

INTERMOLECULAR POTENTIAL*

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Intermolecular potential plays a dominant role in determining the properties of gases, liquids and solids. The equilibrium and transport properties are dependent upon both attractive and repulsive terms in the potential. The scattering cross sections are determined mainly by the repulsive term. Both theoretical and experimental investigations for determining intermolecular potential between helium atoms are fairly extensive. Recent quantum mechanical calculations of interaction energy between two ground state helium atoms are reviewed.

The Hamiltonian of a system consisting of four electrons 1, 2, 3 and 4 and two nuclei a and b shown in Fig 1 can be written in the form

$$K = \sum_{i=1}^4 H(i) + \sum_{i>j}^4 \frac{1}{r_{ij}} + \frac{4}{R} \quad (1)$$

where r_{ai} & r_{bi} are distances of electron i from nuclei a and b respectively, r_{ij} is interelectronic distance, and R is internuclear distance. The interaction energy E is calculated by making use of a suitable wave function. Repulsive energy $V(R)$ is given by the expression

$$V(R) = E(R) - 2E(He) \quad (2)$$

where $2E(He)$ represents energy of two helium atoms in ground state. It is convenient to express distances in Bohr radii ($a = 0.529 \text{ \AA}$) and energy in Hartree units ($H_0 = 27.204 \text{ eV}$).

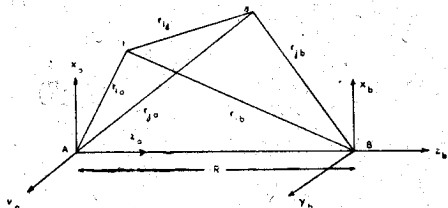


Fig. 1—Electronic configuration of He_2 system.

Rosen¹ has employed valence bond method in evaluation of repulsive energy. He assumes that system He_2 is stable if there is a bond between electrons 1 and 2 as well as between electrons 3 and 4. This implies that spins of electrons 1 and 2 are paired and so are those of electrons 3 and 4. The eigen functions which give eigen values zero under influence of the operator S_z —sum of z components of spins—are given by Bauli's determinants

$$\begin{aligned} \phi_1 &= | \chi_1(1) \alpha(1) \chi_2(2) \beta(2) \chi_3(3) \alpha(3) \chi_4(4) \beta(4) | \\ \phi_2 &= | \chi_1(1) \alpha(1) \chi_2(2) \beta(2) \chi_3(3) \beta(3) \chi_4(4) \alpha(4) | \\ \phi_3 &= | \chi_1(1) \beta(1) \chi_2(2) \alpha(2) \chi_3(3) \alpha(3) \chi_4(4) \beta(4) | \\ \phi_4 &= | \chi_1(1) \beta(1) \chi_2(2) \alpha(2) \chi_3(3) \beta(3) \chi_4(4) \alpha(4) | \end{aligned} \quad (3)$$

where $\chi_1 = \left(\frac{\zeta_1^3}{\pi} \right)^{\frac{1}{2}} \exp(-\zeta_1 r_1)$, ζ_1 is effective nuclear charge and α and β are

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the orthogonal spin functions. The bond function $\psi_{12,34}$ may be represented by the expression

$$\psi_{12,34} = (\phi_1 - \phi_2 - \phi_3 + \phi_4) \quad (4)$$

By making use of wave function (4) and Hamiltonian (1), repulsive energy between ground state helium atoms has been calculated by Rosen. His results are shown in Fig. 2.

