University of Windsor
Scholarship at UWindsor

Electronic Theses and Dissertations

1973

The round state interatomic potential between pairs of closed-shell atoms.

Maureen E. Pillon
University of Windsor

Recommended Citation

Pillon, Maureen E., "The round state interatomic potential between pairs of closed-shell atoms." (1973). *Electronic Theses and Dissertations.* Paper 4254.

THE GROUND STATE INTERATOMIC POTENTIAL BETWEEN PAIRS OF CLOSED-SHELL ATOMS

by

Maureen E. Pillon

A Thesis
Submitted to the Faculty of Graduate Studies through the Department
of Physics in Partial Fulfillment of the Requirements for
the Degree of Master of Science at the
University of Windsor

Windsor, Ontario

1973

ABSTRACT

A theoretical expression is derived to determine the ground-state interatomic potential between a pair of closed-shell atoms. The total interaction is a sum of terms representing electrostatic interaction, antisymmetry "orthogonality" repulsion, interatomic exchange and long-range (van der Waals) polarization (interatomic correlation). The theory is successfully applied to the following systems: Ne-Ne, Ne-Ar, Ne-Kr, Ar-Ar, Ar-Kr and Kr-Kr; that is, the well parameters(ϵ and r_m) determined for each of the above pairs fall within the accepted range of values. Since the theory uses electron densities in tabulated rather than analytical form, there is no extra complication for heavier atoms. The calculations also provide the core-core interaction for the computation of interatomic potentials between atoms with unclosed electron shells.

ACKNOWLEDGEMENTS

I would like to thank Dr. William E. Baylis for his guidance, encouragement and support during the development of this thesis and for his reading and correcting of the final manuscript. Thanks are also due to Mr. Anil K. Pradhan for his helpful comments and discussions and to my family for their support throughout the research and development of this thesis.

I am indebted to the Department of Physics for financial support in the form of a teaching assistantship and to the University of Windsor for their assistance in the form of a postgraduate scholarship.

TABLE OF CONTENTS

TABLE OF CONTENTS (cont'd)

LIST OF TABLES

LIST OF FIGURES

I INTRODUCTION

A detailed knowledge of the interatomic potential is essential to the solution of a number of problems arising in the study of the solid, liquid and gaseous states. There is considerable interest in the interatomic repulsive potentials because of their importance in such topics as the study of transport phenomena, gas scattering and electrode sputtering.

In recent years, much attention has been focused on the determination of noble-gas pair potentials. The availability of information about equilibrium and transport properties of gases and crystals over wide temperature ranges makes it possible to calculate interatomic potentials which will give the best agreement with these observed bulk properties. Researchers have successfully fitted multiparameter potentials in the short and intermediate ranges to second virial-coefficient data[1] and to the following dilute-gas equilibrium and transport properties: coefficient of viscosity, coefficient of thermal conductivity, thermal-diffusion factor and diffusion coefficients[2-20].

Experimentally, some investigators have made use of the technique of molecular beam scattering. Using crossed-beam differential elastic scattering measurements, the interatomic potentials of Ne-Ar, Ne-Kr, and Ne-Xe[21], Ar-Kr, and Ar-Xe[22], He-He and Ne-Ne[23] and Ar-Ar[24] have been calculated.

Other methods for the experimental determination of interatomic potentials exist and are diverse indeed. For example, Jonah[25] has made a direct determination of the pair potential for argon from fluid X-ray-scattering data, and, by measuring the absorption spectrum of diatomic argon in the ultraviolet, Takana and Yoshino[26] evaluated the well depth of the ground state Ar-Ar potential.

Theoretical methods for calculating interatomic potentials have been developed which, unfortunately for the most part, are valid only over certain ranges of internuclear separation.

In the short-range region, multiconfiguration self-consistent-field calculations are useful but possess the drawback that they are virtually unmanageable in length and complexity as one considers atoms heavier than helium or perhaps neon.

Previous attempts at writing a simplified expression for the short-range interaction have been numerous. One of the earliest general expressions is the Born-Mayer potential[27]

$$V(r) = Z_1 Z_2 e^2 r^{-1} \exp(-r/\beta) \qquad (1\text{-}1)$$

This potential represents the Coulomb interaction between two nuclei of charges $Z_1 e$ and $Z_2 e$ being screened by the surrounding electron cloud. The factor β, called the screening length, is given by Bohr as

$$\beta = a_o (Z_1^{2/3} + Z_2^{2/3})^{-1/2} \qquad (1\text{-}2)$$

where a_o (= 0.529 angstroms) is the first Bohr radius in hydrogen. The negative exponential factor simulates the progressive screening, with increasing r, of the interacting nuclei by their electron clouds, and gives the correct limits of $Z_1 Z_2 e^2/r$ for small r and zero for large r.

Another theoretical expression, given by Firsov[28] and based on the Thomas-Fermi statistical model of the atom, is

$$V(r) = Z_1 Z_2 e^2 r^{-1} \phi(\chi) \tag{1-3}$$

The Thomas-Fermi screening function $\phi(\chi)$ has been both tabulated[29-31] and approximated analytically[32] where χ is defined as

$$\chi = (Z_1^{\frac{1}{2}} + Z_2^{\frac{1}{2}})^{2/3} r/0.8853a_o \tag{1-4}$$

However since the short-range repulsive forces arise by way of the overlap of the electron clouds, a correct theoretical treatment must take into account exchange and possible correlation effects involving all or most of the electrons of both atoms. It is for this reason that the aforementioned multiconfiguration-self-consistent field calculations are favoured.

One who dealt extensively in these short-range calculations was Abrahamson who approached the problem of the determination of short-range repulsive potentials by the application of a variational minimization-and-maximization principle to the Thomas-Fermi-Dirac (TFD) statistical model of the atom[33]. He proceeded to determine the repulsive interaction potentials between noble-gas homonuclear[34] and heteronuclear[35] two-centre systems. Using the TDF model, he also determined potentials between closed-shell ions[36].

In recent years, additional theoretical work on the short-range part of the ground state potential for He-He and other noble-gas pairs has been carried out using various ab initio methods[37-43].

Since potentials computed by the above methods, used to describe strictly short-range interactions, are repulsive in nature (as they must be), they cannot be used in the intermediate region where the interatomic potential minimum lies since it is in this region that attraction exists. In this intermediate range, theoretical potential calculations have been done by Murrell and Shaw[44,45] and by Bertoncini and Wahl[46]. Experimental investigations in this region have been carried out by the groups of Lee[21-24], Scoles[47] and others.

Gordon and Kim[48] described the interatomic potential between two noble-gas atoms (all combinations of helium, neon, argon and krypton) in the short and intermediate ranges by a single "a priori" expression involving a Coulombic part plus kinetic-energy, exchange and correlation contributions calculated in the statistical approximation. Adopting Gordon and Kim's method, Schneider[49] added the ground state interatomic potentials of Xe-He, Xe-Ne, Xe-Ar, Xe-Kr and Xe-Xe.

In the region of large internuclear separation, calculation of the weak, long-range attractive interaction can be handled in various ways, one of which is many-body perturbation theory[50]. Convergence, however, is slow and the calculation tedious.

Other methods which have been used to describe the long-range attraction, particularly for He-He, include variational calculations[51] and time-dependent Hartree-Fock theory[52]. Many semiempirical calculations have been made of interaction coefficients[53], some using sum rules and Padé approximants for interpolation. Portions of the potential curves calculated by different methods have been pieced together as one potential curve, appropriately matched at the joining points (piecewise defined potential). This has been done quite recently for He-Ne, He-Ar, Ne-Ne, Ne-Ar, Ar-Ar, Ar-Kr, Kr-Kr and Xe-Xe by Konowalow and Zakheim[54].

In this thesis a theoretical expression for the ground-state interatomic potential between pairs of closed-shell atoms is developed. The total potential consists of the sum of four separate terms - electrostatic interaction, antisymmetry "orthogonality" repulsion interaction, interatomic exchange interaction and long-range van der Waals (interatomic correlation) interaction.

A major motivation for this work is the need for core-core interactions for two-centre systems involving one or more valence electrons. Such interactions can provide the foundation for calculations of interatomic potentials of both ground and excited states of arbitrary diatomic systems.

Sections II, III, IV and V, respectively, deal with each of the above interactions explicitly. Section VI describes some details of the calculation including the numerical calculation of integrals and the form of the electron density.

Section VII presents the results of the calculation including comparisons with results, both theoretical and experimental, by other investigators.

Section VIII contains conclusions and suggestions for possible improvements in the calculations and suggestions for future work.

II ELECTROSTATIC INTERACTION

The term designated the electrostatic interaction is derived from a common expression of electrodynamics: if a point charge q_i is brought from infinity to a point $\underline{x}_i$ in a region where the scalar potential Φ (which vanishes at infinity) is produced by an array of (n-1) charges q_j ($j=1,2,\ldots,n-1$) at positions $\underline{x}_j$, the work done on the charge (and hence its potential energy) is given by

$$W_i = q_i \sum_{j=1}^{n-1} q_j \left| \underline{x}_i - \underline{x}_j \right|^{-1} = q_i \Phi \qquad (2\text{-}1)$$

The total potential energy of all the charges due to all the forces acting between them is

$$W = \tfrac{1}{2} \sum_{i} \sum_{\substack{j \\ i \neq j}} q_i q_j \left| \underline{x}_i - \underline{x}_j \right|^{-1} \qquad (2\text{-}2)$$

For a continuous charge distribution of density $-e\rho$, the potential energy becomes

$$W = \frac{e^2}{2} \iint \frac{\rho(\underline{x})\, \rho(\underline{x}')}{|\underline{x} - \underline{x}'|}\, d^3x\, d^3x' \qquad (2\text{-}3)$$

In the present investigation the "charge distribution" consists of two closed-shell atoms. These form weakly bound (van der Waals) diatomic molecules in which the distortion of the separate atomic densities is relatively small - small enough that one can, to a good approximation, use undistorted densities to calculate the electrostatic, antisymmetry and exchange interactions (polarization effects are considered separately in Section V). Of course at very small internuclear separations, considerable distortion must occur and here an independent check of the interatomic potential is called for (see below). However in the range of internuclear separation on which we concentrate, this assumption should be valid. Thus the density of the molecule is expressed as the sum of the individual undistorted atomic densities:

$$\rho = \rho_A^{\text{atomic}} + \rho_B^{\text{atomic}} \tag{2-4}$$

With this relation, W becomes

$$\begin{aligned} W = \frac{e^2}{2} \iint \frac{\rho_A^{\text{atomic}}(\underline{x})\, \rho_A^{\text{atomic}}(\underline{x}')}{|\underline{x} - \underline{x}'|} d^3x\, d^3x' \\ + \frac{e^2}{2} \iint \frac{\rho_B^{\text{atomic}}(\underline{x})\, \rho_B^{\text{atomic}}(\underline{x}')}{|\underline{x} - \underline{x}'|} d^3x\, d^3x' \\ + e^2 \iint \frac{\rho_A^{\text{atomic}}(\underline{x})\, \rho_B^{\text{atomic}}(\underline{x}')}{|\underline{x} - \underline{x}'|} d^3x\, d^3x' \end{aligned} \tag{2-5}$$

where the first two terms represent the electrostatic interaction of an atomic charge distribution with itself and the third term represents the electrostatic interaction between the two atomic charge distributions. It is this third term alone that is considered.

The nuclear density is included in the expression for the atomic density by means of a delta function

$$\rho_A^{\text{atomic}}(\underline{r}) = \rho_A(\underline{r}) - Z_A\delta(\underline{r}) \qquad (2\text{-}6)$$

This representation is a valid one since the "radius" of the nucleus is of the order of 10^{-5} that of the radius of the first Bohr orbit. Thus the expression for the electrostatic interaction takes the form

$$V(R) = e^2\int d^3r\int d^3r''\frac{(\rho_A(\underline{r}) - Z_A\delta(\underline{r}))(\rho_B(\underline{r}'') - Z_B\delta(\underline{r}''))}{\left|\underline{r}'' + \underline{R} - \underline{r}\right|} \qquad (2\text{-}7)$$

where e is the charge on the electron; $\rho_A(\underline{r})$ ($\rho_B(\underline{r}'')$) is the electron density of atom A (B); Z_A (Z_B) is the atomic number of atom A (B); $\underline{R}$ is a vector whose magnitude is the internuclear separation and whose direction is from A to B; $\underline{r}$ and $\underline{r}''$ are defined as shown in Figure 1.

The electron densities used in the present investigation are of course ground state densities. Excitation to higher states is ignored. This model is appropriate when the two atoms approach each other slowly, i.e. "thermal" encounters where the kinetic energy is much smaller than the atomic excitation energy ($\gtrsim$10 e.v. for closed-shell atoms). The resulting theoretical interaction energies are independent of collision energy and are called "adiabatic potentials".

Expansion of expression (2-7) shows three types of interactions which are present, namely the repulsive nuclear-nuclear interaction

$$Z_A Z_B e^2 R^{-1} ,$$

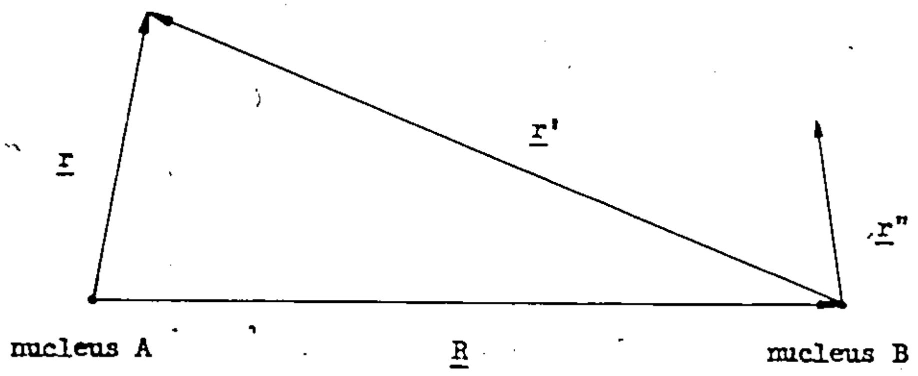

Figure 1: Electron density position vectors $\underline{r}$ and $\underline{r}''$ for the spherically symmetric closed-shell atoms A and B respectively. $\underline{R}$ is the internuclear separation vector and $\underline{r}' = \underline{r} - \underline{R}$.

the attractive electron-nuclear interaction

$$-e^2 Z_A \int d^3r'' \frac{\rho_B(\underline{r}'')}{|\underline{R} + \underline{r}''|} \quad - e^2 Z_B \int d^3r \frac{\rho_A(\underline{r})}{|\underline{R} - \underline{r}|} \quad ,$$

and the repulsive electron-electron interaction

$$e^2 \int d^3r \int d^3r'' \frac{\rho_A(\underline{r}) \; \rho_B(\underline{r}'')}{|\underline{r}'' + \underline{R} - \underline{r}|} \quad .$$

An important assumption made in this investigation and previously mentioned is that the atoms are "closed-shelled". By this term is meant that all the (n, ℓ) orbitals of the atom are filled, e.g. He, Ne, Ar, Kr, Xe, ... By restricting the study to this class of atoms, the electron density is therefore spherically symmetric (Unsöld's theorem[55]) and the angular integration over the azimuthal angle ϕ (taken around the internuclear axis) results simply in 2π.

Simple manipulation of the above equation yields

$$V(R) = z_A z_B e^2 R^{-1} - Z_A e^2 \chi_B(R) - z_B e^2 \chi_A(R)$$
$$+ e^2 \int d^3r \; \rho_A(\underline{r}) \chi_B(\underline{r}') \qquad (2\text{-}8)$$

where z_A (z_B) is the ionicity of atom A (B). By the term "ionicity" is meant the difference between the atomic number of the neutral atom and the number of electrons. Obviously for the neutral atom $z = 0$; for the singly charged ion $z = 1$. The function $\chi(R)$ is

$$\chi(R) = 4\pi \int_R^\infty dr'' \, r'' \left(1 - \frac{r''}{R} \right) \rho(r'') \tag{2-9}$$

Now

$$\int d^3r \, \rho(\underline{r}) \left| \underline{R} - \underline{r} \right|^{-1} = 4\pi \int_0^R dr \, r^2 \rho(r) R^{-1}$$

$$+ 4\pi \int_R^\infty dr \, r^2 \rho(r) r^{-1}$$

$$= \frac{Z - z}{R} + 4\pi \int_R^\infty dr \, r^2 \rho(r) \left(\frac{1}{r} - \frac{1}{R} \right)$$

$$= \frac{Z - z}{R} + \chi(R) \tag{2-10}$$

Thus $-e\chi(R)$ can be thought of as the electrostatic potential at R due to a positive nucleus of charge $(Z - z)$ at the origin and the electron distribution $\rho(r)$. The numerical calculation of $\chi(R)$ and the integral

$$\int d^3r \; \rho_A(\underline{r}) \chi_B(\underline{r}')$$

is discussed in Section VI and in Appendix C.

III ANTISYMMETRY REPULSION

The effect of the Pauli exclusion principle - that the total wavefunction must be antisymmetric[57] - manifests itself in the antisymmetry "orthogonality" repulsion. This repulsion is represented mathematically by a pseudopotential.

