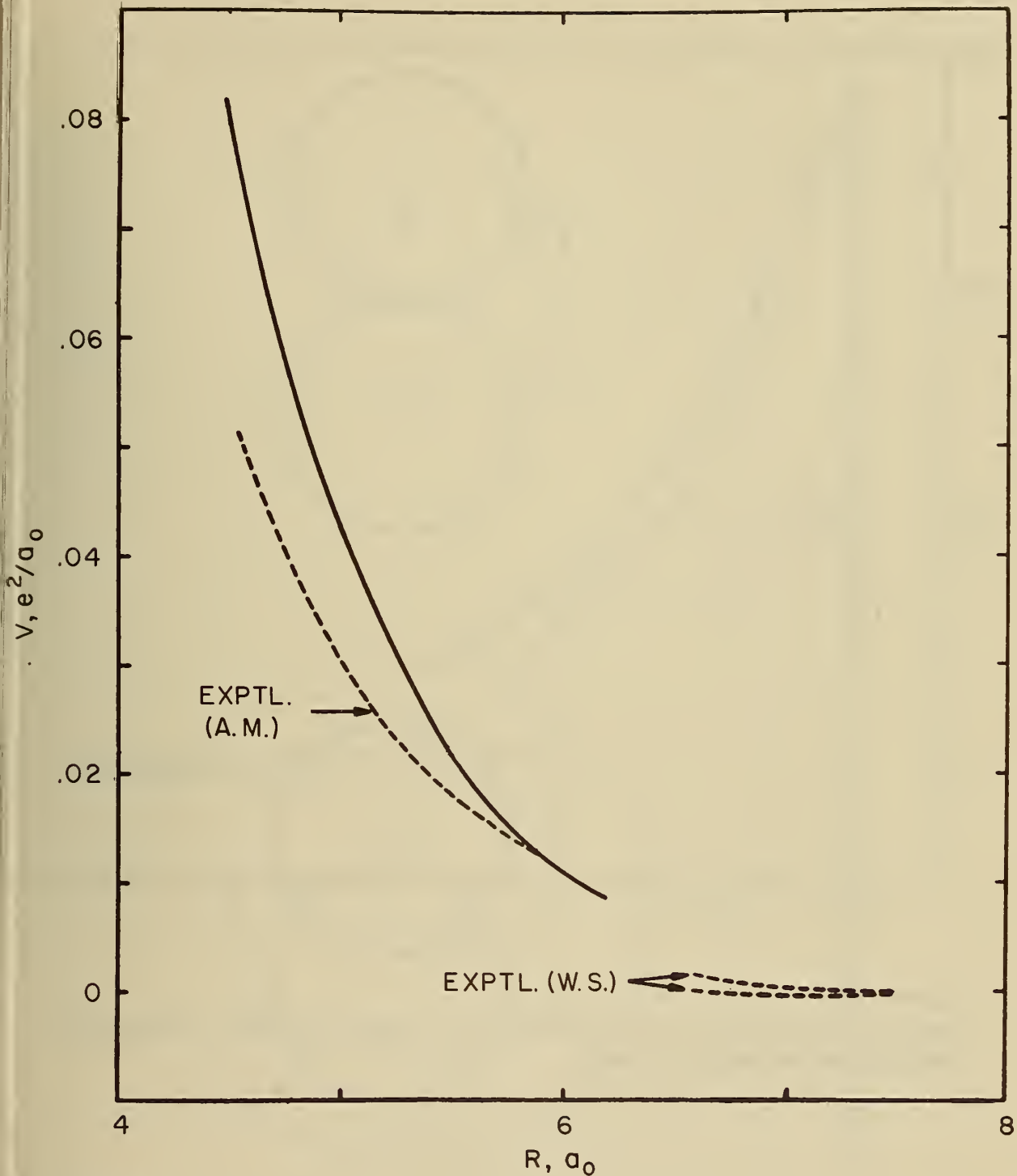


Figure 19 -

Energy of interaction of two krypton atoms. The solid curve is calculated from the delta-function model.