Griffing and Wehner² have employed molecular orbital approach. The four electrons are assigned to the following two molecular orbitals $1\sigma_g$ and $1\sigma_u$ which extend over the whole molecule

$$\begin{aligned} 1\sigma_g &= N_g (\chi_a + \chi_b) \\ 1\sigma_u &= N_u (\chi_a - \chi_b) \end{aligned} \quad (5)$$

where $N_g = (2+2S_{ab})^{-\frac{1}{2}}$ and $N_u = (2-2S_{ab})^{-\frac{1}{2}}$ are normalizing factor; $S_{ab} = \int \chi_a \chi_b d\tau$ is an overlap integral. The molecular wave function is assumed to be of the form

$$\psi = \left(\frac{1}{24}\right)^{\frac{1}{2}} \sum_{\lambda} (-1)^{\lambda} P_{\lambda} \left[(\sigma_g \alpha)^1 (\sigma_g \beta)^2 (\sigma_u \alpha)^3 (\sigma_u \beta)^4 \right] \quad (6)$$

where P_{λ} is an operator permuting the superscripts which denote electrons. The exponent ζ in both the functions has been assigned a value of $\zeta = 1.6875A^{-1}$. By making use of Rootan's theory the total energy of the system is found to be

$$E = 2H_g + 2H_u + J_{gg} + J_{uu} + 4J_{gu} - 2K_{gu} + \frac{4}{R} \quad (7)$$

$$\text{where } H_g = \int 1\sigma_g(1) H(1) 1\sigma_g(1) d\tau_1$$

$$H_u = \int 1\sigma_u(1) H(1) 1\sigma_u(1) d\tau_1$$

$$J_{gg} = \iint 1\sigma_g(1) 1\sigma_g(1) \frac{1}{r_{12}} 1\sigma_g(2) 1\sigma_g(2) d\tau_1 d\tau_2$$

$$J_{uu} = \iint 1\sigma_u(1) 1\sigma_u(1) \frac{1}{r_{12}} 1\sigma_u(2) 1\sigma_u(2) d\tau_1 d\tau_2$$

$$J_{gu} = \iint 1\sigma_g(1) 1\sigma_g(1) \frac{1}{r_{12}} 1\sigma_u(2) 1\sigma_u(2) d\tau_1 d\tau_2$$

The results of calculation are shown in Fig. 2 which are fairly in agreement with experimental results at interatomic distance $R=2A$.

Griffing and Wehner² have also calculated interaction energy at $R=3.11A$ by including $2P_z$ orbitals. The molecular orbitals employed by them are

$$\phi_g = N_1 [\{(1s)_a + (1s)_b\} + \lambda_g \{(2p_z)_a + (2p_z)_b\}] \quad (8)$$

$$\phi_u = N_2 [\{(1s)_a - (1s)_b\} + \lambda_u \{(2p_z)_a - (2p_z)_b\}]$$

where N_1 and N_2 are normalising factors and

$$(2 p_z) = \left(\frac{\zeta_p^2}{\pi} \right)^{\frac{1}{2}} \times r \cos \theta \text{Exp} (-\zeta_p r).$$

A variational treatment gives an attractive energy of 2.14×10^{-5} a.u. when $\lambda_1 = -\lambda_2 = 1.4 \times 10^{-3}$. This value may be compared with experimental result of 3.4×10^{-5} a.u.

Hashino and Huzinaga³ have extended the calculations and observed that λ_g is positive and λ_u is negative in the range of internuclear distances investigated. A positive value of λ_g implies that orbital ϕ_g has a tendency to contract and a negative value of λ_u means that ϕ_u tends to extend into outer space. Calculations of Hashino and Huzinaga give repulsive energy of 21.65 eV at $R=0.627A$ compared with corresponding value of 24.86 eV given by Wehner and Griffing.

Dooling and Piper⁴ have carried out similar calculations. They have employed linear combinations of atomic orbitals 1s, 2s and 2p. Their results are shown in Fig. 3.