The development of the term for the antisymmetry repulsion begins with the assumption that the electrons of the closed-shell atoms can be treated statistically, as in a free electron gas. The Fermi energy (i.e. the energy below which all states are occupied at absolute zero according to Fermi statistics) for this gas is

$$E_F = \frac{p_o^2}{2m_e} + V(r) \qquad (3\text{-}1)$$

where p_o is the Fermi momentum and m_e is the mass of the electron. Now the volume $h^3/2$ which one electron occupies in phase space (the factor $\frac{1}{2}$ arises from spin degeneracy) multiplied by the number of electrons must equal the volume in momentum space that all the electrons occupy multiplied by the volume in co-ordinate space. Dividing through by the volume yields

$$\frac{h^3}{2}\,\frac{N}{V} = \frac{4\pi}{3}p_o^3 \qquad (3\text{-}2)$$

whereupon

$$E_F = (2m)^{-1}(3h^3\rho/8\pi)^{2/3} + V(r) \tag{3-3}$$

Thus if the density ρ is increased, the additional states occupied must have an energy of at least $(2m)^{-1}(3h^3\rho/8\pi)^{2/3}$ above the potential energy $V(r)$. This term, as Baylis[56] points out, can be identified as the " ...Pauli-exclusion pseudopotential for the [repulsive] interaction of a single electron with a ground state electron distribution of density ρ ... ".

The integral $\int d^3r \int_0^{\rho_{total}} d\rho$ over the pseudopotential yields the total energy arising from the pseudointeraction of an electron distribution with itself, namely

$$W(R) = 3\hbar^2(10m_e)^{-1}(3\pi^2)^{2/3}\int d^3r\,\rho^{5/3}(\underline{r}) \tag{3-4}$$

As above the density for the electron distribution of the pair is taken to be the sum of the separate electron densities,

$$\rho(\underline{r}) = \rho_A(\underline{r}) + \rho_B(\underline{r}') \tag{3-5}$$

Thus the antisymmetry repulsion between the two atoms becomes the pseudointeraction energy of ρ minus the pseudointeractions of ρ_A and ρ_B separately:

$$W(R) = 3\hbar^2(10m_e)^{-1}(3\pi^2)^{2/3}\int d^3r\,\Big(\big(\rho_A(\underline{r}) + \rho_B(\underline{r}')\big)^{5/3} - \rho_A^{5/3}(\underline{r}) - \rho_B^{5/3}(r')\Big) \tag{3-6}$$

The numerical calculation of $W(R)$ is discussed in Section VI.

IV INTRA-ATOMIC AND INTERATOMIC EXCHANGE INTERACTION

The electrostatic potential energy of a group of electrons and nuclei can be written as an integral

$$W = \tfrac{1}{2}\int \rho(\underline{x})\Phi(\underline{x})\, d^3x \tag{4-1}$$

where ρ is the charge density and Φ is the electrostatic potential arising from ρ. This, however, incorrectly includes the electrostatic interaction of each electron with itself (self-interaction): Φ should represent the potential exerted by all other electrons except the one under consideration. Due to the Pauli exclusion principle[57], other electrons of like spin tend to avoid this electron. The effect of the exclusion principle, or of exchange, on the distribution of the other electrons of the same spin surrounding the given one is that this distribution approaches a constant density at large distances from the given electron but as it is approached, the density decreases to zero. Thus it can be said that surrounding any electron, the other electrons of the same spin avoid a "hole" centred on the electron in question and large enough to include one electron. The radius r of this hole can be estimated as follows: if one electron is to be included in it, and if the density of like-spin electrons is N/2V electrons per unit volume

$$1 = \frac{4}{3}\pi r^3\left[\frac{N}{2V}\right] \tag{4-2}$$

or

$$r \propto (N/V)^{-1/3} \tag{4-3}$$

Since the potential is proportional to the inverse of r, this leads to an exchange potential of the form[58]

$$U_x \propto \rho^{1/3} \tag{4-4}$$

ρ being the density of the charge distribution.

This is the effect on the distribution of electrons of the same spin; there will be no effect at all on the distribution of electrons of the opposite spin as long as only the exclusion principle is considered, though, of course, electrostatic repulsion will tend to keep these electrons away as well.

The exact form of the exchange potential U_x is given as[58]

$$U_x = -\kappa_x \rho^{1/3} \tag{4-5}$$

where

$$\kappa_x = \frac{3}{4}(3/\pi)^{1/3} e^2 \tag{4-6}$$

From this, one can determine the exchange potential energy to be

$$\int d^3r \int_0^{\rho_{total}} d\rho\, U_x = -\kappa_x \int d^3r\, \rho^{4/3}(\underline{r}) \tag{4-7}$$

Again ρ is the sum of the electron densities of the two atoms

$$\rho(\underline{r}) = \rho_A(\underline{r}) + \rho_B(\underline{r}') \tag{4-8}$$

so the exchange interaction between the two atoms becomes

$$V_x(R) = -\kappa_x \int d^3r \left(\left(\rho_A(\underline{r}) + \rho_B(\underline{r}') \right)^{4/3} - \rho_A^{4/3}(\underline{r}) - \rho_B^{4/3}(\underline{r}') \right) \tag{4-9}$$

Note that the exchange interaction is attractive (hence the negative sign). If exchange effects did not exist, electrons of the same spin would be free to approach each other more closely, the potential between them governed only by the simple law of electrostatics

$$V(r) = e^2 r^{-1} \tag{4-10}$$

where r is the inter-electron separation. However because of the existence of exchange, like-spin electrons tend to avoid each other, hence the repulsive potential between them is less. So the added exchange interaction must be negative.

The numerical calculation of the interatomic exchange interaction is explained in Section VI.

V LONG-RANGE ATTRACTIVE INTERACTION

The attractive interaction between two atoms may be usually characterized either by a weak van der Waals interaction or by a strong chemical interaction. Weak dispersion or dynamic polarization (van der Waals interaction) generally may dominate if one or both of the atoms are noble gases, if the electron spins in the two atoms are parallel (e.g. $H_2\,{}^3\Sigma$) or if for some other reason chemical bonding is not possible.

Quantum mechanically, electrons in an atom cannot be "at rest" since by the uncertainty principle

$$\Delta p \Delta x \gtrsim \hbar \qquad (5\text{-}1)$$

Although in an atom with a spherical charge distribution there is no mean angular or linear momentum or dipole moment, random fluctuations in the electron distribution create instantaneous multipoles (their average is zero) which are able to produce transient fields. These fields polarize the other atom creating attractive forces. That is, if the one atom is considered, say, to be an instantaneous dipole (separation of the centre of negative charge from the centre of positive charge) then it will induce a dipole moment parallel or antiparallel to itself in the other atom. This alignment gives rise to an attractive potential, termed a dispersion interaction by London[59,60] of the form

$$V(r) \propto - r^{-6} \qquad (5\text{-}2)$$

Thus it is the mutual perturbation of the electrons in the two atomic systems that creates this potential.

This interaction can be considered to represent the interatomic correlation since, due to this interaction, the electron cloud of one atom assumes a certain orientation with respect to that of the other atom and vice versa. (The absence of a term representing intra-atomic correlation is justified since this does not change during the encounter.)

The complete form of the interaction can be found by expanding the total Coulombic potential energy of the interacting pair of atoms in a multipole series[61,62]; one gets in second-order perturbation theory the asymptotic series :

$$U(R)_{\text{van der Waals}} = - C_6 R^{-6} - C_8 R^{-8} - C_{10} R^{-10} - \ldots \qquad (5\text{-}3)$$

The terms in the expansion represent, respectively, the dipole-dipole, dipole-quadrupole, quadrupole-quadrupole plus dipole-octupole, ... interactions.

This van der Waals interaction, dominated asymptotically, of course, by the inverse sixth power interaction, can yield a maximum attractive energy of 0.001 - 0.05 e.v.; it extends to distances greater than ten angstroms which is large compared with the "size" of the atoms. This attraction can give rise, at low temperatures, to dimers such as Ar_2 and $(O_2)_2$.

An early expression for the dispersion constant C_6 was developed using a variational calculation by Slater and Kirkwood[63].

It took the form

$$C_6 = C_{disp} = \frac{3e\hbar}{2m_e^{\frac{1}{2}}} \frac{\alpha_1\alpha_2}{(\alpha_1/N_1)^{\frac{1}{2}} + (\alpha_2/N_2)^{\frac{1}{2}}} \tag{5-4}$$

where m_e is the electron mass, and α_1 and α_2 are the electric dipole polarizabilities of atom 1 and atom 2 respectively and N_1 and N_2 are the number of outer shell electrons for atom 1 and atom 2 respectively. Mavroyannis and Stephen[64] and Salem[65] reinterpreted the Slater-Kirkwood formula and from their result, it followed that the total number of electrons in the atom should be used for N_1 and N_2. A good approximate formula developed by London[60,66] and Margenau[61] is

$$C_{disp} = \frac{3}{2}(E_1E_2/(E_1 + E_2))\alpha_1\alpha_2 \tag{5-5}$$

The energies E_1 and E_2 were found to be close to the ionization energies E_{I1} and E_{I2} of the atoms. Similar expressions along this line were also developed for C_8 and C_{10}[62]; more recent treatments have been given by Hirschfelder and Löwdin[63,64]. Recently determined values of the C_6[65-74] and C_8[50,51,75,76] coefficients, utilizing various theoretical methods, are available in the literature.

If the asymptotic van der Waals formula (5-3) is extended to the short-range region, $U_{vdW}(R)$ diverges as R^{-6}. One therefore seeks an analytical expression to represent the polarization interaction which has the appropriate behavior at large and small distances - that is, one which remains finite as r goes to zero and possesses the asymptotic form

$$-C_6R^{-6}-C_8R^{-8}-\ldots$$

The higher order terms

$$-C_{10}R^{-10}-C_{12}R^{-12}-\ldots$$

are generally small in comparison to the first two and will be omitted.

The construction of this analytical expression is equivalent to the use of a "cutoff". The concept of a cutoff has been used by others such as Bates[77] in a study of the effect of polarization on the distribution of intensity in a continuous spectrum beyond the series limit and by Biermann[78] to examine polarization effects on the energy levels of the terms of various optical spectra.

The form constructed for the polarization interaction in the present investigation is

$$V_{PI}(R)=-C_6R^2(R^2+R_o^2)^{-4}-AR^4(R^2+R_o^2)^{-6} \qquad (5\text{-}6)$$

where R_o is the cutoff length and A is a constant to be determined. The above form vanishes as R^2 as R approaches zero. By expanding $V_{PI}(R)$ for the case of large R and comparing this expansion to the van der Waals long-range expression (5-3), A is found to be

$$A=C_8+4C_6R_o^2 \qquad (5\text{-}7)$$

All that remains is to determine R_o. But many different analytical formulae exist which display the required behavior at large and small R values. Only one of these has been chosen for the present investigation. Therefore R_o, which must have units of length, cannot be expected to correspond exactly to anything physical. However it is logical to assume that it should somehow depend equally on the two atoms considered. The choice of R_o is discussed below (Section VI).

VI METHOD OF CALCULATION

The expression for the total interatomic potential between two closed-shell atoms (having, of course, spherically symmetric charge distributions) is

$$
\begin{aligned}
V_{total}(R) = {} & z_A z_B e^2 R^{-1} - Z_A e^2 \chi_B(R) - z_B e^2 \chi_A(R) \\
& + e^2 \int d^3 r \; \rho_A(\underline{r}) \, \chi_B(\underline{r}') \\
& + \frac{3}{5} \frac{\hbar^2}{2m_e} (3\pi^2)^{2/3} e^2 \int d^3 r \left(\left(\rho_A(\underline{r}) + \rho_B(\underline{r}') \right)^{5/3} \right. \\
& \qquad \left. - \rho_A^{5/3}(\underline{r}) - \rho_B^{5/3}(\underline{r}') \right) \\
& - \frac{3}{4} (3/\pi)^{1/3} e^2 \int d^3 r \left(\left(\rho_A(\underline{r}) + \rho_B(\underline{r}') \right)^{4/3} \right. \\
& \qquad \left. - \rho_A^{4/3}(\underline{r}) - \rho_B^{4/3}(\underline{r}') \right) \\
& - e^2 \left(C_6 R^2 (R^2 + R_o^2)^{-4} + (C_8 + 4 C_6 R_o^2) R^4 \times \right. \\
& \qquad \left. (R^2 + R_o^2)^{-6} \right)
\end{aligned}
\tag{6-1}
$$

Calculation of the first and seventh terms presents no difficulty as it is very straightforward. The three integrals can be handled collectively utilizing Gauss-Legendre and Gauss-Laguerre integration methods to carry out the integral over the volume. By changing to elliptical co-ordinates, the details of which are explained in Appendix A, the integral over the volume element can be re-written as

$$\int d^3r = \frac{\pi R^3}{4} \int_0^\infty dx \int_{-1}^{1} dy \, \left((x+1)^2 - y^2 \right) \qquad (6\text{-}2)$$

where the integral over "x" from zero to infinity is handled using the Gauss-Laguerre method and the integral over "y" from minus one to plus one by the Gauss-Legendre method. A 15-point Gauss-Laguerre[79] integration coupled with a 32-point Gauss-Legendre[80] integration proves to be a good compromise between speed and accuracy.

In the Gauss-Laguerre integration over x (see Appendix A (ii)) the integrand is essentially fitted to a polynomial in x (of 29'th order for a 15-point integration) times an exponential factor exp($-x/\kappa$). The optimum value of the parameter κ is different for the three integrations performed (fourth, fifth and sixth terms on the right hand side of equation (6-1)). A single value of κ was however found which would work satisfactorily with all integrations. It is (see Appendix A (ii) for details)

$$\kappa^{-1} = 2^{1/2} \left(I_A^{1/2} + I_B^{1/2} \right) R \qquad (6\text{-}3)$$

where I_A (I_B) is the ionization energy in a.u. of atom A (B).

Thus all three integrals can be evaluated at once, yielding a savings of nearly a factor of three in computer calculation time and a significant increase in accuracy. The latter arises because the integrals largely cancel one another at some values of R, and considerable error is eliminated by subtracting the integrands, which have a numerical error of only about 10^{-14}, rather than the integrals, whose error may be as high as 10^{-5}.

In the early stages of this work, the Gombás[81] form of the electron density was used since it possessed a convenient form with which to work. However it is not as accurate as the one selected for use in the final computations[82]. Using the Roothan-Hartree-Fock method, Clementi[83,84] has calculated wavefunctions for atomic orbitals which can be used to derive electron densities for the atom. The determination of the densities is done in the following manner: Slater-type basis functions $\chi^{(i)}_{n\ell m}$[85] for each orbital are defined as

$$\chi^{(i)}_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi) \tag{6-4}$$

where $Y_{\ell m}(\theta,\phi)$ are normalized spherical harmonics and

$$R_{n\ell}(r) = ((2n_{n\ell})!)^{-\frac{1}{2}}(2\zeta_{n\ell})^{\left[n_{n\ell}+\frac{1}{2}\right]} r^{\left[n_{n\ell}-1\right]} \exp(-\zeta_{n\ell} r) \tag{6-5}$$

The wavefunction of a particular orbital is then defined as

$$\phi_{n\ell} = \sum_{i=1}^{N} a_i \chi^{(i)}_{n\ell} \tag{6-6}$$

For the first thirty-six elements (H to Kr) Clementi has tabulated values of n and ζ (orbital exponent) for each basis function and a set of a_i (weight factors) for each orbital.

The electron density of the atom is given by

$$\rho = \sum_{s} \nu_s \left|\psi_s\right|^2 / Z \tag{6-7}$$

where ν_s is the occupation number of the s'th orbital. Since the class of atoms under consideration (closed-shell atoms) possess spherically symmetric charge distributions, the contribution made to $|\phi|^2$ by the factor $|Y_{\ell m}(\theta,\phi)|^2$ will always be $(4\pi)^{-1}$. Therefore the "Clementi" wavefunctions simplify to

$$\phi_{n\ell} = (4\pi)^{-\frac{1}{2}} \sum_{i=1}^{N} a_i R^{(i)}_{n\ell}(r) \qquad (6\text{-}8)$$

The ϕ's are already appropriately normalized, that is, the integral over all space of $|\phi|^2$ is one.

Because (6-7) proves to be progressively more time-consuming as heavier and heavier atoms are considered, a more efficient means of determining the "Clementi" electron density at a point is to define the density as a set of points spaced at certain intervals rather than as an analytical formula. This will also allow the use of electron densities which are available only in tabular form. If the electron density is to be accurately described by a set of points, more points must be specified in the rapidly-varying region (small r) than in the slowly-varying region (large r). This is conveniently handled by utilizing a log grid or mesh, that is, by defining the electron density not as a function of r but as a function of y where r = exp(y). Thus r can range from zero to plus infinity by varying y from minus infinity to plus infinity (Figure 2).