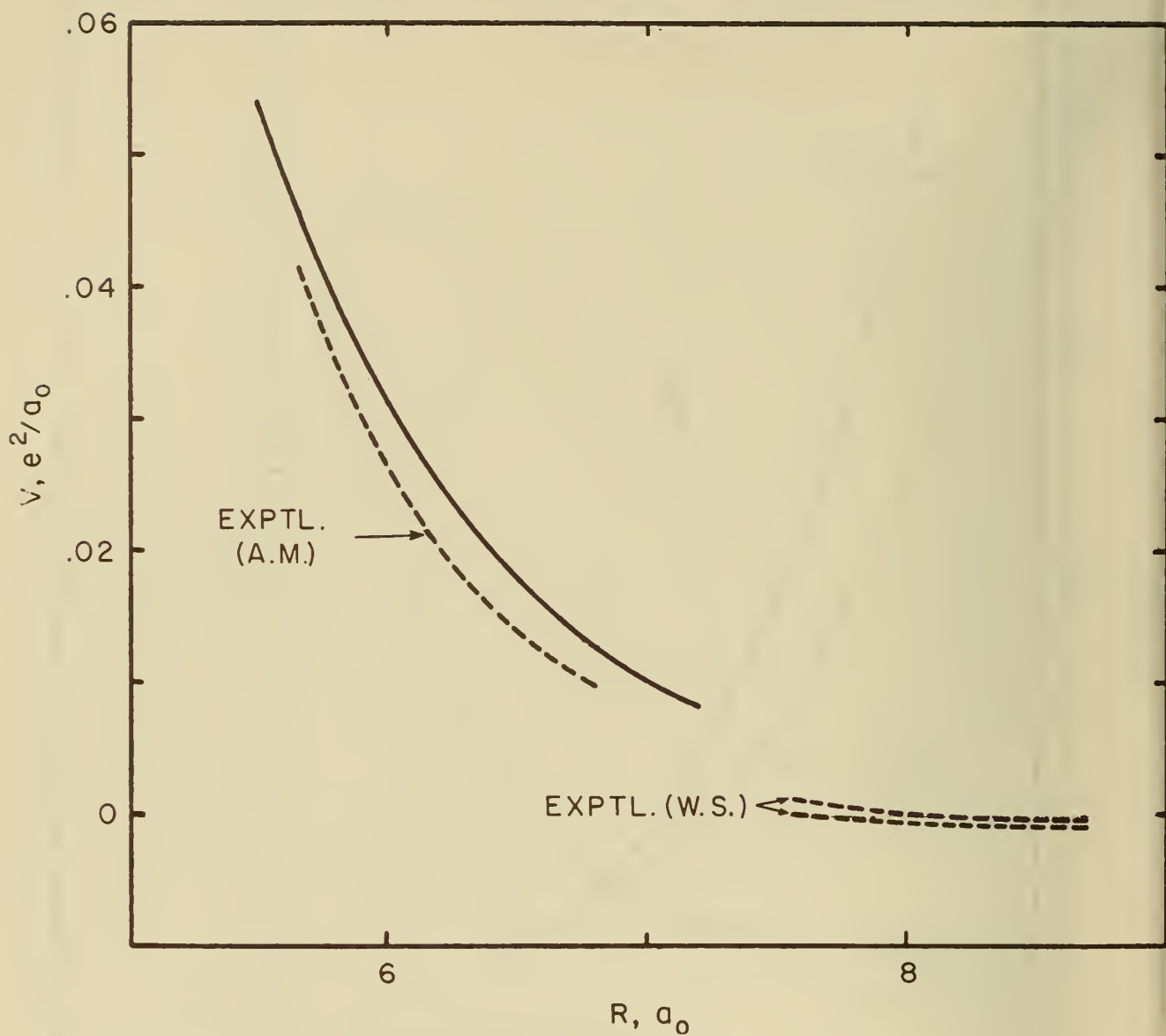


Figure 20 -
 Energy of interaction of two xenon atoms. The solid curve is calculated from the delta-function model.