Spherically symmetric 1s functions do not possess sufficient flexibility to allow for mutual polarization. To achieve polarization effect Moore⁵ has modified the wave function. Principal modified diagonal term w may be written as

$$\begin{aligned} w = & \chi_1(1) \alpha(1) \chi_2(2) \beta(2) \chi_3(3) \alpha(3) \chi_4(4) \beta(4) \\ & (1 + \gamma \zeta^2 (x_{a_1} x_{b_3} + x_{a_1} x_{b_4} + x_{a_2} x_{b_3} + x_{a_2} x_{b_4}) \\ & + \gamma \zeta^2 (y_{a_1} y_{b_3} + y_{a_1} y_{b_4} + y_{a_2} y_{b_3} + y_{a_2} y_{b_4}) \\ & + \delta \zeta^2 (z_{a_1} z_{b_3} + z_{a_1} z_{b_4} + z_{a_2} z_{b_3} + z_{a_2} z_{b_4})] \end{aligned} \quad (9)$$

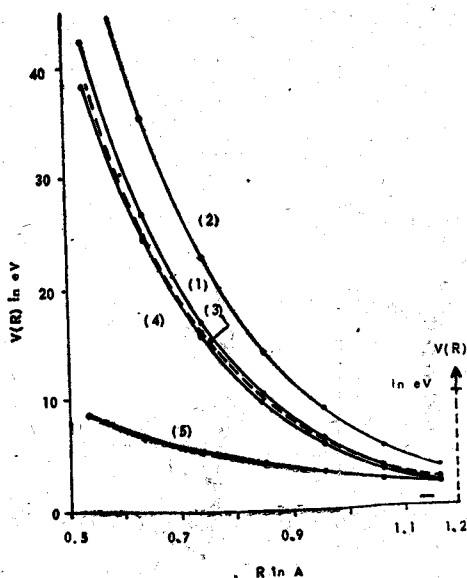


Fig. 2—He-He repulsive potential V vs interatomic distance R . (1) Slater (2) P-Rosen (3) Griffing-Wehner (4) Sakamoto-Ishiguro (5) Amdur-Harkness' exp.

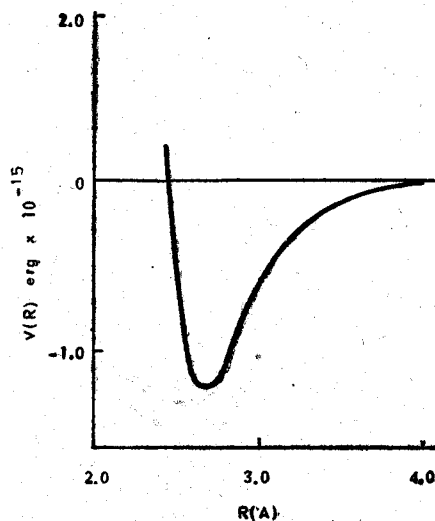


Fig. 3—Potential $V(R)$ versus distance R in attractive region.

where γ , δ & ζ are variational parameters. The system of coordinates is shown in Fig. 1. A negative value of γ implies that the term involving γ in the state function is largest when an electron on one atom and another electron on the second atom are on opposite side of Z -axis. A positive value of δ signifies that for a given pair of electrons—one belonging to each atom, there is a tendency for one and only one electron to be between the two nuclei. The disadvantage of the present function is that both electrons on the same atom tend to be near one another. The advantage of using function (9) is that integrals involved in calculations of energy can be exactly evaluated. There is considerable simplification if following points are kept in view (i) orthogonality of spin functions makes contributions from large number of terms zero, (ii) hermiticity of the Hamiltonian makes large number of terms equal and (iii) symmetry properties give invariance during exchange of two nuclei. It is interesting to note that Moore's function gives rise to van der Waals minimum and provides information regarding mutual polarization of the atoms. The method possesses poor extensibility. Moore's results are given in Fig. 4.

Ransil⁶ has given a treatment based upon molecular orbital approach which gives appreciable van der Waals energy. By making use of self consistent procedure he has derived molecular orbitals in the form of linear combinations of atomic orbitals $1s$, $2s$ and $2p$. The exponents ζ in these orbitals have been assumed to be equal. The variation of ζ at each interatomic distance has been restricted to finding best value of ζ common to all STO 's and both $1\sigma_g$ and $1\sigma_u$. Ransil's results are given in Fig. 5.