Very few, if any, of the actual read-in points will be called for in the potential calculation. This necessitates the construction of an interpolation procedure to determine the electron density at the required points. A variation of the Lagrange three-point (parabolic fit) interpolation method is used, the details of which

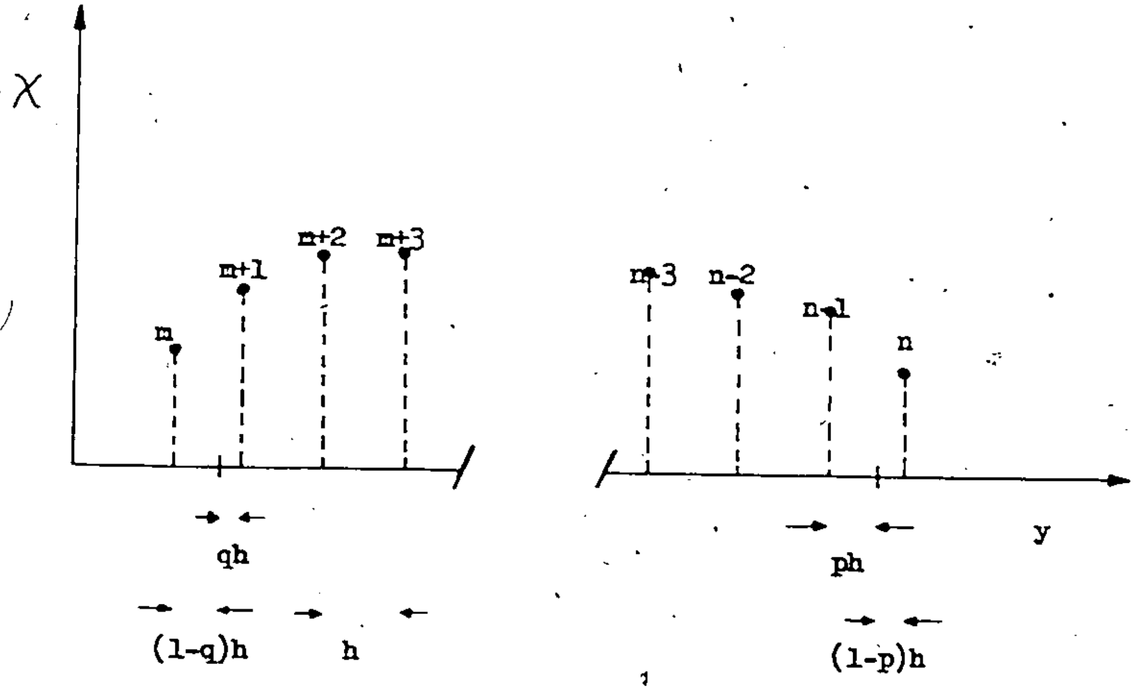

Figure 2: χ integrand calculated at evenly spaced intervals on the log grid

are outlined in Appendix B. Adoption of this method sacrifices small errors[86] in the required density points for speed of calculation.

The remaining two terms in the total interaction are

$$- Z_A e^2 \chi_B(R) - z_B e^2 \chi_A(R) \quad .$$

As shown previously

$$\chi(r) = 4\pi \int_r^\infty dr'' \, r'' \left(1 - r''/r \right) \rho(r'') \qquad (6\text{-}9)$$

Using the Gombás densities

$$\rho(r) = \sum_s \gamma_s \, r^{\alpha_s} \exp(-2\beta_s r) \qquad (6\text{-}10)$$

it is possible to evaluate $\chi(R)$ analytically. However since a numerical form of the electron density is being used, $\chi(R)$ must be done numerically. Using the log grid

$$r = \exp(y) \qquad dr = \exp(y) dy \qquad (6\text{-}11)$$

the integral

$$\chi(R) = \int_R^\infty dr \, D(r) \left(r^{-1} - R^{-1} \right) \qquad (6\text{-}12)$$

where

$$D(r) = 4\pi r^2 \rho(r) \qquad (6\text{-}13)$$

can be written as

$$\chi(R) = \int_{\ln R}^{\infty} dy\ D(y)\ (\ 1 - \exp(\ y\ )/R\ ) \qquad (6\text{-}14)$$

Equation (6-14) is evaluated by the "double quadratic integration method" (Appendix B (ii)) over the range of equally spaced density values and by an analytic approximation (Appendix C (i)) outside this range.

At this point, the three interactions - electrostatic, antisymmetry and interatomic exchange - can be calculated at any internuclear separation. The fourth interaction, namely the long-range polarization, is completely defined except for the choice of the cutoff R_o. As mentioned previously, it is known that R_o must have units of length and it is assumed to depend equally on each of the two interacting atoms. The possible forms for R_o considered were

$$R_o = A(\langle r^n\rangle_A^{1/n} + \langle r^n\rangle_B^{1/n}) \qquad (6\text{-}15)$$

where $\langle r^n\rangle_A$ ($\langle r^n\rangle_B$) is the average value of r^n for atom A (B) and A is a real multiplicative constant. Using the "Clementi" electron densities and the parameters in Table 1, the simple form

$$R_o = \langle r^6\rangle_A^{1/6} + \langle r^6\rangle_B^{1/6} \qquad (6\text{-}16)$$

was found to reproduce satisfactorily experimental well depths ϵ and positions r_m of diatomic neon, argon and krypton combinations.

TABLE 1

PARAMETERS FOR THE LONG-RANGE POLARIZATION INTERACTION *

ELEMENT	$\langle r^2 \rangle^{87}$	$\langle r^4 \rangle^{87}$	$\langle r^6 \rangle^{87}$
Neon	0.9372	2.719	16.36
Argon	1.446	8.044	83.45
Krypton	1.098	6.828	84.11

NOBLE-GAS PAIR	C_6^{71}	C_8^{88}	R_o
Ne-Ne	6.3	54.83	3.187
Ne-Ar	19.5	247.6	3.684
Ne-Kr	27	369.4	3.686
Ar-Ar	65	1085	4.181
Ar-Kr	91	1608	4.184
Kr-Kr	128	2388	4.186

* a.u. used (energy in hartrees, lengths in bohr)

VII RESULTS

The results of the calculations using densities constructed from Clementi's Hartree-Fock wavefunctions,[84] Dalgarno's C_6 values,[71] Starkschall and Gordon's C_8 formula,[76] and a cutoff of the form

$$R_o = \langle r^6\rangle_A^{1/6} + \langle r^6\rangle_B^{1/6}$$

are presented in the following manner. Tables 2 through 7 contain values of the total ground state interatomic potential at internuclear separations ranging from 0.2 bohr to 15 bohrs. Figures 3 through 8 show the data from Tables 2-7 plotted along with the results of other investigators. Tables 8 through 13 compare the well parameters from the present investigation with those determined by others.

TABLE 2

Ne-Ne GROUND STATE POTENTIAL

R (bohrs)	TOTAL POTENTIAL (e.v.) *
0.2	0.7342D4
0.4	0.2282D4
0.6	0.9892D3
0.8	0.4924D3
1.0	0.2713D3
1.2	0.1613D3
1.4	0.1004D3
1.6	0.6378D2
1.8	0.4079D2
2.0	0.2606D2
2.2	0.1657D2
2.4	0.1047D2
2.6	0.6571D1
2.8	0.4096D1
3.0	0.2533D1
3.2	0.1553D1
3.4	0.9435D0
3.6	0.5665D0
3.8	0.3352D0
4.0	0.1945D0
4.2	0.1098D0
4.4	0.5958D-1
4.6	0.3023D-1
4.8	0.1348D-1

TABLE 2

Ne-Ne GROUND STATE POTENTIAL (cont'd)

R (bohrs)	TOTAL POTENTIAL (e.v.)
5.0	0.4240D-2
5.2	-0.5973D-3
5.4	-0.2904D-2
5.6	-0.3796D-2
5.8	-0.3934D-2
6.0	-0.3697D-2
6.2	-0.3300D-2
6.4	-0.2858D-2
6.6	-0.2432D-2
6.8	-0.2048D-2
7.0	-0.1715D-2
7.2	-0.1433D-2
7.4	-0.1198D-2
7.6	-0.1003D-2
7.8	-0.8434D-3
8.0	-0.7118D-3
9.0	-0.3283D-3
10.0	-0.1699D-3
11.0	-0.9562D-4
12.0	-0.5700D-4
13.0	-0.3547D-4
14.0	-0.2284D-4
15.0	-0.1515D-4

* Dx = 10^{x} D-y = 10^{-y}

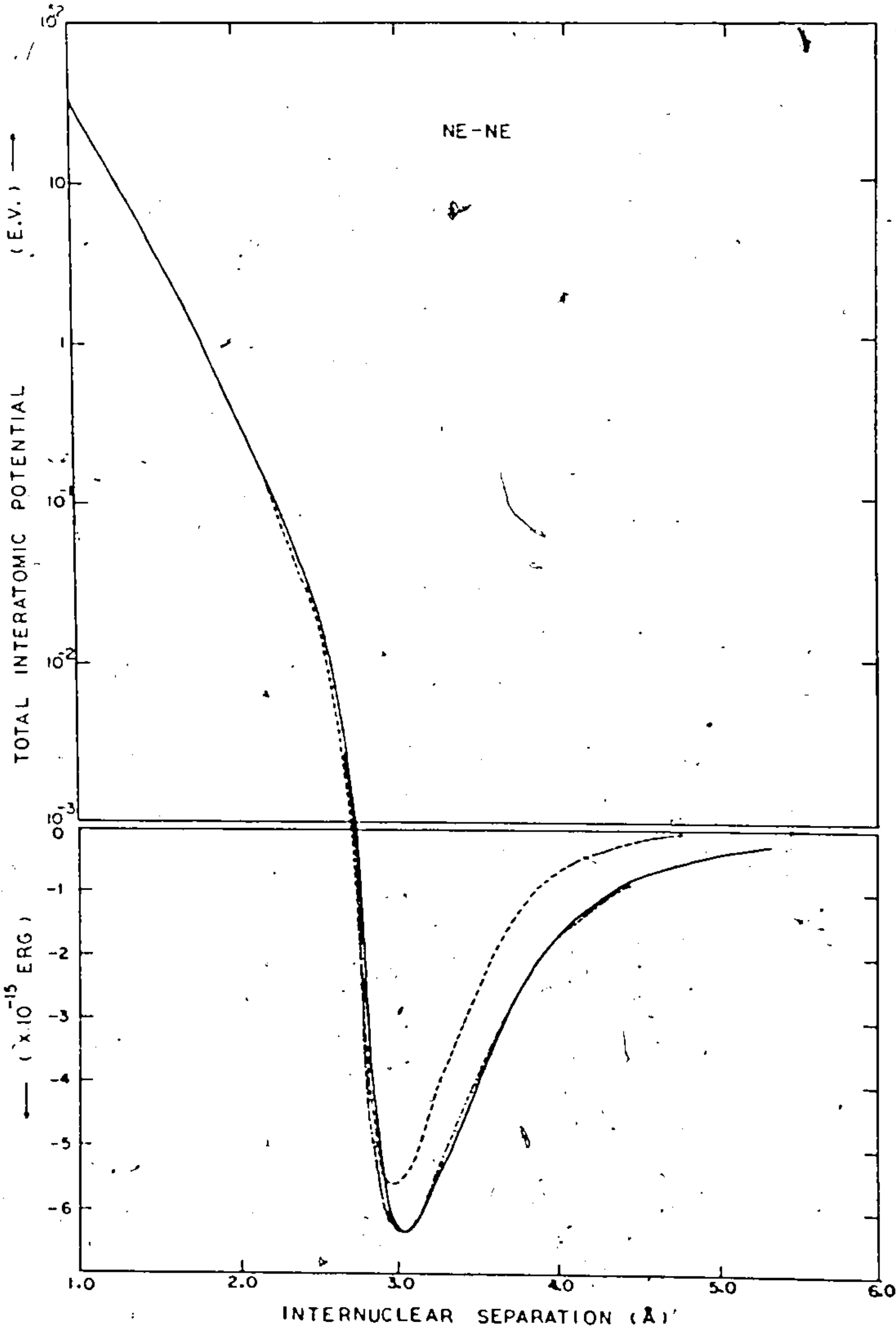

Figure 3: Ne-Ne ground state interatomic potential. - - - Gordon and Kim (Reference 48); -.-.- Siska et al. (Reference 23); —— Present Investigation

TABLE 3

Ne-Ar GROUND STATE POTENTIAL

R (bohrs)	TOTAL POTENTIAL (e.v.)
0.1	0.3351D5
0.2	0.1232D5
0.3	0.6251D4
0.4	0.3651D4
0.5	0.2312D4
0.6	0.1550D4
0.7	0.1083D4
0.8	0.7785D3
0.9	0.5700D3
1.0	0.4231D3
1.1	0.3177D3
1.2	0.2416D3
1.3	0.1861D3
1.4	0.1455D3
1.5	0.1154D3
1.6	0.9271D2
1.7	0.7539D2
1.8	0.6191D2
1.9	0.5122D2
2.0	0.4260D2
2.1	0.3556D2
2.2	0.2975D2
2.3	0.2490D2
2.4	0.2084D2

TABLE 3

Ne-Ar GROUND STATE POTENTIAL (cont'd)

R (bohrs)	TOTAL POTENTIAL (e.v.)
2.5	0.1743D2
2.6	0.1456D2
2.7	0.1214D2
2.8	0.1011D2
2.9	0.8395D1
3.0	0.6960D1
3.1	0.5758D1
3.2	0.4753D1
3.4	0.3217D1
3.6	0.2158D1
3.8	0.1433D1
4.0	0.9412D0
4.2	0.6106D0
4.4	0.3903D0
4.6	0.2449D0
4.8	0.1501D0
5.0	0.8895D-1
5.2	0.5021D-1
5.4	0.2611D-1
5.6	0.1149D-1
5.8	0.2942D-2
6.0	-0.1802D-2
6.2	-0.4204D-2
6.4	-0.5205D-2

TABLE 3

Ne-Ar GROUND STATE POTENTIAL (cont'd)

R (bohrs)	TOTAL POTENTIAL (e.v.)
6.6	-0.5401D-2
6.8	-0.5161D-2
7.0	-0.4711D-2
7.2	-0.4182D-2
7.4	-0.3649D-2
7.6	-0.3150D-2
7.8	-0.2702D-2
8.0	-0.2311D-2
9.0	-0.1072D-2
10.0	-0.5414D-3
11.0	-0.2989D-3
12.0	-0.1765D-3
13.0	-0.1094D-3
14.0	-0.7040D-4
15.0	-0.4672D-4

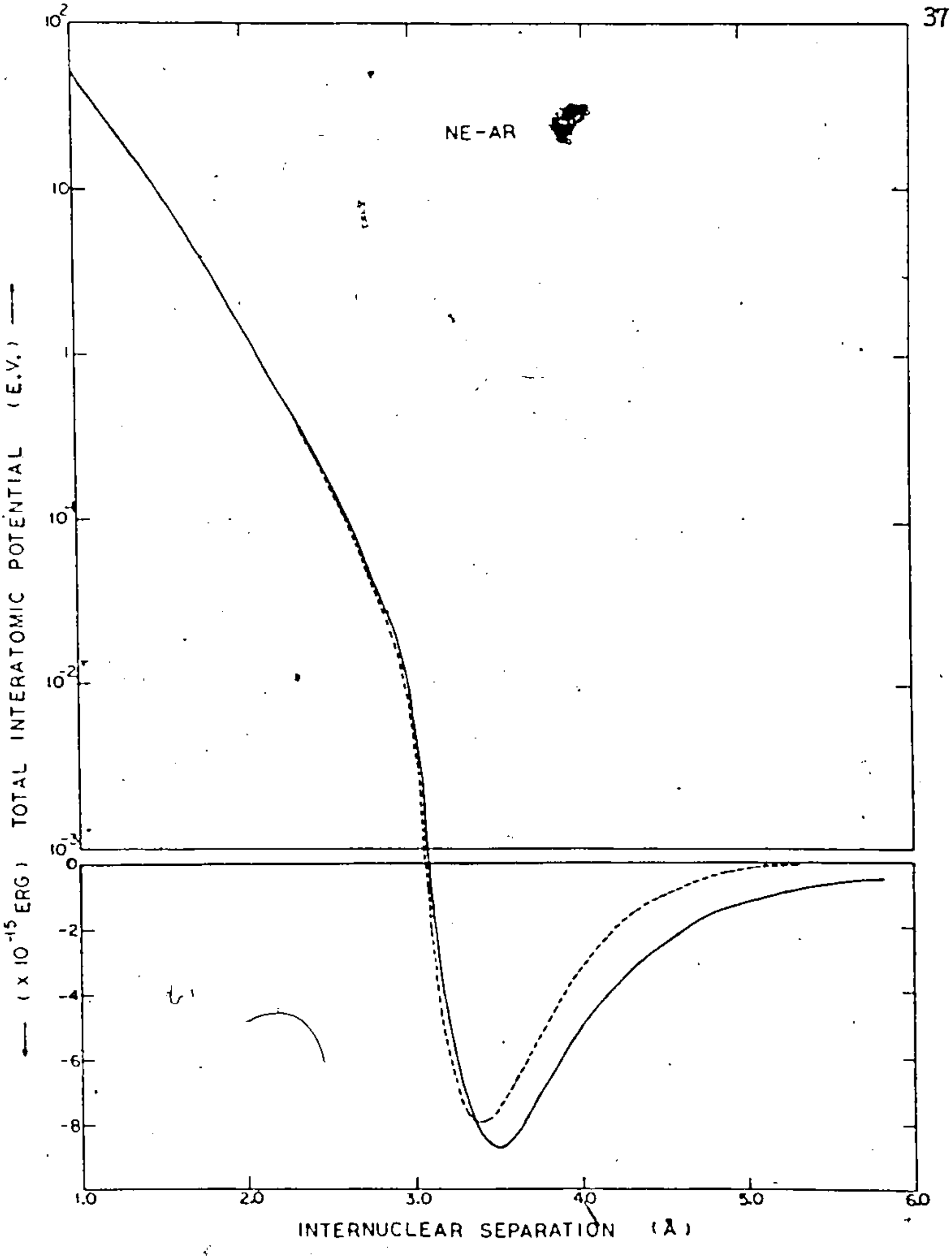

Figure 4: Ne-Ar ground state interatomic potential. - - - Gordon and Kim (Reference 48); —— Present Investigation