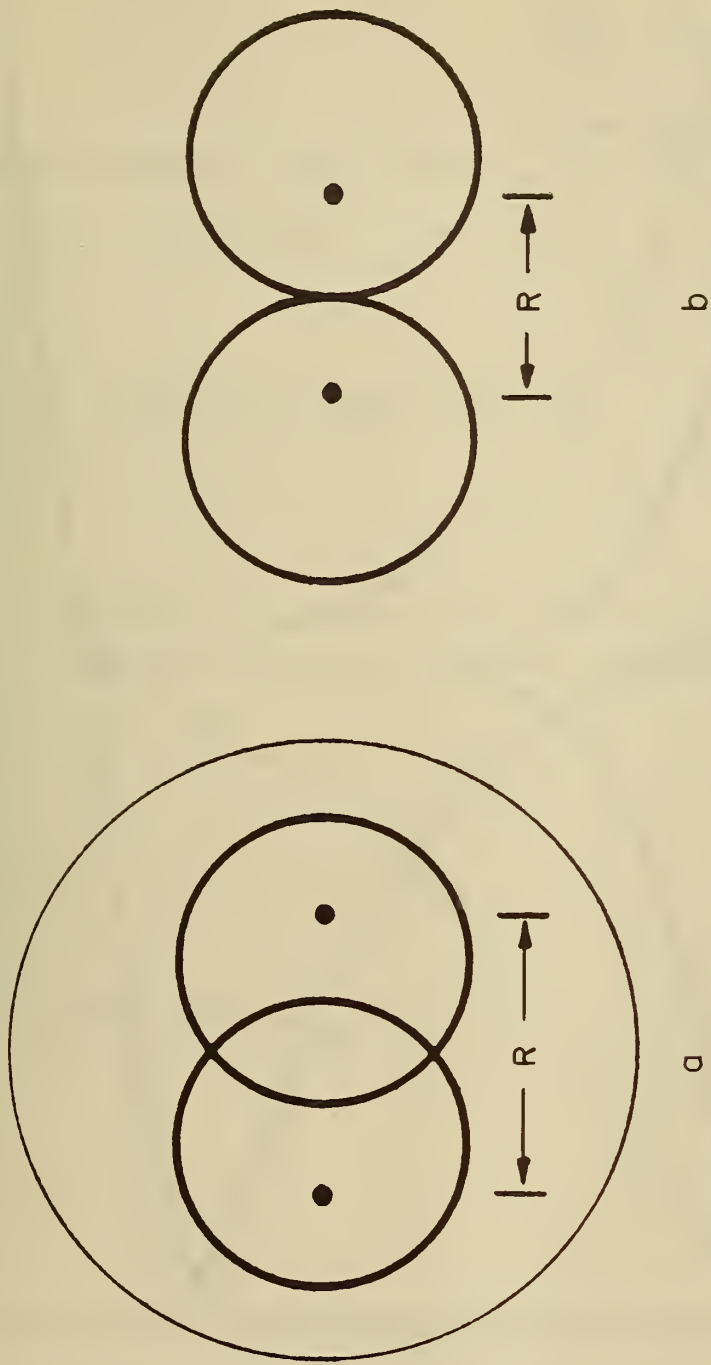


Figure 21 - Semi-classical model of a homonuclear diatomic molecule (after Jefimenko).