At distances greater than $0.75A$ Ransil's energies are fairly low. The energy of separated helium atoms on extrapolation is found to be $-5.6953 a.u.$ The coefficient of $2p\sigma$ is small in the molecular wave function. The percentage of p character is, however, adequate

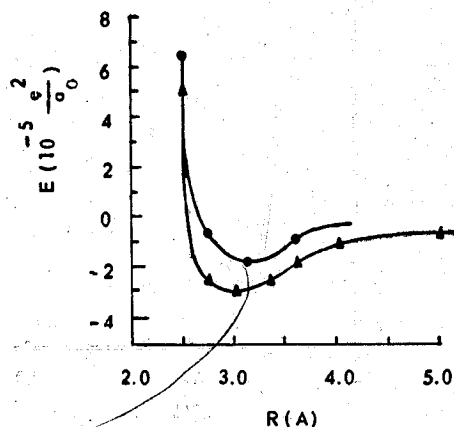


Fig. 4—He-He interaction potential—attractive region.
 Δ = Slater—Kirkwood; \bullet = Moore.

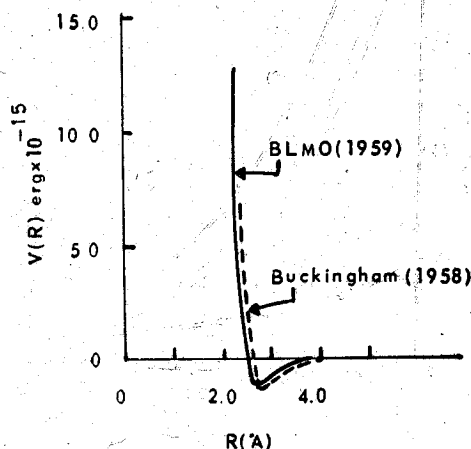


Fig. 5—Van der Waals region for interaction of two He atoms.

to produce mutual polarization and yield a minimum in the van der Waals region. The electron overlap population is negative in the region $0.5A$ to $1.0A$ indicating antibonding character. The bonding character is found to be maximum in the region near $2.0A$.

Sakamoto and Ishiguro⁷ have attempted to improve repulsive energy by taking into account mutual distortion of the electron clouds. For this purpose, it is convenient to introduce spherical coordinates

$$\lambda = \left(\frac{r_a + r_b}{R} \right), \quad \mu = \left(\frac{r_a - r_b}{R} \right) \quad (10)$$

The atomic orbitals may be written in the form

$$\left. \begin{aligned} \chi_a &= N_a e^{-\zeta \frac{R}{2} (\lambda + \mu)} \\ \chi_b &= N_b e^{-\zeta \frac{R}{2} (\lambda - \mu)} \end{aligned} \right\} \quad (11)$$

The distortion of electron clouds by neighbouring atoms is taken into account by modifying the atomic orbitals which may be assumed to have the forms

$$\left. \begin{aligned} \chi_a &= N_a e^{-\alpha \lambda - \beta \mu} \\ \chi_b &= N_b e^{-\alpha \lambda + \beta \mu} \end{aligned} \right\} \quad (12)$$

By assigning suitable values to two parameters α and β these investigators have obtained slight improvement in repulsive energy. A comparison of results obtained by investigators including Rosen, Griffing & Wehner and Sakamoto & Ishiguro are given in Fig. 2. It may be noted that variation of even two parameters in expressions at (12) does not produce sufficient deformation of two orbitals. Limitations of this method are quite apparent.

There are certain disadvantages in inclusion of $1\sigma_u$ function to describe the ground state of H_{e_2} . Function $1\sigma_u$ assumes a p -like character as R goes to zero. The united atom formed from molecules configuration $(1\sigma_g)^2(1\sigma_u)^2$ is beryllium atom in excited state $(1s)^2(2p)^2$. A simple explanation of why it is so is as follows:

Function $1\sigma_u$ is a difference function $[(1s)_a - (1s)_b]$ which may be approximated by

the expression $\frac{de^{-\zeta r}}{dz}$ or $\frac{ze^{-\zeta r}}{r}$ where z is along the line of two centres. This expression

shows a nodal behaviour at the centre of united atom. Further spectroscopic⁸ studies show that $\zeta = 3.7A^{-1}$ for $1s$ state. The value of the exponent is less than one for p -state of helium. For this reason it is desirable to assign different values to ζ in molecular orbitals $1\sigma_g(1s)$ and $1\sigma_u(1s')$.