TABLE 4

Ne-Kr GROUND STATE POTENTIAL

R (bohrs)	TOTAL POTENTIAL (e.v.)
0.2	0.2271D5
0.4	0.6402D4
0.6	0.2588D4
0.8	0.1249D4
1.0	0.6753D3
1.2	0.3864D3
1.4	0.2283D3
1.6	0.1394D3
1.8	0.8846D2
2.0	0.5834D2
2.2	0.3969D2
2.4	0.2756D2
2.6	0.1934D2
2.8	0.1362D2
3.0	0.9580D1
3.2	0.6709D1
3.4	0.4670D1
3.6	0.3228D1
3.8	0.2214D1
4.0	0.1506D1
4.2	0.1014D1
4.4	0.6757D0
4.6	0.4445D0
4.8	0.2880D0

TABLE 4

Ne-Kr GROUND STATE POTENTIAL (cont'd)

R (bohrs)	TOTAL POTENTIAL (e.v.)
5.0	0.1829D0
5.2	0.1132D0
5.4	0.6749D-1
5.6	0.3799D-1
5.8	0.1932D-1
6.0	0.7811D-2
6.2	0.9707D-3
6.4	-0.2866D-2
6.6	-0.4814D-2
6.8	-0.5604D-2
7.0	-0.5711D-2
7.2	-0.5438D-2
7.4	-0.4977D-2
7.6	-0.4441D-2
7.8	-0.3898D-2
8.0	-0.3386D-2
9.0	-0.1590D-2
10.0	-0.7803D-3
11.0	-0.4203D-3
12.0	-0.2453D-3
13.0	-0.1516D-3
14.0	-0.9758D-4
15.0	-0.6480D-4

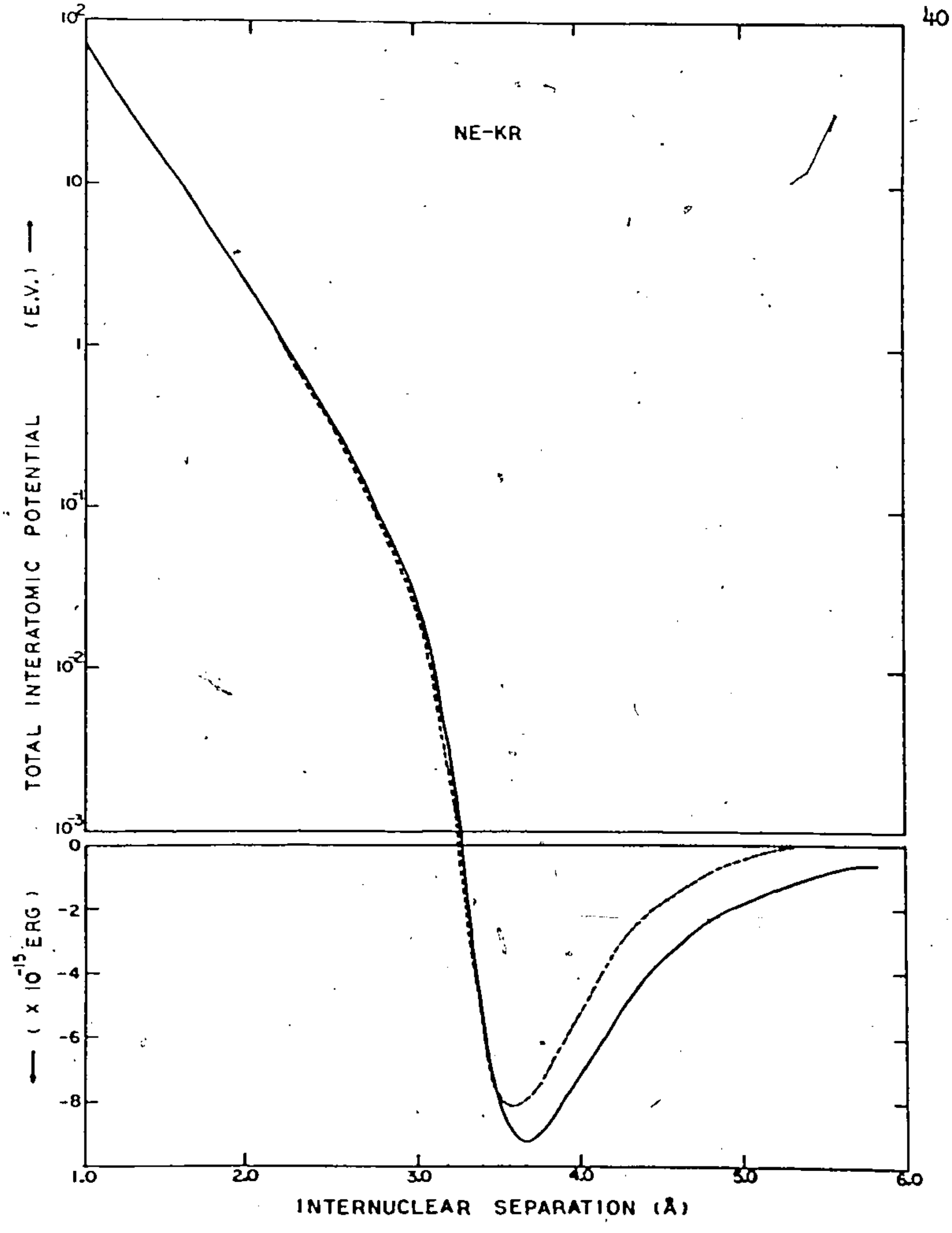

Figure 5: Ne-Kr ground state interatomic potential. - - - Gordon and Kim (Reference 48); —— Present Investigation

TABLE 5

Ar-Ar GROUND STATE POTENTIAL

R (bohrs)	TOTAL POTENTIAL (e.v.)
0.2	0.2124D5
0.4	0.6120D4
0.6	0.2557D4
0.8	0.1261D4
1.0	0.6947D3
1.2	0.4114D3
1.4	0.2515D3
1.6	0.1558D3
1.8	0.9808D2
2.0	0.6345D2
2.2	0.4250D2
2.4	0.2946D2
2.6	0.2099D2
2.8	0.1521D2
3.0	0.1111D2
3.2	0.8128D1
3.4	0.5923D1
3.6	0.4288D1
3.8	0.3080D1
4.0	0.2190D1
4.2	0.1541D1
4.4	0.1071D1
4.6	0.7345D0
4.8	0.4953D0

TABLE 5

Ar-Ar GROUND STATE POTENTIAL (cont'd)

R (bohrs)	TOTAL POTENTIAL (e.v.)
5.0	0.3272D0
5.2	0.2106D0
5.4	0.1309D0
5.6	0.7714D-1
5.8	0.4167D-1
6.0	0.1882D-1
6.1	0.1083D-1
6.2	0.4586D-2
6.3	0.2234D-3
6.4	-0.3868D-2
6.5	-0.6571D-2
6.6	-0.8518D-2
6.7	-0.9860D-2
6.8	-0.1072D-1
6.9	-0.1121D-1
7.0	-0.1141D-1
7.1	-0.1139D-1
7.2	-0.1120D-1
7.3	-0.1089D-1
7.4	-0.1049D-1
7.5	-0.1003D-1
7.6	-0.9536D-2
7.7	-0.9024D-2
7.8	-0.8506D-2

TABLE 5

Ar-Ar GROUND STATE POTENTIAL (cont'd)

R (bohrs)	TOTAL POTENTIAL (e.v.)
7.9	-0.7992D-2
8.0	-0.7490D-2
9.0	-0.3688D-2
10.0	-0.1852D-2
11.0	-0.1006D-2
12.0	-0.5874D-3
13.0	-0.3623D-3
14.0	-0.2329D-3
15.0	-0.1546D-3

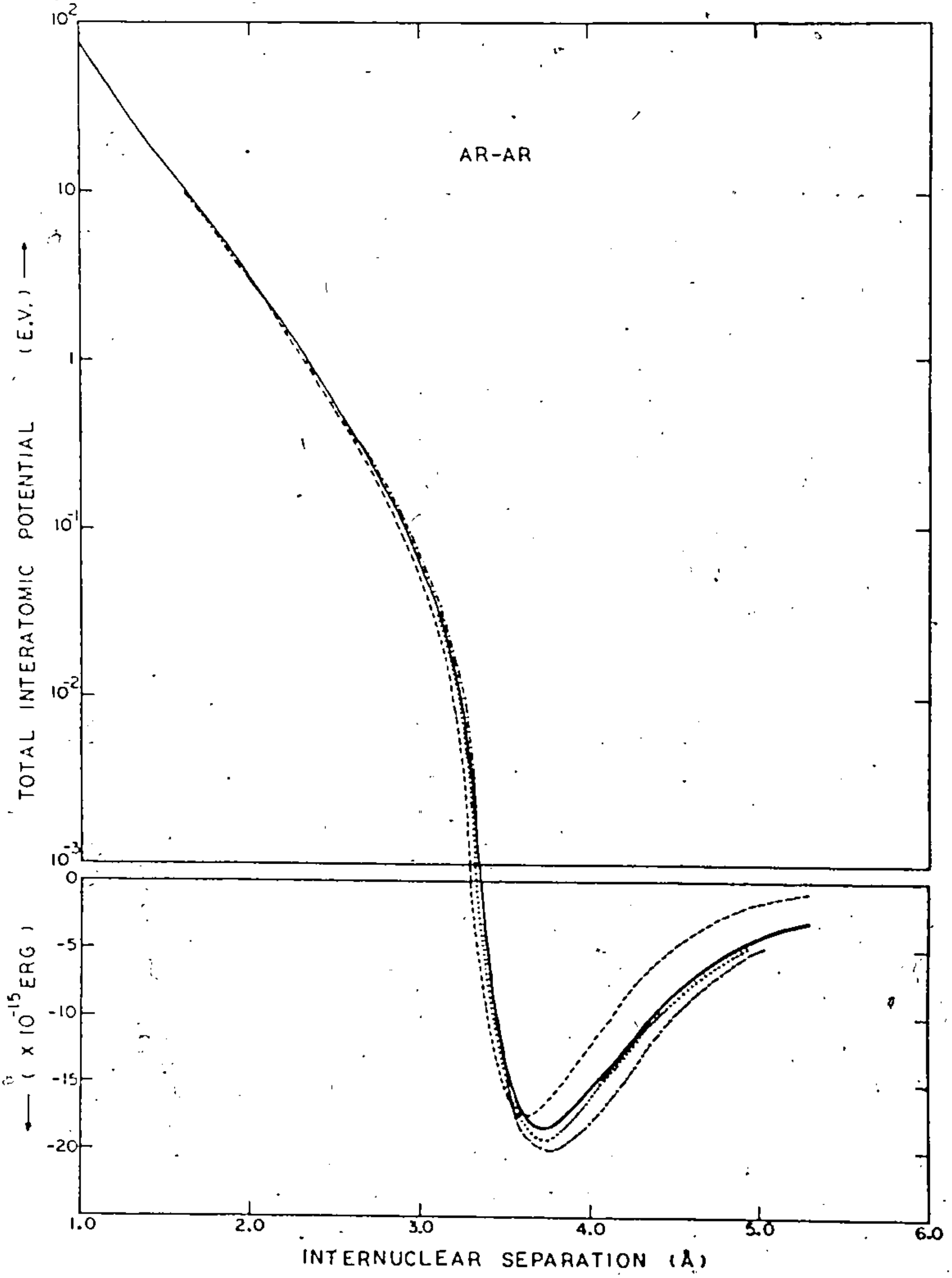

Figure 6: Ar-Ar ground state interatomic potential. - - - Gordon and Kim (Reference 48); ... Parson et al. (Reference 89) ; -.-.- Barker and Pompe (Reference 12); ___ Present Investigation

TABLE 6

Ar-Kr GROUND STATE POTENTIAL

R (bohrs)	TOTAL POTENTIAL (e.v.)
0.2	0.3940D5
0.4	0.1076D5
0.6	0.4271D4
0.8	0.2028D4
1.0	0.1066D4
1.2	0.6107D3
1.4	0.3745D3
1.6	0.2379D3
1.8	0.1531D3
2.0	0.9940D2
2.2	0.6545D2
2.4	0.4398D2
2.6	0.3023D2
2.8	0.2124D2
3.0	0.1517D2
3.2	0.1097D2
3.4	0.7970D1
3.6	0.5795D1
3.8	0.4203D1
4.0	0.3032D1
4.2	0.2172D1
4.4	0.1541D1
4.6	0.1081D1
4.8	0.7495D0

TABLE 6

Ar-Kr GROUND STATE POTENTIAL (cont'd)

R (bohrs)	TOTAL POTENTIAL (e.v.)
5.0	0.5114D0
5.2	0.3422D0
5.4	0.2232D0
5.6	0.1406D0
5.8	0.8409D-1
6.0	0.4617D-1
6.2	0.2126D-1
6.4	0.5393D-2
6.6	-0.4280D-2
6.8	-0.9782D-2
7.0	-0.1254D-1
7.2	-0.1354D-1
7.4	-0.1347D-1
7.6	-0.1276D-1
7.8	-0.1173D-1
8.0	-0.1057D-1
9.0	-0.5453D-2
10.0	-0.2718D-2
11.0	-0.1446D-2
12.0	-0.8315D-3
13.0	-0.5091D-3
14.0	-0.3264D-3
15.0	-0.2166D-3

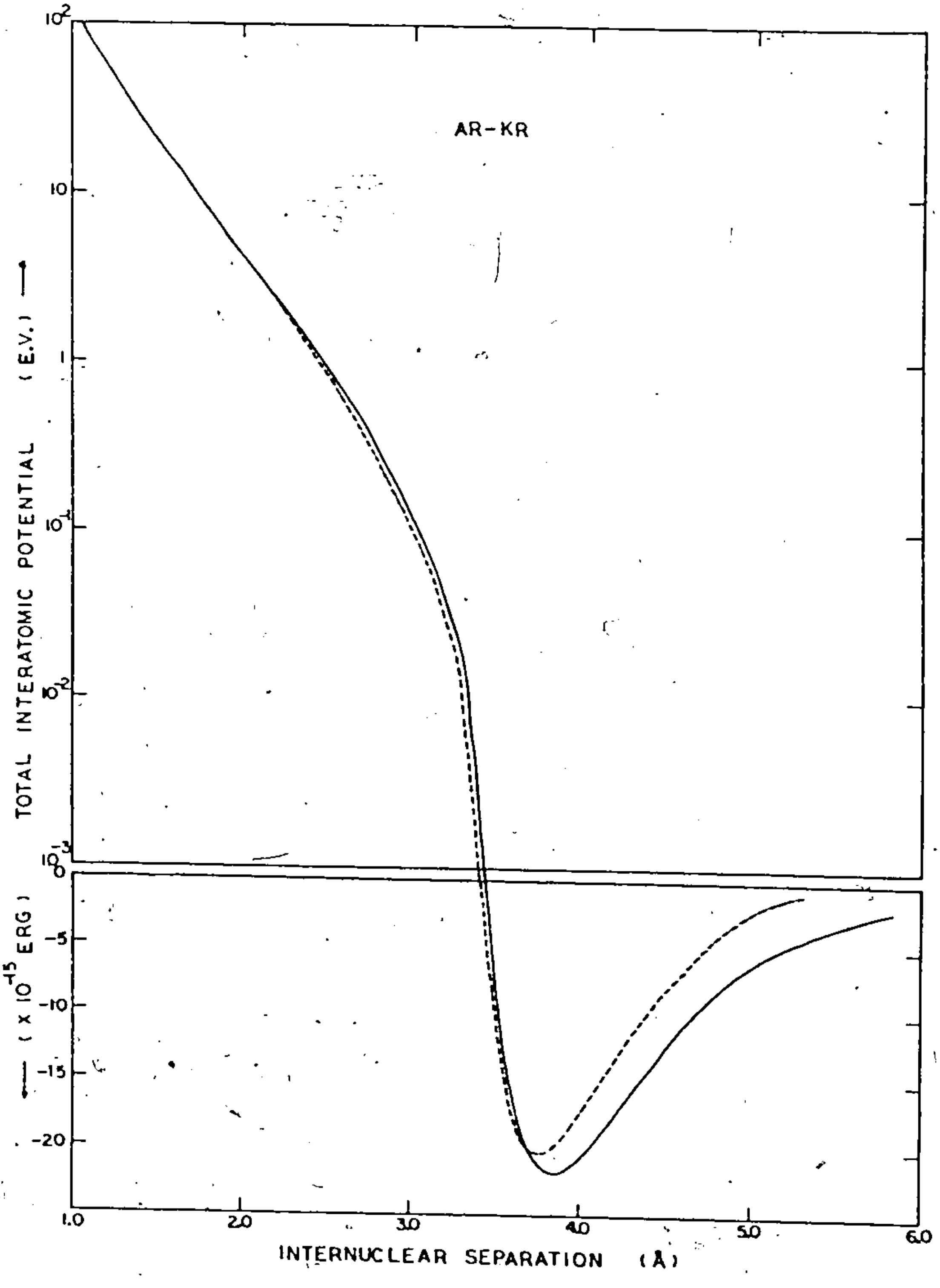

Figure 7: Ar-Kr ground state interatomic potential. - - - Gordon and Kim (Reference 48); —— Present Investigation