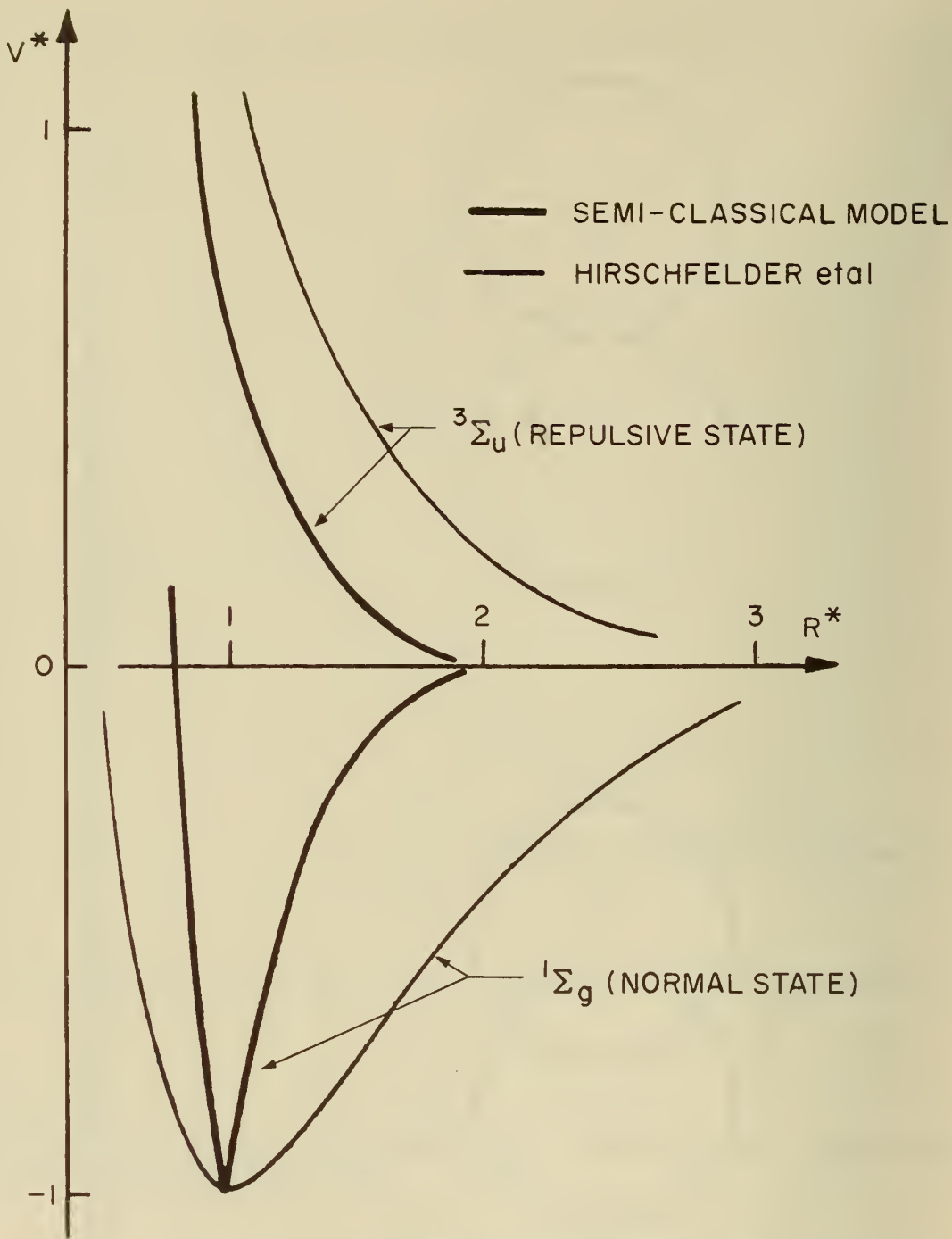


Figure 22 - Observed and calculated potential curves for H_2 .