Huzinaga⁹ has made a powerful suggestion that exponents ζ 's in molecular orbitals $1\sigma_g$ and $1\sigma_u$ may be assigned different values. At each internuclear distance two exponents ζ in $1\sigma_g$ ($1s$) and $1\sigma_u$ ($1s'$) are optimised by variational technique. The molecular function obtained in this way is called $MO-\zeta$ wave function. Independent variation of ζ in $1\sigma_g$ ($1s$) and $1\sigma_u$ ($1s'$) permits deformation of these orbitals. The $1\sigma_g$ ($1s$) molecular orbital tends to contract and $1\sigma_u$ ($1s'$) tends to expand as R gets smaller. Independent variation of exponents in two molecular orbitals gives dramatic improvements in repulsive energy. The results of these calculations are given in Fig. 6.

For comparison results of Griffing & Wehner and experimental data in the form of Buckingham¹⁰ function

$$V = \frac{8}{R} e^{-2.48R} (1 + 0.265R - 2.419R^2 + 2.618R^3 - 0.436R^4) \quad (13)$$

are also given.

This expression fits into data from scattering experiments and transport properties. This function also gives correct energy of beryllium atom when two helium atoms coalesce at $R = 0$.

It is remarkable that a simple modification suggested by Huzinaga gives results which are fairly close to Buckingham curve. The $MO-\zeta$ function representing electronic configuration $(\sigma_g 1s)^2 (\sigma_u 1s')^2$ also provides some indication about van der Waals attraction energy which arises mainly from the fact that even at large distance ($\sigma_u 1s'$) function possesses some p -character. The bonding, however, is not adequate. The minimum occurs at 3.3 \AA instead of 2.9 \AA . The magnitude of computed energy of attraction is only a small percentage of experimental value.

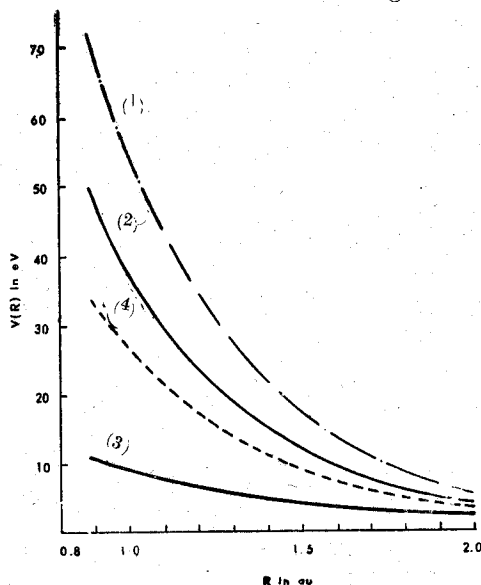


Fig. 6—Comparison of the results of various investigators (1) Rosen (2) Sakamoto and Ishiguro (3) Experimental result of Landur and Harkness and (4) S. Huzinaga.

Further improvement in interaction energy is possible if correlation of electrons is taken into account. A proper correlation ensures that at $R = \infty$ the He_2 system will separate into two helium atoms in their ground state and at $R = 0$ the system will coalesce into beryllium atom in its ground state. An inter-electronic vector may be included in the wave function to allow for correlation¹¹. Alternatively configuration interaction may be employed to ensure proper correlation. This implies that electrons should not be assigned to private molecular orbitals but may spread over various configurations. Correlation energy may be defined as difference between non-relativistic energy derived from function providing for correlation and Hartree Fock energy which is lowest energy obtained from a single anti-symmetric orbital function.