TABLE 7

Kr-Kr GROUND STATE POTENTIAL

R (bohrs)	TOTAL POTENTIAL (e.v.)
0.2	0.7374D5
0.4	0.1945D5
0.6	0.7391D4
0.8	0.3380D4
1.0	0.1725D4
1.2	0.9413D3
1.4	0.5505D3
1.6	0.3431D3
1.8	0.2224D3
2.0	0.1470D3
2.2	0.9808D2
2.4	0.6599D2
2.6	0.4491D2
2.8	0.3101D2
3.0	0.2174D2
3.2	0.1545D2
3.4	0.1110D2
3.6	0.8019D1
3.8	0.5814D1
4.0	0.4214D1
4.2	0.3044D1
4.4	0.2188D1
4.6	0.1560D1
4.8	0.1102D1

TABLE 7

Kr-Kr GROUND STATE POTENTIAL (cont'd)

R (bohrs)	TOTAL POTENTIAL (e.v.)
5.0	0.7680D0
5.2	0.5276D0
5.4	0.3553D0
5.6	0.2333D0
5.8	0.1477D0
6.0	0.8849D-1
6.2	0.4833D-1
6.4	0.2163D-1
6.6	0.4402D-2
6.8	-0.6235D-2
7.0	-0.1238D-1
7.2	-0.1552D-1
7.4	-0.1669D-1
7.6	-0.1663D-1
7.8	-0.1583D-1
8.0	-0.1463D-1
9.0	-0.8031D-2
10.0	-0.4023D-2
11.0	-0.2104D-2
12.0	-0.1189D-2
13.0	-0.7205D-3
14.0	-0.4601D-3
15.0	-0.3050D-3

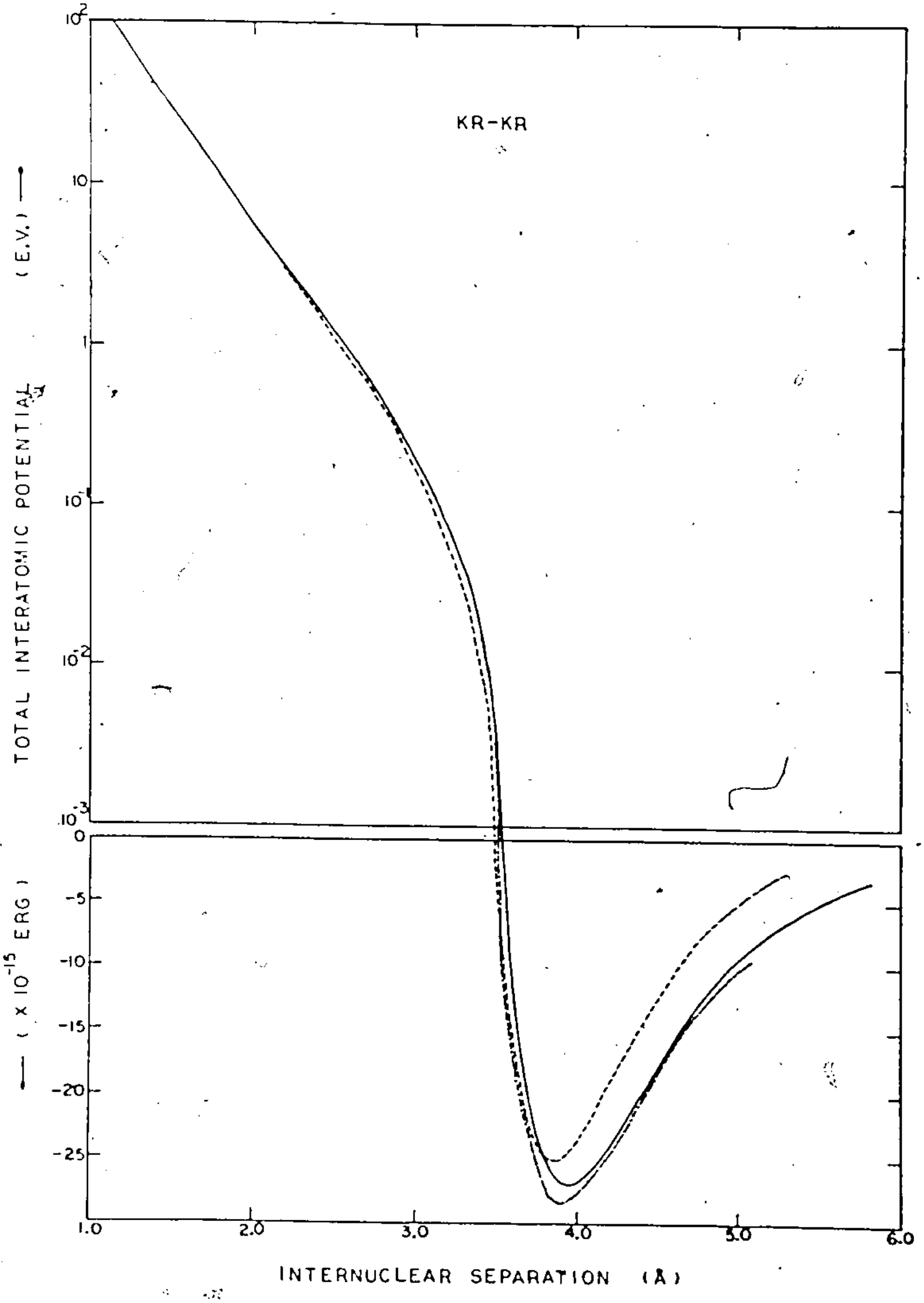

Figure 8: Kr-Kr ground state interatomic potential. - - - Gordon and Kim (Reference 48); -.-.- Kestin et al. (Reference 90); —— Present Investigation

The effect on the short-range potential due to the distortion of the electron distributions must be small since in this region the potentials of Tables 2-7 approach the short-range Thomas-Fermi potential. Hence these potentials should be able to reproduce data such as high-energy scattering cross-sections.

Results have not been presented for xenon or helium. In the case of xenon, accurate Hartree-Fock-type densities were not readily available[91] at the time that the research was completed. As for helium, the cutoff, which worked so well for homonuclear and heteronuclear diatomic molecules of neon, argon and krypton, was not satisfactory. For He-He, the well depth was over three times larger than the accepted value. It may well be that the theory presented here with its particular form for the cutoff will produce accurate well parameters for the He-Ne, He-Ar and He-Kr pairs, but this was not attempted due to the results of the He-He calculation.

One should not judge the present calculation by the graphs alone. For the heteronuclear pairs, the only curves[92] available were by Gordon and Kim[48] and for the homonuclear pairs, the curves available for plotting[92] happened to have deeper potential wells. A truer test of these calculations comes in the comparison of the well parameters as shown in Tables 8 through 13.

TABLE 8

WELL PARAMETERS FOR THE Ne-Ne POTENTIAL

ϵ/k (°K)	ϵ(x 10^{-15} erg)	r_m (Å)	σ(Å)**	Reference
38.0	5.25	3.147	-	93
38.0	5.25	3.147	-	94
35.7	4.93	2.789	-	95
42	5.8	3.00-3.16	-	2
36.3	5.01	3.16	-	2 (12:6)[96]
40.6	5.60	3.13	-	97
44	6.1	2.98	2.69	7
36.3	5.01	3.16	-	98 (12:6)
37.1	5.12	3.16	-	98
66.6	9.19	2.96	-	99
45.9	6.33	3.03	2.73	23
35.7	4.93	-	2.789	95 (12:6)
27.5	3.80	-	2.858	95 (12:6)
50.918	7.0292	3.5661	3.1993	54
50.634	6.9900	3.5676	3.2007	54
52.658	7.2694	3.5572	3.1904	54
49.049	6.7712	3.0447	2.7295	54
48.987	6.7626	3.0450	2.7298	54
55.094	7.6057	3.0183	2.7031	54
53.064	7.3254	2.9529	2.6584	54
56.552	7.8070	2.9394	2.6449	54
58.948	8.1377	2.9306	2.6361	54
52.162	7.2009	2.9629	2.6650	54
55.106	7.6073	2.9511	2.6532	54

TABLE 8: WELL PARAMETERS FOR THE Ne-Ne POTENTIAL (cont'd)

ϵ/k (^{0}K)	ϵ(x 10^{-15} erg)	r_m (Å)	σ(Å)	Reference
58.194	8.0336	2.9393	2.6415	54
51.636	7.1283	2.9698	2.6698	54
54.199	7.4821	2.9593	2.6593	54
57.751	7.9725	2.9456	2.6456	54
41	5.6	2.99	2.71	48
46.0	6.35	3.03	2.74	present

** distance between nuclear centres where potential is zero

5

TABLE 9

WELL PARAMETERS FOR THE Ne-Ar POTENTIAL

ϵ/k (°K)	ϵ ($\times 10^{-15}$ erg)	r_m (Å)	σ (Å)	Reference
63.8	8.81	3.638	-	100
63.79	8.806	3.638	-	101
73.7	10.2	3.443	-	93
68.42	9.445	3.491	-	94
64.60	8.918	-	3.092	90
56.59	7.812	-	3.157	90
42.8	5.91	3.83	-	102
49.8	6.87	3.68	-	102
55.1	7.61	3.58	-	102
60.9	8.41	3.50	-	102
64.5	8.90	-	3.098	103
69.5	9.59	-	3.067	103
67.6	9.33	-	3.079	103
66.6	9.19	-	3.104	103
75.3	10.4	3.48	-	21
70.3	9.7	3.48	-	21
64.5	8.9	3.48	-	21 (12:6)
81.929	11.310	3.6193	3.2448	54
81.014	11.184	3.6223	3.2479	54
88.936	12.278	3.5971	3.2227	54
69.478	9.5914	3.3981	3.0294	54
70.090	9.6759	3.3958	3.0270	54
79.854	11.024	3.3611	2.9924	54
74.458	10.279	3.5444	3.1629	54

TABLE 9: WELL PARAMETERS FOR THE He-Ar POTENTIAL (cont'd)

ϵ/k ($^\circ$K)	ϵ (x 10^{-15} erg)	r_m (Å)	σ(Å)	Reference
73.462	10.141	3.5481	3.1666	54
82.382	11.373	3.5166	3.1351	54
56.9	7.85	3.42	3.09	48
62.7	8.66	3.48	3.13	present

TABLE 10

WELL PARAMETERS FOR THE Ne-Kr POTENTIAL

ϵ/k ($^\circ$K)	ϵ($\times 10^{-15}$ erg)	r_m (Å)	σ(Å)	Reference
95.3	13.2	3.449	-	93
71.74	9.904	3.701	-	94
52.8	7.29	3.94	-	102
60.5	8.35	3.80	-	102
65.8	9.08	3.71	-	102
72.0	9.94	3.62	-	102
67.5	9.32	-	3.257	103
63.5	8.77	-	3.291	103
64.9	8.96	-	3.287	103
82.4	11.4	-	3.200	103
78.2	10.8	3.60	-	21
73.2	10.1	3.60	-	21
59	8.1	3.60	3.27	48
66.5	9.18	3.67	3.31	present

TABLE 11

WELL PARAMETERS FOR THE Ar-Ar POTENTIAL

ϵ/k (°K)	ϵ(x 10^{-15} erg)	r_m (Å)	σ(Å)	Reference
123.2	17.01	3.866	-	93
123.2	17.01	3.866	-	94
117.7	16.25	3.933	3.504	3 (12:6)
152.0	20.98	3.644	3.302	3
147.2	20.32	3.677	3.314	3
137.5	18.98	3.812	-	97
140.1	19.34	3.801	-	104
142.9	19.73	3.735	3.36	4
138.0	19.05	3.761	-	105
149	20.6	3.67	3.32	7
146.8	20.27	3.793	3.28	6
147.7	20.39	3.756	-	12
176	24.3	3.535	-	106
123.2	17.01	3.87	-	98
148.0	20.43	3.68	-	99
124.0	17.12	3.418	-	99 (12:6)
124.0	17.12	3.418	-	95 (12:6)
144	19.9	3.70-3.90	-	2
138	19.1	3.81	-	97
119	16.4	3.87	-	2 (12:6)
149	20.6	3.67	3.32	7
119	16.4	3.87	-	98 (12:6)
119.8	16.5	-	3.405	20 (12:6)
145(?)	20.0(?)	3.7(?)	-	20

TABLE 11: WELL PARAMETERS FOR THE Ar-Ar POTENTIAL (cont'd)

ϵ/k ($^{\circ}$K)	ϵ(x 10^{-15} erg)	r_m (Å)	σ(Å)	Reference
119.53	16.501	-	3.5149	8
132.64	18.311	-	3.5540	8
132.59	18.304	-	3.5477	8
128.11	17.685	-	3.4791	8
144.8	19.990	-	3.386	8
141	19.5	3.70	3.32	89
144.4	19.94	3.715	-	24
140.7	19.43	3.760	-	24
124	17.1	-	3.418	95 (12:6)
116	16.0	-	3.465	95 (12:6)
163.92	22.6290	3.6146	3.2323	54
164.97	22.7740	3.6128	3.2305	54
174.87	24.1406	3.5967	3.2145	54
142.06	19.6113	3.7783	3.3343	54
141.18	19.4898	3.7803	3.3363	54
150.95	20.8385	3.7589	3.3148	54
151.51	20.9158	3.8261	3.4179	54
150.76	20.8123	3.8276	3.4194	54
160.58	22.1679	3.8090	3.4008	54
141.78	19.5726	3.9200	3.4814	54
141.06	19.4732	3.9216	3.4830	54
149.19	20.5955	3.9039	3.4653	54
146.43	20.215	-	3.321	5
163.7	22.60	-	3.15	107
132	18.2	-	-	26

TABLE 11: WELL PARAMETERS FOR THE Ar-Ar POTENTIAL (cont'd)

ϵ/k ($^{\circ}$K)	ϵ ($\times 10^{-15}$ erg)	r_m (Å)	σ (Å)	Reference
127	17.5	3.63	3.28	48
132	18.3	3.71	3.33	present

TABLE 12

WELL PARAMETERS FOR THE Ar-Kr POTENTIAL

ϵ/k (°K)	ϵ(x 10^{-15} erg)	r_m (Å)	σ(Å)	Reference
143	19.7	3.947	-	93
129.2	17.84	4.099	-	94
169.79	23.439	-	3.443	90
171.67	23.699	-	3.408	90
120	16.6	4.22	-	102
133	18.4	4.10	-	102
144	19.9	4.01	-	102
153	21.1	3.93	-	102
155.0	21.40	-	3.526	103
162	22.36	-	3.495	103
153.2	21.15	-	3.514	103
121	16.7	-	3.609	110
172	23.8	3.80	-	22
194.97	26.915	3.7490	3.3623	54
196.02	27.060	3.7475	3.3608	54
207.83	28.691	3.7312	3.3445	54
164.58	22.720	3.9260	3.4617	54
163.37	22.553	3.9285	3.4642	54
174.20	24.048	3.9070	3.4427	54
147	20.3	3.78	3.40	48
158	21.8	3.85	3.45	present

TABLE 13

WELL PARAMETERS FOR THE Kr-Kr POTENTIAL

ϵ/k (°K)	ϵ(x 10^{-15} erg)	r_m (Å)	σ(Å)	Reference
158.3	21.85	4.056	-	93
135.5	18.71	4.341	-	94
164.0	22.6	-	3.827	3 (12:6)
215.6	29.76	-	3.521	3
213.9	29.53	-	3.551	3
203	28.0	3.95-4.17	-	2
159	21.9	4.04	-	2 (12:6)
191	26.4	4.08	-	97
210	29.0	3.93	3.54	7
210.3	29.03	-	3.47	6
159	21.9	4.04	-	98 (12:6)
190	26.2	-	3.61	95 (12:6)
192.24	26.539	-	3.6257	8
199.59	27.553	-	3.5609	8
199.33	27.517	-	3.5625	8
182.7	25.22	-	3.510	8
236.10	32.593	3.8816	3.4904	54
236.94	32.709	3.8806	3.4894	54
248.47	34.301	3.8672	3.4759	54
196.58	27.138	4.0771	3.5906	54
195.25	26.954	4.0795	3.5930	54
205.44	28.361	4.0616	3.5751	54
211.50	29.197	-	3.550	5

TABLE 13: WELL PARAMETERS FOR THE Kr-Kr POTENTIAL (cont'd)

ϵ/k ($^\circ$K)	ϵ (x 10^{-15} erg)	r_m (Å)	σ(Å)	Reference
213.9	29.53	-	3.42	107
180	24.8	3.89	3.48	48
195	26.9	3.95	3.53	present

The well parameters determined in this investigation compare favourably with those derived by other methods. The ϵ and r_m parameters presented here are consistently greater than those of Gordon and Kim but this can attributed to the fact that Gordon and Kim did not include any long-range polarization interaction in their theoretical expression for the potential and used a statistical approximation for interatomic correlation. It is for this reason that their potential, in the region of the outer wall, tends to zero faster than those derived experimentally and, in particular, the one given here. In the repulsive region of the interaction, where the present method and that of Gordon and Kim are quite similar (but numerical techniques are different), the results are in good agreement.