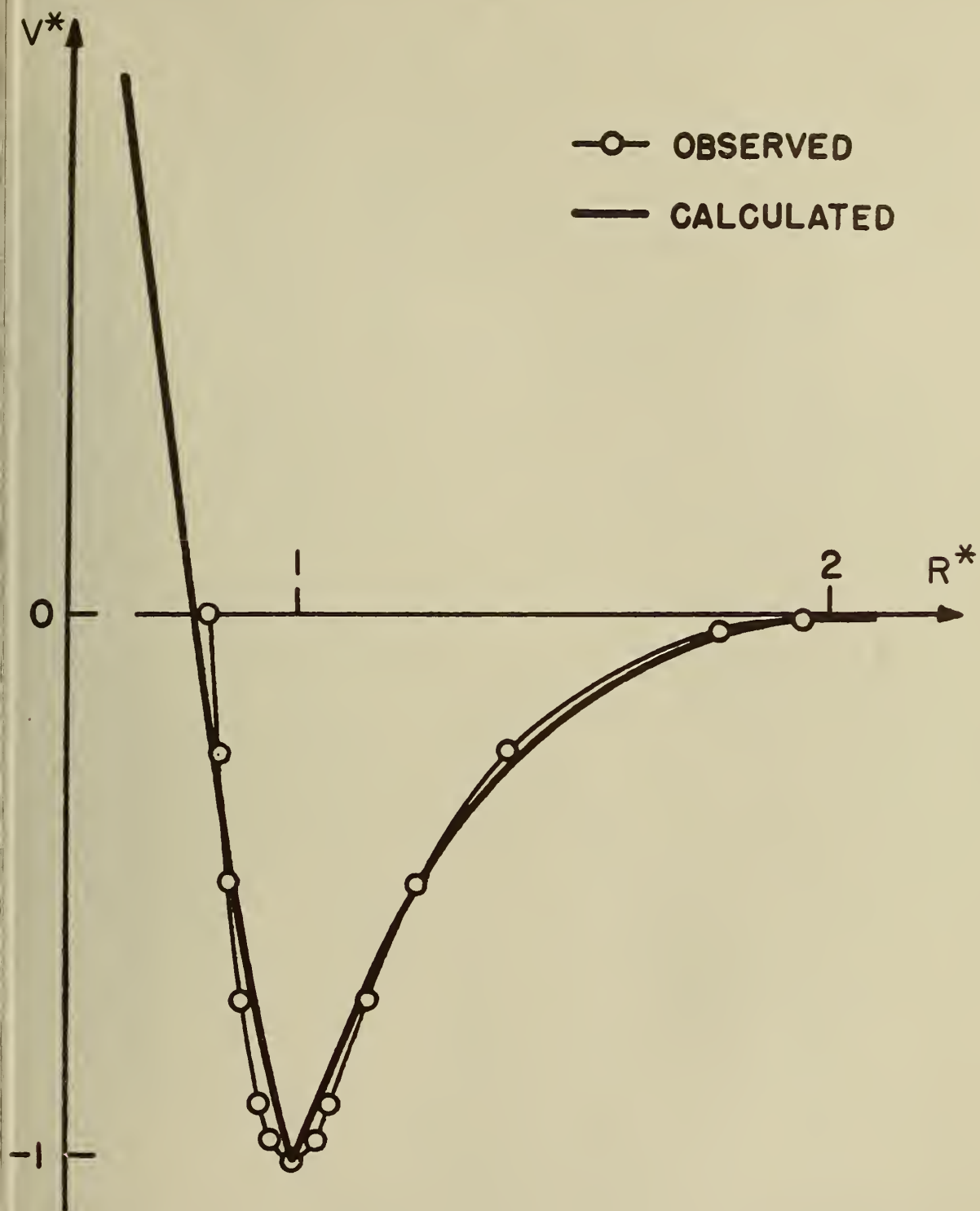


Figure 23 - Observed and calculated potential curves for I_2 .