VIII CONCLUSIONS

An expression has been developed to determine ground state interatomic potentials for homonuclear and heteronuclear pairs of closed-shell atoms. It successfully determines accurate well parameters for the following diatomic molecules: Ne-Ne, Ne-Ar, Ne-Kr, Ar-Ar, Ar-Kr and Kr-Kr. The calculation does not become more complicated as heavier and heavier systems are considered since the electron densities used are in a tabulated form rather than an analytical expression.

There are a few areas in which the results of the interatomic potential calculations could be improved. These include the obvious one of increasing the number of steps in the Gauss-Legendre and Gauss-Laguerre integrations and using more density points spaced closer together. However the huge increase in computer calculation time would probably not be worth the small improvement in the results which are probably already at the limit of accuracy inherent in the method.

Another would be to try forms of the cutoff other than those investigated for the long-range correlation. It is indeed possible that another form of R_o may exist which would improve on the well parameters or the shape of the well.

The C_6 values used in this investigation are those due to Dalgarno[71]. Using C_6 values of other investigators[66,67,69,72,73] coupled with a change in the form of R_o might somewhat improve the results given here.

The theory outlined here opens up other avenues for future work. There are many closed-shell pairs which can also be considered such as xenon interactions and combinations of, for example, mercury with the noble gases. It is hoped that the form of R_o given here will continue to provide accurate well parameters for these new calculations.

One could try using these potentials to generate second virial coefficient data, scattering cross-sections, etc. and compare the results with that obtained experimentally. This would provide additional tests for the accuracy of the whole potential.

With a trivial modification of the polarization interaction term, the theory developed here can also be used to determine the interaction between a closed-shell ion and a closed-shell atom. Investigations in this area would prove to be useful in themselves and as a starting point in alkali-noble-gas and alkaline-earth-ion-noble-gas potentials.

APPENDIX A

MATHEMATICAL DETAILS FOR NUMERICAL INTEGRATION

(i) TRANSFORMATION OF THE INTEGRAL OVER THE VOLUME ELEMENT

$$\int d^3 r \;=\; 2\pi \int_0^\infty dr\, r^2 \int_{-1}^{1} d\xi \qquad \text{(A-1)}$$

where ξ is the cosine of the angle between $\underline{r}$ and $\underline{R}$. Now

$$r' \;=\; \left(r^2 + R^2 - 2rR\xi \right)^{\frac{1}{2}} \quad \text{(See Figure 1)} \qquad \text{(A-2)}$$

$$r'\, dr \;=\; -\, rR\, d\xi \qquad \text{(A-3)}$$

Therefore

$$2\pi \int_0^\infty dr\, r^2 \int_{-1}^{1} d\xi \;=\; \frac{2\pi}{R} \int_0^\infty dr\, r \int_{|r-R|}^{r+R} dr'\, r' \qquad \text{(A-4)}$$

If the variables $r_{\pm}$ are defined as

$$r_{\pm} \;=\; r' \pm r \qquad \text{(A-5)}$$

Then

$$\frac{2\pi}{R} \int_0^\infty dr \int_{|r-R|}^{r+R} dr' \;=\; \pi \int_R^\infty dr_+ \int_{-R}^{R} dr_- \qquad \text{(A-6)}$$

Further definitions

$$x = r_+/R - 1 \qquad\qquad y = r_-/R \qquad \text{(A-7)}$$

convert the double integral into the form

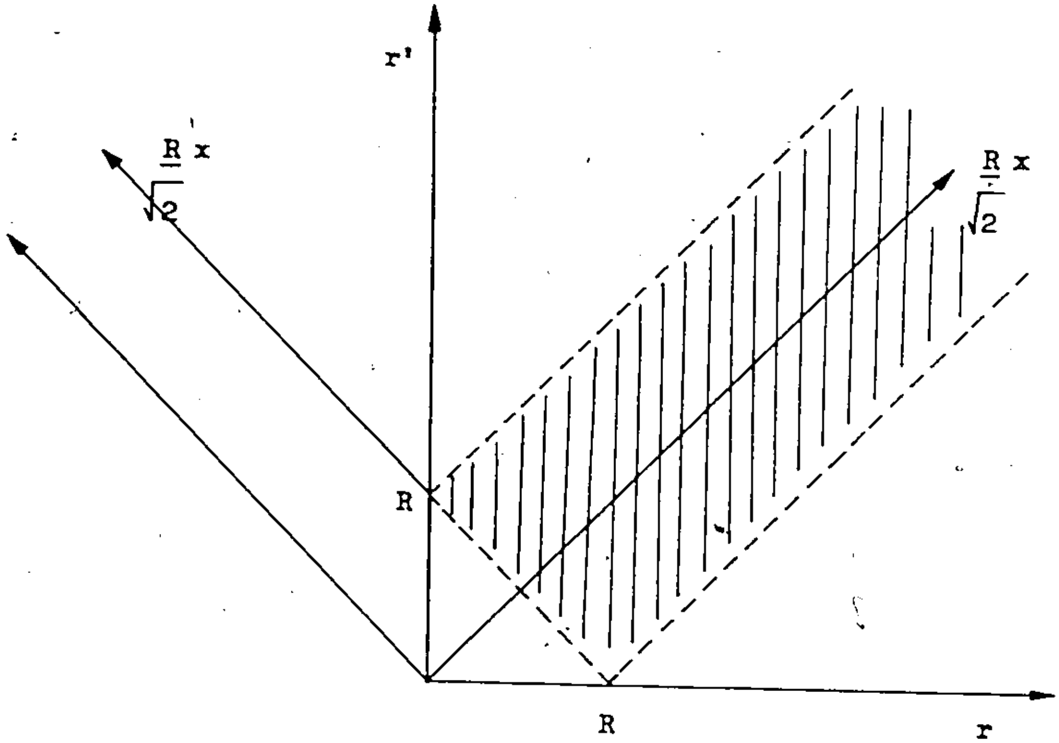

Figure 9: Co-ordinate system. Hatched region is the domain of integration.

$$\pi R^2 \int_0^\infty dx \int_{-1}^{1} dy$$

With the integrand rr' written in terms of x and y as

$$rr' = \frac{R^2}{4} \left((x + 1)^2 - y^2 \right) \qquad \text{(A-8)}$$

the integral over the volume element can be written as

$$\int d^3 r = \frac{\pi R^3}{4} \int_0^\infty dx \int_{-1}^{1} dy \left((x + 1)^2 - y^2 \right) \qquad \text{(A-9)}$$

(The co-ordinate system is shown in Figure 9.)

(ii) GAUSS-LAGUERRE PARAMETER κ

A definite integral can be approximated by

$$\int_a^b w(x)f(x)dx \simeq \sum_{i=1}^{N} A_i f(x_i) \qquad \text{(A-10)}$$

where w(x) is a function for which the moments

$$c_k = \int_a^b w(x)x^k\, dx \qquad (k = 1, 2, \ldots) \qquad \text{(A-11)}$$

are defined and finite and $c_0 \geqslant 0$.

A quadrature formula has "degree of precision" 'm' if it is exact whenever f(x) is a polynomial of degree $\leqslant$ m (or equivalently, whenever $f(x) = 1, x, \ldots, x^m$) and it is not exact for $f(x) = x^{m+1}$. The x_i are called the "points" of the formula and the A_i are called "weights". If w(x) is non-negative in $\left[a,b \right]$, then n points and weights can be found to make (A-10) exact for all polynomials of degree $\leqslant$ (2n - 1); this is the highest degree of precision which can be obtained using n points. Such formulas are usually called Gaussian quadrature formulas.

The Gauss-Laguerre quadrature formula is for the special case:

$$\int_0^{\infty} \exp(-x)f(x)dx \simeq \sum_{i=1}^{n} A_i f(x_i) \qquad \text{(A-12)}$$

In the present theory, the electrostatic, antisymmetry and interatomic exchange integrands are fitted to a polynomial of the

29'th order ($N = 15$) times an exponential factor $\exp(-x/\kappa)$. The particular form of the exponential factor can derived by considering, for example, the exchange term integrand

$$\rho_A^{4/3}(r)\ \frac{3}{4}\left((1 + x)^{4/3} - 1 - x^{4/3} \right) \qquad \text{(A-13)}$$

$$x = \rho_B(r')/\rho_A(r) \qquad \text{(A-14)}$$

It is approximated by the expression

$$\rho_A^{4/3}(r)\ x\ (1 + x^{\frac{1}{2}})^{-4/3}$$

which holds true for small and large x. Substitution for x and rearrangement of the resulting expression yields

$$\left(\frac{\rho_A^{\frac{1}{2}}(r)\ \rho_B^{\frac{1}{2}}(r')}{\rho_A^{\frac{1}{2}}(r) + \rho_B^{\frac{1}{2}}(r')} \right)^{4/3} \left(\rho_A^{1/3}(r)\ \rho_B^{1/3}(r') \right)$$

which can be shown to be less than $\rho_A^{2/3}(r)\,\rho_B^{2/3}(r')$. Thus the exchange term integrand is bounded from above by $\rho_A^{2/3}(r)\,\rho_B^{2/3}(r')$. In the asymptotic region

$$\rho_A(r) \sim \exp(-2\beta_A r) \qquad \text{(A-15)}$$

$$\rho_B(r') \sim \exp(-2\beta_B r') \qquad \text{(A-16)}$$

$$r = \frac{R}{2}(x - y + 1) \qquad \text{(A-17)}$$

$$r' = \frac{R}{2}(x + y + 1) \tag{A-18}$$

whereupon

$$\rho_A^{2/3}(r)\,\rho_B^{2/3}(r') \sim \exp\Big(- \frac{2R}{3}(\beta_A + \beta_B)x - \frac{2R}{3}((\beta_A + \beta_B) + (\beta_A + \beta_B)y) \Big) \tag{A-19}$$

Thus

$$\kappa = \left(\frac{2R}{3}(\beta_A + \beta_B) \right)^{-1} \tag{A-20}$$

Similarly in the electrostatic calculation,

$$\kappa = \left(R(\beta_A + \beta_B) \right)^{-1} \tag{A-21}$$

and in the antisymmetry repulsion calculation

$$\kappa = \left(\frac{5R}{6}(\beta_A + \beta_B) \right)^{-1} \tag{A-22}$$

So the integrals used in the calculation have the general form

$$\int_0^{\infty} dx\; f(x)\, \exp(-x/\kappa)$$

By letting $X = x/\kappa$, the integral becomes

$$\kappa \int_0^{\infty} dX\; f(\kappa X)\, \exp(-X) = \kappa \sum_{i=1}^{n} A_i\, f(\kappa X_i) \tag{A-23}$$

Because all three integrands approach the same form in the asymptotic region with similar exponential coefficients, one expression for κ can be used for all three integrals without significant error.

In initial calculations, the form of the electron density used was that due to Gombás[81] - namely a sum over all N electron orbitals[82]

$$\rho_G(r) = \sum_{s=1}^{N} \gamma_s \, r^{\alpha_s} \exp(-2\beta_s r) \tag{A-24}$$

where γ_s represents the normalization factor

$$\gamma_s = \frac{\nu_s}{4\pi} \frac{(2\beta_s)^{\alpha_s + 3}}{(\alpha_s + 2)!} \tag{A-25}$$

ν_s being the occupation number of the s'th orbital. For any orbital of atoms A and B, the expression for κ which produced the least amount of error when used in the electrostatic, antisymmetry and exchange interactions is

$$\kappa = ((\beta_A + \beta_B)R)^{-1} \tag{A-26}$$

Now from W.K.B. theory

$$\psi \sim \exp(-\kappa' r) \tag{A-27}$$

where

$$\hbar^2 \kappa'^2 (2m)^{-1} = I \tag{A-28}$$

and I is the ionization potential of the atom. Since (A-27) is true, the density ρ must be

$$\rho \sim \exp(-2\kappa' r) \qquad \text{(A-29)}$$

Looking back at the Gombás expression for the electron density of the s'th orbital

$$\rho_G^{(s)}(r) \sim \exp(-2\beta_s r) \qquad \text{(A-30)}$$

a comparison of (A-29) and (A-30) shows that β, a parameter for a specific, chosen form for the electron density, can be expressed, in atomic units, as a function of an atomic property, namely

$$\beta = (2I)^{\frac{1}{2}} \qquad \text{(A-31)}$$

Thus κ can be written as

$$\kappa = \left(\left(I_A^{\frac{1}{2}} + I_B^{\frac{1}{2}} \right) 2^{\frac{1}{2}} R \right)^{-1} \qquad \text{(A-32)}$$

and it retains the same form regardless of the expression used for the atomic electron density.

APPENDIX B

INTERPOLATION PROCEDURES

(i) LAGRANGE INTERPOLATION

Suppose that $x_o, x_1, \ldots, x_n$ are (n+1) distinct points and that the values of a function f(x) are known at these points. The problem is to find a polynomial

$$P(x) = a_1 + a_2 x + a_3 x^2 + \ldots + a_{n+1} x^n \qquad \text{(B-1)}$$

with the property that

$$P(x_i) = f(x_i) \qquad i = 0, 1, 2, \ldots, n \qquad \text{(B-2)}$$

The resulting polynomial, called the Lagrange interpolating polynomial to f(x), is given by

$$P(x) = L_o(x)f(x_o) + L_1(x)f(x_1) + \ldots + L_n(x)f(x_n) \qquad \text{(B-3)}$$

where the functions $L_i(x)$, called the Lagrange coefficient polynomials, are defined by

$$L_i(x) = \frac{(x-x_o)(x-x_1)\ldots(x-x_{i-1})(x-x_{i+1})\ldots(x-x_n)}{(x_i-x_o)(x_i-x_1)\ldots(x_i-x_{i-1})(x_i-x_{i+1})\ldots(x_i-x_n)} \qquad \text{(B-4)}$$

In the present investigation, the function f(x) is the electron density $\rho(y)$. Linear interpolation ($n = 1$) is simple but too crude. Therefore a polynomial of higher degree must be used. However if the degree chosen is too high, incorrect interpolations can result. For example, as shown in Figure 10, the polynomial $P_3(y_o)$ incorrectly determines the value of the function at the point y_o.

This problem can be partially solved by using the "double parabolic interpolation" method. As shown in Figure 11, the method makes use of four points, two on either side of the required point. First a parabolic interpolation P_1 using the points y_1, y_2 and y_3 yields the interpolated value $P_1(y_o)$ at y_o. Similarly, a second parabolic interpolation P_2 using the points y_2, y_3 and y_4 yields $P_2(y_o)$ at y_o. Since they are meant to represent the same thing, $P_1(y_o)$ and $P_2(y_o)$ are used in a weighted average to determine the final result $f(y_o)$.

A simple average

$$f(y_o) = (P_1(y_o) + P_2(y_o))/2 \tag{B-5}$$

could lead to erroneous results as illustrated in Figure 12. To safeguard against large errors being generated in the averaging procedure, a weighted average

$$P(y_o) = \alpha P_1(y_o) + (1 - \alpha)P_2(y_o) \tag{B-6}$$

$$\alpha = \frac{\left| P_L(y_o) - P_2(y_o) \right|}{\left| P_L(y_o) - P_2(y_o) \right| + \left| P_L(y_o) - P_1(y_o) \right|} \tag{B-7}$$

is used. $P_L(y_o)$ is the linear interpolation for f at y_o using one

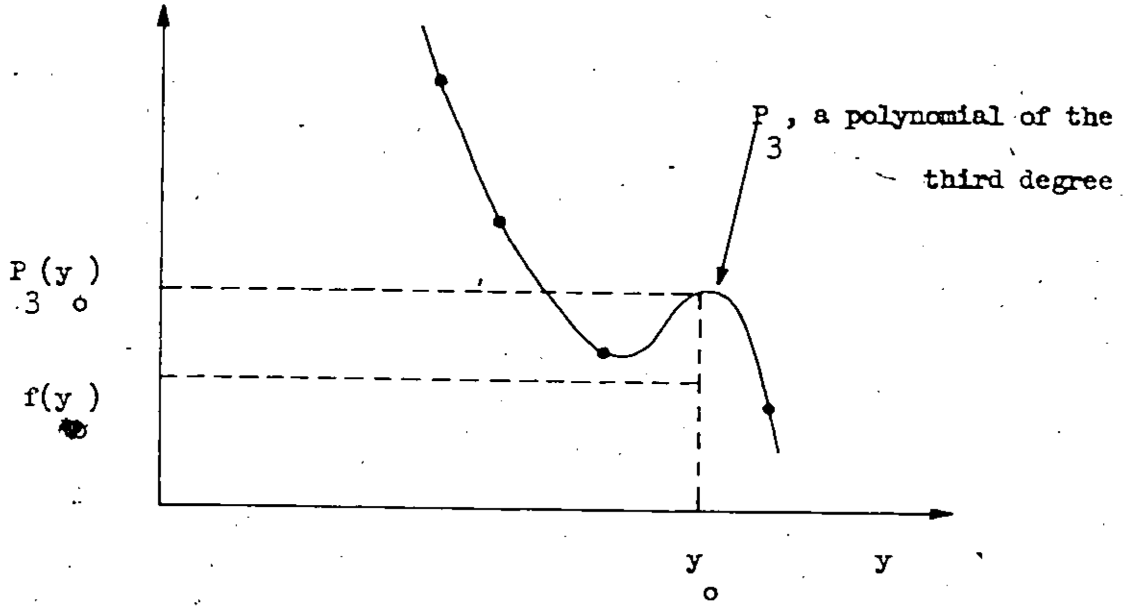

Figure 10: Cubic fit to four electron density points.

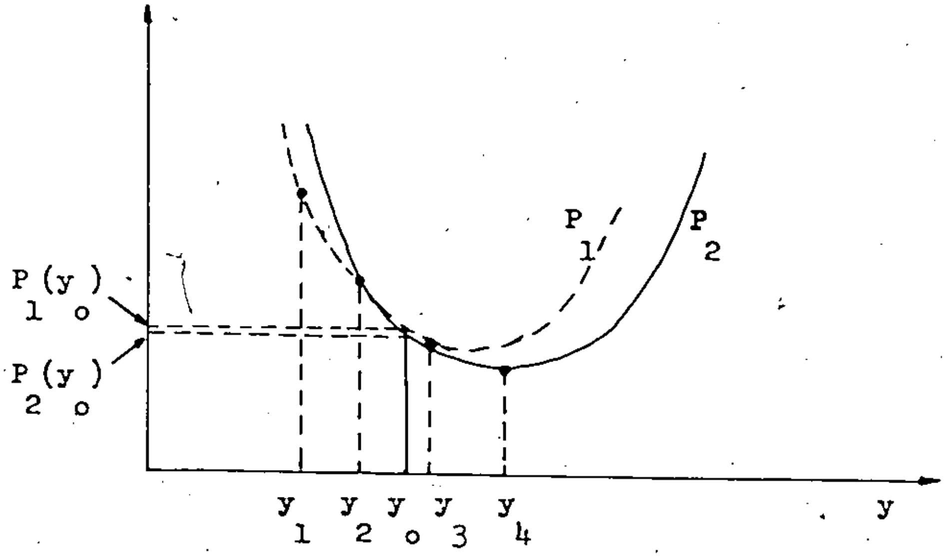

Figure 11: Parabolic fit to three electron density points.

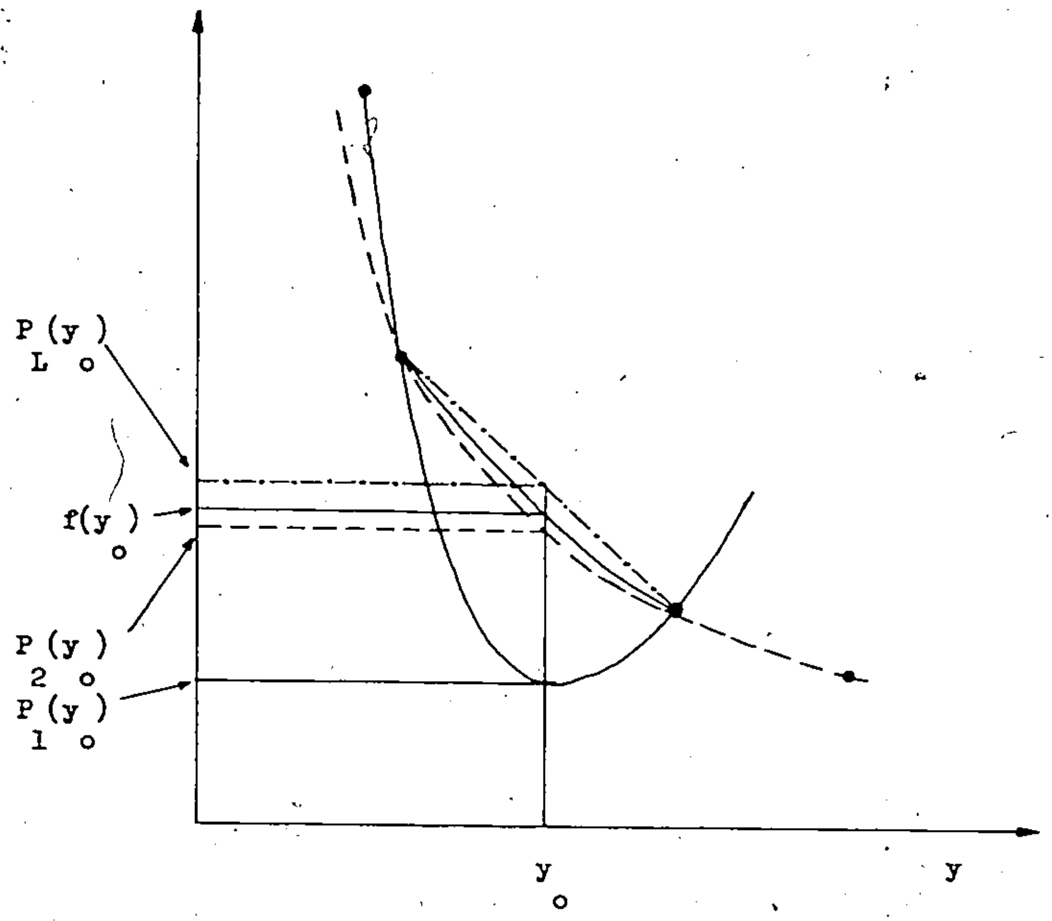

Figure 12: Double parabolic interpolation method.

$P_1(y_o)$ first parabolic interpolation for $f(y_o)$
$P_2(y_o)$ second parabolic interpolation for $f(y_o)$
$P_L(y_o)$ linear interpolation for $f(y_o)$
$f(y_o)$ is the true value of the function at y_o

point on either side of y_o,

$$f(y_1 + ph) = (1 - p)f_1 + pf_2 \qquad \text{(B-8)}$$

It will always be a little greater than the correct value $\rho(y_o)$ in regions of positive curvature of the function $\rho(y)$. If

$$P_1(y_o) = P_2(y_o) \qquad \text{(B-9)}$$

then $\alpha = \frac{1}{2}$ and $P_1(y_o)$ and $P_2(y_o)$ share equally in their contributions to $P(y_o)$. If $P_1(y_o)$ is much too large, then $\alpha \rightarrow 0$ making $P(y_o) \simeq P_2(y_o)$. Similarly if $P_2(y_o)$ is too large, $P(y_o) \simeq P_1(y_o)$.

Obviously a problem will exist if there are not two read-in points on one side or the other of the required point. If there is only one read-in point to the left of the required one, a single parabolic interpolation is done using this point and two points immediately to the right. If no read-in points exist to the left, a single parabolic interpolation is carried out using the value of the density at the origin[109] and the two immediately to the right of the required one.

It is possible that either none or only one read-in point will be to the immediate right of the required one. This will occur only in the asymptotic region (large r) since enough points are read-in to ensure the presence of a few points there. In this region the density can be written as a function of r (the log mesh is abandoned in this situation)

$$\rho(r) \sim \rho_o \exp(-ar) \qquad \text{(B-10)}$$

ρ_o and 'a' can be determined by considering the value of the density at the last two read-in points $\rho(r_{n-1})$ and $\rho(r_n)$:

$$a = (\ \ln(\ \rho(r_{n-1})/\rho(r_n)\ )\ )/(\ r_n - r_{n-1}\ ) \tag{B-11}$$

$$\rho_o = \rho(r_n)\exp(\ ar_n\ ) \tag{B-12}$$

So in this situation, the density at a required point r_o in the asymptotic region is calculated from the analytical formula

$$\rho(r_o) \simeq \rho_o \exp(\ -ar_o\ ) \tag{B-13}$$

One realizes that the above asymptotic form is exactly correct only for helium; for larger atoms, it should be

$$\rho(r) = (\ \rho_o + \rho_1 r + \rho_2 r^2 + \ldots\ )\exp(\ -br\ ) \tag{B-14}$$

since for these larger atoms, the electron densities do not fall off as a simple exponential. However ρ is so small in this region that any differences between (B-13) and (B-14) would have negligible effect on the final result at the expense of increased computer calculation time. It is for this reason that (B-13) is used.

(ii) DOUBLE QUADRATIC INTEGRATION FORMULA

In Figure 13, $f(x)$ can be written, using the Lagrange three point interpolation formula as

$$f(x) = \sum_{i=1}^{N} a_i(x) f_i(x) \qquad \text{(B-15)}$$

where $N = 3$ and

$$a_i(x) = \prod_{\substack{j \\ j \neq i}} (x - x_j)(x_i - x_j)^{-1} \qquad \text{(B-16)}$$

If x_i is written as

$$x_i = (i - 2)h \qquad i = 1, 2, 3 \qquad \text{(B-17)}$$

then

$$f(x) = \frac{1}{2}(x/h)^2 (f_1 - 2f_2 + f_3) + x(2h)^{-1}(f_3 - f_1) + f_2 \qquad \text{(B-18)}$$

$$\int_A^B f(x)dx = (6h^2)^{-1}(f_1 - 2f_2 + f_3)(B^3 - A^3) + (4h)^{-1}(f_3 - f_1)(B^2 - A^2) + f_2(B - A) \qquad \text{(B-19)}$$

Extending this scheme for use with 'n' points,

$$\int_{-h}^{-h/2} f(x)dx = \frac{h}{2}\left(2f_1/3 + 5f_2/12 - f_3/12 \right) \qquad \text{(B-20)}$$

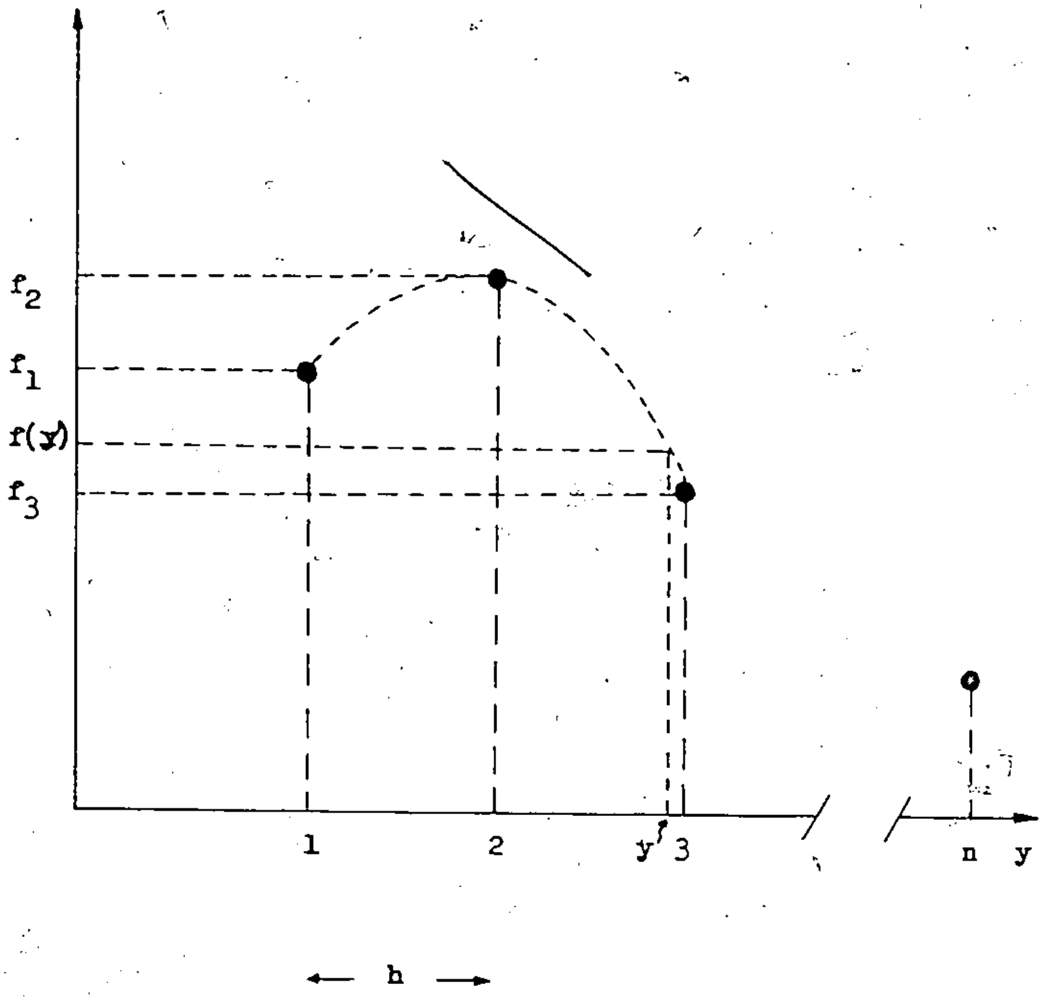

Figure 13: Electron density points used in the double parabolic interpolation method.

$$\int_{-h/2}^{h/2} f(x)dx = \frac{h}{24}\left(f_1 + 22f_2 + f_3 \right) \tag{B-21}$$

$$\int_{h/2}^{h} f(x)dx = \frac{h}{24}\left(f_2 + 22f_3 + f_4 \right) \tag{B-22}$$

$$\vdots$$

The integral from point 1 to point n can be found by summing the individual sections:

$$\begin{aligned} I = \int_{\text{point } 1}^{\text{point } n} f(x)dx = \frac{h}{24}\Big(& 8f_1 + 5f_2 - f_3 \\ + & f_1 + 22f_2 + f_3 \\ + & \qquad f_2 + 22f_3 + f_4 \\ + & \\ & \vdots \qquad\qquad\qquad \Big) \end{aligned}$$

$$= h\left(\frac{3}{8}(f_1 + f_n) + \frac{7}{6}(f_2 + f_{n-1}) + \frac{23}{24}(f_3 + f_{n-2}) + \sum_{m=4}^{n-3} f_m \right) \tag{B-23}$$

Similar theory can be used to evaluate the integral from "a" to "b" as in Figure 2.

$$I_{ab} = \int_a^b f(y)dy = h\left(-\frac{1}{24}(f_m + f_n) + \frac{1}{2}(f_{m+1} + f_{n-1}) + \frac{25}{24}(f_{m+2} + f_{n-2}) + \sum_{i=m+3}^{n-3} f_i \right.$$

$$+ q(f_m (2q + 3)q/12 + f_{m+1} (1 - q^2/3) + f_{m+2} (2q - 3)q/12)$$

$$+ p(f_{n-2} (2p - 3)p/12 + f_{n-1} (1 - p^2/3) + f_n (2p + 3)p/12)) \qquad \text{(B-24)}$$

For the case of $p = q = 1$, this formula reduces to the expression for I.

The factors involving q and p are derived using the formula for $\int_A^B f(x)dx$:

$$\int_{-qh}^{0} f(x)dx = (6h^2)^{-1} (f_m - 2f_{m+1} + f_{m+2})q^3 h^3$$

$$- (4h)^{-1} (f_{m+2} - f_m q^2 h^2 + f_{m+1} qh$$

$$= \frac{h}{6}(f_m - 2f_{m+1} + f_{m+2})q^3 - \frac{h}{4}(f_{m+2} - f_m)q^2$$

$$+ f_{m+1} qh \qquad \text{(B-25)}$$

Rearrangement yields

$$\int_{-qh}^{0} f(x)dx = qh(f_m (2q + 3)q/12 + f_{m+1} (1 - q^2/3)$$

$$+ f_{m+2} (2q - 3)q/12) \qquad \text{(B-26)}$$

A similar integral results in the expression involving p.