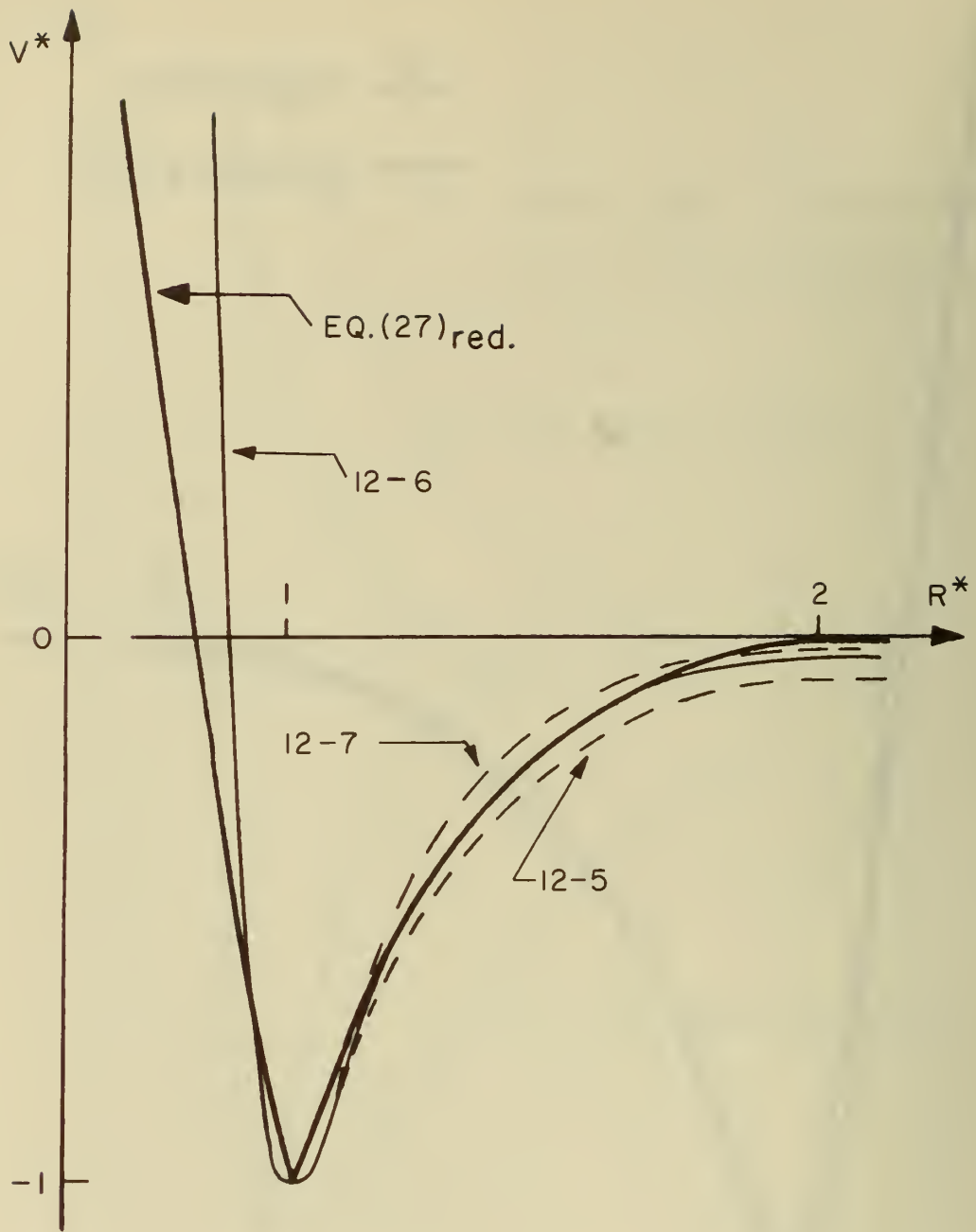


Figure 24 - Comparison of the potential curve resulting from the semi-classical model with the curves resulting from Lennard-Jones (5-12), (6-12), and (7-12) potentials.



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