APPENDIX C

CALCULATION OF $\chi(R)$

(i) ANALYTICAL FORMULA FOR THE ASYMPTOTIC CONTRIBUTION

$$\chi_{asym}(R) = \int_{r_n}^{\infty} dr\, D(r)\, (r^{-1} - R^{-1}) \qquad \text{(C-1)}$$

Since

$$D(r) = 4\pi r^2 \rho(r) \qquad \text{(C-2)}$$

$\chi_{asym}(R)$ becomes

$$\chi_{asym}(R) = 4\pi \int_{r_n}^{\infty} dr\, r^2 \rho(r)\, (r^{-1} - R^{-1}) \qquad \text{(C-3)}$$

But the asymptotic form for $\rho(r)$ is

$$\rho(r) \backsim \rho_o \exp(-ar) \qquad \text{(C-4)}$$

Therefore

$$\chi_{asym}(R) = 4\pi\rho_o \int_{r_n}^{\infty} dr\, r^2 \exp(- ar)(r^{-1} - R^{-1})$$

$$= 4\pi\rho_o (\int_{r_n}^{\infty} dr\, r \exp(-ar) - R^{-1} \int_{r_n}^{\infty} dr\, r^2 \exp(-ar)) \qquad \text{(C-5)}$$

Integrating the second term by parts once yields

$$\chi_{asym}(R) = 4\pi\rho_o \left(\int_{r_n}^{\infty} dr\, r \exp(-ar)(1 - 2/aR) - (aR)^{-1} r_n^2 \exp(-ar_n) \right) \qquad \text{(C-6)}$$

The remaining integral can be evaluated simply and, after some rearrangement,

$$\chi_{asym}(R) = \frac{4\pi\rho_o}{a} \left(- r_n^2 R^{-1} + (1 - 2/aR)(r_n + 1/a) \right) \times \exp(-ar_n) \qquad \text{(C-7)}$$

(ii) NUMERICAL CALCULATION

$$I = \int_R^{r_1} dr\, D(r)\left(\frac{1}{r} - \frac{1}{R} \right) = 4\pi \int_R^{r_1} dr\, r\, \rho(r)\left(1 - \frac{r}{R} \right) \qquad (C-8)$$

The integrand can be approximated by

$$f(x) = x(\, a_3 x^2 + a_2 x + a_1 \,)(\, 1 - x/R \,) \qquad (C-9)$$

if the electron density in this region is approximated by a parabola.

To solve for a_1, a_2 and a_3, three simultaneous equations are used:

$$a_3 x_1^2 + a_2 x_1 + a_1 = \rho(x_1) \qquad (C-10)$$

$$a_3 x_2^2 + a_2 x_2 + a_1 = \rho(x_2) \qquad (C-11)$$

$$a_3 x_3^2 + a_2 x_3 + a_1 = \rho(x_3) \qquad (C-12)$$

where the ρ's and the x_i's are defined as in Figure 13.

Manipulation of (C-10), (C-11) and (C-12) yields

$$a_1 = \rho(x_1) - a_3 x_1^2 - a_2 x_1 \qquad (C-13)$$

$$a_2 = \frac{\rho(x_2) - \rho(x_1) - a_3(x_2^2 - x_1^2)}{x_2 - x_1} \qquad (C-14)$$

$$a_3 = \frac{\rho(x_3) - \rho(x_1) - (x_3 - x_1)\left(\dfrac{\rho(x_2) - \rho(x_1)}{x_2 - x_1}\right)}{x_3^2 - x_1^2 - (x_3 - x_1)(x_2^2 - x_1^2)/(x_2 - x_1)} \qquad \text{(C-15)}$$

Therefore

$$I = 4\pi\Big(- a_3 (5R)^{-1} (r_1^5 - R^5) + \frac{(a_3 - a_2/R)}{4}(r_1^4 - R^4)$$

$$+ \frac{(a_2 - a_1/R)}{3}(r_1^3 - R^3) + \frac{a_1}{2}(r_1^2 - R^2) \Big) \qquad \text{(C-16)}$$

REFERENCES

1 The quantity $z = pV/NRT$ is called the compressibility factor. The expansion of z in powers of the inverse volume is called the virial expansion. This is of the form

$$z = 1 + B(N/V) + C(N/V)^2 + D(N/V)^3 + \ldots..$$

The coefficients B, C, D, ... are functions of the temperature. B is called the second virial coefficient.

2 R. J. Munn, J. Chem. Phys. 40, 1439 (1964)

3 A. E. Sherwood, J. M. Prausnitz, J. Chem. Phys. 41, 429 (1964)

4 J. A. Barker, W. Fock, F. Smith, Physics Fluids, 7, 897 (1964)

5 A. E. Kingston, J. Chem. Phys. 42, 719 (1965)

6 J. H. Dymond, M. Rigby, E. B. Smith, J. Chem. Phys. 42, 2801 (1965)

7 R. J. Munn, F. J. Smith, J. Chem. Phys. 43, 3998 (1965)

8 D. D. Konowalow, S. Carrá, Physics Fluids, 8, 1585 (1965)

9 D. A. Jonah, J. S. Rowlinson, Trans. Faraday Soc. 62, 1067 (1966)

10 L. W. Bruch, I. J. McGee, J. Chem. Phys. 46, 2959 (1967)

11 J. H. Dymond, J. Chem. Phys. 49, 3673 (1967)

12 J. A. Barker, A. Pompe, Aust. J. Chem. 21, 1683 (1968)

13 D. E. Beck, Mol. Phys. 14, 311 (1968)

14 H. J. M. Hanley, J. Klein, J. Chem. Phys. 50, 4765 (1969)

15 J. H. Dymond, B. J. Alder, J. Chem. Phys. 51, 309 (1969)

16 J. M. Keller, W. L. Taylor, J. Chem. Phys. 51, 4829 (1969)

17 G. C. Maitland, E. B. Smith, J. Chem. Phys. 52, 3848 (1970)

18 L. W. Bruch, I. J. McGee, J. Chem. Phys. 52, 5884 (1970)

19 J. Klein, H. J. M. Hanley, J. Chem. Phys. 53, 4722 (1970)

20 J. A. Barker, R. A. Fisher, R. O. Watts, Mol. Phys. 21, 657 (1971)

21 J. M. Parson, T. P. Schafer, F. P. Tully, P. E. Siska, Y. C. Wong, Y. T. Lee, J. Chem. Phys. 53, 2123 (1970)

22 J. M. Parson, T. P. Schafer, P. E. Siska, F. P. Tully, Y. C. Wong, Y. T. Lee, J. Chem. Phys. 53, 3755 (1970)

23 P. E. Siska, J. M. Parson, T. P. Schafer, Y. T. Lee, J. Chem. Phys. 55, 5762 (1971)

24 J. M. Parson, P. E. Siska, Y. T. Lee, J. Chem. Phys. 56, 1511 (1972)

25 D. A. Jonah, Mol. Phys. 21, 755 (1971)

26 Y. Takana, K. Yoshino, J. Chem. Phys. 53, 2012 (1970)

27 N. Bohr, Kgl. Danske Videnskab. Selskab, Mat.-Fys. 18, No. 8 (1948)

28 O. B. Firsov, Soviet Physics J. E. T. P. 6, 534 (1958)

29 V. Bush, S. H. Caldwell, Phys. Rev. 38, 1898 (1931)

30 E. Fermi, Z. Phys. 48, 73 (1928)

31 S. Kobayashi, T. Masukuma, S. Nagai, K. Umeda, J. Phys. Soc. Jap. 10, 759 (1955)

32 A. van Wijngaarden, B. Miremadi, W. E. Baylis, Can. J. Phys. 50, 1938 (1972)

33 A. A. Abrahamson, R. D. Hatcher, G. H. Vineyard, Phys. Rev. 121, 159 (1961)

34 A. A. Abrahamson, Phys. Rev. 130, 693 (1963)

35 A. A. Abrahamson, Phys. Rev. 133, A990 (1964)

36 A. A. Abrahamson, Phys. Rev. 185, 44 (1969)

37 D. Y. Kim, Z. Physik, 166, 359 (1962)

38 P. E. Phillipson, Phys. Rev. 125, 1981 (1962)

39 N. R. Kestner, O. Sinanoğlu, J. Chem. Phys. 45, 194 (1966)

40 J. E. Jordan, I. Amdur, Advan. Chem. Phys. 10, 29 (1966)

41 T. L. Gilbert, A. C. Wahl, J. Chem. Phys. 47, 3425 (1967)

42 H. Matsumoto, C. F. Bender, E. R. Davidson, J. Chem. Phys. 46, 402 (1967)

43 D. J. Klein, C. E. Rodriguez, J. C. Browne, F. A. Matsen, J. Chem. Phys. 47, 4862 (1967)

44 J. N. Murrell, G. Shaw, Mol. Phys. 12, 475 (1967)

45 J. N. Murrell, G. Shaw, Mol. Phys. 15, 325 (1968)

46 P. Bertoncini, A. C. Wahl, Phys. Rev. Letters, 25, 991 (1970)

47 P. Cantini, M. G. Dondi, G. Scoles, F. Torello, J. Chem. Phys. 56, 1946 (1972)

48 R. G. Gordon, Y. S. Kim, J. Chem. Phys. 56, 3122 (1972)

49 B. Schneider, J. Chem. Phys. 58, 4447 (1973)

50 N. R. Kestner, J. Chem. Phys. 45, 208 (1966)

51 W. D. Davison, Proc. Phys. Soc. (London) 87, 133 (1966)

52 A. Dalgarno, G. A. Victor, Proc. Phys. Soc. (London) 90, 605 (1967)

53 P. W. Langhoff, M. Karplus, J. Chem. Phys. 53, 233 (1970)

54 D. D. Konowalow, D. S. Zakheim, J. Chem. Phys. 57, 4375 (1972)

55 Unsöld's Theorem (A. Unsöld, Ann. Physik 82, 355 (1927)) states that the sum over "m" (magnetic quantum number) of the squares of the magnitudes of the wavefunctions of all states with the same " ℓ " (orbital quantum number) values, but different m's is independent of angle.

56 W. E. Baylis, J. Chem. Phys. 51, 2665 (1969)

57 An ensemble of particles with half integer spin (fermions with $s = \pm \hbar/2$) has a totally antisymmetric wavefunction, that is the

wavefunction changes sign but is otherwise unaltered upon interchange of the co-ordinates, including spin, of any pair of particles. Thus, in the case of an atom, each electron has its own set of quantum numbers - n (principal quantum number), ℓ (orbital quantum number), m(magnetic quantum number) and s (spin quantum number).

58 J. C. Slater, Quantum Theory of Atomic Structure Vol. II, McGraw-Hill Book Company, Inc., New York, Appendix 22, p323.

59 R. Eisenschitz, F. London, Z. Phys. 60, 491 (1930)

60 F. London, Z. Phys. 63, 245 (1930)

61 H. Margenau, Rev. Mod. Phys. 11, 1 (1939)

62 H. Margenau, J. Chem. Phys. 6, 896 (1938)

63 J. O. Hirschfelder, P. O. Löwdin, Mol. Phys. 2, 229 (1959)

64 J. O. Hirschfelder, P. O. Löwdin, Mol. Phys. 9, 491 (1965)

65 A. Dalgarno, A. E. Kingston, Proc. Roy. Soc. Ser. A 259, 424 (1960)

66 A. Dalgarno, A. E. Kingston, Proc. Roy. Soc. 78, 607 (1961)

67 A. E. Kingston, Phys. Rev. 135, A1018 (1964)

68 J. A. Barker, P. J. Leonard, Phys. Letters 13, 127 (1964)

69 R. J. Bell, Proc. Phys. Soc. (London) 86, 17 (1965)

70 R. J. Bell, A. E. Kingston, Proc. Phys. Soc. (London) 90, 901 (1967)

71 A. Dalgarno, I. M. Morrison, R. M. Pengelly, Intern. J. Quantum Chem. 1, 161 (1967)

72 R. G. Gordon, J. Chem. Phys. 48, 3929 (1968)

73 G. Starkschall, R. G. Gordon, J. Chem. Phys. 54, 663 (1971)

74 D. A. McQuarrie, J. Terebey, S. J. Shire, J. Chem. Phys. 51,

4683 (1969)

75 W. D. Davison, J. Phys. Soc. B1, 139 (1968)

76 G. Starkschall, R. G. Gordon, J. Chem. Phys. 56, 2801 (1972)

77 D. R. Bates, Proc. Roy. Soc. 188, 350 (1947)

78 L. Biermann, E. Trefftz, Z. Astrophys. 30, 275 (1953)

79 M. Abramowitz, I. A. Segun, *Handbook of Mathematical Functions*, Dover Publications, Inc., New York, 1968, p923. Additional positions and weights for N greater than 15 have been determined by A. H. Stroud, D. Secrest, *Gaussian Quadrature Formulas*, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1966.

80 M. Abramowitz, I. A. Segun, *Handbook of Mathematical Functions*, Dover Publications, Inc., New York, 1968, p916.

81 P. Gombás, T. Szondy, Acta Physica Academiae Scientiarum Hungaricae 25, 345 (1968). $a = 2K - 2$, $\beta = \lambda$

82 Gombás uses a simplified self-consistent field method to procure his density parameters. However in his method, he combines orbitals according to their "n" quantum number.

83 E. Clementi, I. B. M. J. Res. Develop. 9, 2 (1965)

84 E. Clementi, *Tables of Atomic Functions*, International Business Machines Corporation, San José, California, 1965.

85 Clementi's basis functions χ are Slater-type orbitals. This means that the wavefunctions are constructed using Slater determinants so that they will be antisymmetric and thus include intra-atomic exchange. (Intra-atomic correlation would be taken into account by using as large a linear combination of these Slater determinants as possible, each determinant representing

a different configuration of the atom. This has not been done however.

86 The error becomes more and more apparent as larger and larger r values are considered. However at these points, the densities are of the order of 10^{-17} or less and their inaccuracy has negligible effects on the final result.

87 J. B. Mann, Atomic Structure Calculations II Hartree-Fock Wavefunctions and Radial Expectation Values: Hydrogen to Lawrencium, Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico, 1968.

88 The C_8 values are determined using C_6 values from Reference 71 in the formula from Reference 76.

89 J. M. Parson, Y. T. Lee, Third International Symposium on Molecular Beams, June 29, 1971 - July 2, 1971, Cannes.

91 They can be calculated using a theory developed by A. K. Pradhan, Master's Thesis, Department of Physics, University of Windsor, Windsor, Ontario, Canada, 1973.

92 For most potential calculations presented in the literature, usually only the well parameters are given. Very few articles provide tables of the potential versus internuclear separation. Some display their potentials in the form of graphs but reading values of the potential at certain points from them to any satisfactory degree of accuracy is difficult.

93 E. A. Mason, J. Chem. Phys. 23, 49 (1955)

94 K. P. Srivistava, J. Chem. Phys. 28, 543 (1958)

95 J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, Inc., New York, 1954 p 1110

96 Lennard-Jones potential is $V(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right]$ Different values of the parameters σ and ϵ are often available for the same pair, depending on which properties were used to evaluate the parameters (i.e. crystal data, second virial coefficient data). $r_m = 2^{1/6}\sigma$

97 E. A. Guggenheim, M. L. McGlashan, Proc. Roy. Soc. A255, 456 (1960)

98 E. A. Mason, W. E. Rice, J. Chem. Phys. 22, 843 (1954)

99 S. C. Saxena, J. G. Kelley, W. W. Watson, Phys. Fluids, 4, 1216 (1961)

100 D. D. Konowalow, J. Chem. Phys. 50, 12 (1969)

101 R. K. Nesbet, J. Chem. Phys. 48, 1419 (1968)

102 R. J. J. Van Heijningen, J. P. Harpe, J. J. M. Beenakker, Physica 38, 1 (1968)

103 B. N. Srivastava, K. P. Srivastava, J. Chem. Phys. 30, 984 (1959)

104 M. L. McGlashan, Discuss. Faraday Soc. 40, 59 (1965)

105 J. C. Rossi, F. Danon, Discuss. Faraday Soc. 40, 97 (1965)

106 R. Paul, A. J. Howard, W. W. Watson, J. Chem. Phys. 39, 3055 (1963)

107 R. D. Weir, I. W. Jones, J. S. Rowlinson, G. Saville, Trans. Faraday Soc. 63, 1320 (1967)

108 The International Dictionary of Applied Mathematics, D. Van Nostrand Company, Inc., Princeton, N. J., 1960, p 877

109 At the origin, only 's' orbitals ($\ell = 0$) contribute to the electron density. 'p' ($\ell = 1$), 'd' ($\ell = 2$), ... orbitals do not. This is true since near the origin $\psi_{orb} \propto r^{\ell}$ and

$$\rho \propto \left|\psi_{orb}\right|^2.$$

110 A. P. Malinauskas, J. Chem. Phys. 45, 4704 (1966)

VITA AUCTORIS

I was born on July 14, 1949 in Windsor, Ontario. In 1968 I graduated with honours from John L. Forster Collegiate Institute winning an Ontario Scholarship, a University of Windsor Entrance Award and a continuing Chrysler Canada Limited Scholarship and Bursary. I then entered the Honours Physics program at the University of Windsor. In the spring of 1972, I graduated from the University of Windsor with an Honours BSc. degree in Physics. I then enrolled in the Faculty of Graduate Studies at the University of Windsor to pursue a Master of Science degree in the field of Theoretical Atomic Physics and was subsequently awarded a University of Windsor Postgraduate Scholarship.