In superposition of configurations a wave function is expressed as a linear combination

of $1 \sum_g^+$ wave functions each corresponding to different electron configuration. As an approximation it may be assumed that total wave function is linear combination of configurations $^{11} D_{ijk}$ each involving two or three molecular orbitals *i.e.*

$$\psi_n = \sum_{ijk} C_{ijk} D_{ijk} \quad (14)$$

where D_{ijk} is a certain configuration which is a linear combination of four anti-symmetric orbital products and subscript n denotes number of configurations. D_{ijk} may be represented by the expression

$$\begin{aligned} D_{ijk} = & N_{ijk} [|\Phi_i^* (1) \alpha (1) \Phi_i (2) \beta (2) \Phi_j^* (3) \alpha (3) \Phi_k (4) \beta (4) | \\ & + |\Phi_i^* (1) \alpha (1) \Phi_j (2) \beta (2) \Phi_k^* (3) \alpha (3) \Phi_j (4) \beta (4) | \\ & + |\Phi_i^* (1) \alpha (1) \Phi_i (2) \beta (2) \phi_j (3) \alpha (3) \Phi_k^* (4) \beta (4) | \\ & + |\Phi_i^* (1) \alpha (1) \Phi_i (2) \beta (2) \Phi_k (3) \alpha (3) \Phi_j^* (4) \beta (4) |] \quad (15) \end{aligned}$$

*indicates complex conjugate, N_{ijk} is a normalization factor such that each configuration is normalised to one. Configurations of the form $\Phi_i \Phi_j \Phi_k \Phi_l$ in which all molecular orbitals are singly occupied have been excluded.

In the first instance the configurations built up from molecular orbitals

$$\begin{aligned} \sigma_g (1s) &= N_g [(1s)_a + (1s)_b] \\ \sigma_g (1s') &= N'_g [(1s')_a + (1s')_b] \\ \sigma_u (1s) &= N_u [(1s)_a - (1s)_b] \\ \sigma_u (1s') &= N'_u [(1s')_a - (1s')_b] \end{aligned} \quad (16)$$

may be considered. Interaction energy and coefficients in expression (14) have been computed by Phillipson¹². The electronic energy is found to be 1.1 *ev* lower over the single *MO*— ζ configuration in the range 0.5 \AA to 2.0 \AA . The repulsive energy which is difference between E and $2E$, however, remains unchanged. $\psi_{10} (1s, 1s')$ wave function gives energies of separated atoms and united atoms which are respectively 1.84 *ev* and 4.38 *ev* above their exact values.

Next, the effect of admixture of configurations involving functions

$$\begin{aligned} \sigma_g (2s) &= N_{g2s} [(2s)_a + (2s)_b] \\ \sigma_u (2s) &= N_{u2s} [(2s)_a - (2s)_b] \end{aligned} \quad (17)$$

may be considered. It is observed that on admixture of these configurations there is no lowering of electronic energy¹² over the energy given by $\psi_{10} (1s, 1s')$ function. It appears that use of $1s$ and $1s'$ functions with optimized parameters accounts for most of contribution from a electrons. Further 29 configurations containing $2p\sigma$ orbitals may be taken into account. Calculations show that only seven of these configurations contribute towards lowering of electronic energy. The function involving these configurations is denoted by $\psi_{17} (1s, 1s', 2p\sigma)$. Inclusion of 25 configurations involving $\pi_g (2p)$ and $\pi_u (2p)$ orbitals produces 64 configuration wave functions $\psi_{64} (1s, 1s', 2p\sigma \& 2p\pi)$. Out of these

additional 25 configurations, only three make a significant contribution. The significant portion of the wave function may be represented by ψ_{20} ($1s, 1s', 2p\sigma, 2p\pi$). Improvements in electronic energy of 80 per cent and 90 per cent over the $MO-\zeta$ function have been obtained by the use of ψ_{20} ($1s, 1s', 2p\sigma$ and $2p\pi$) and ψ_{64} ($1s, 1s', 2p\sigma, 2p\pi$) functions respectively. This improvement is mainly due to correlation of the motion of electrons arising from superposition of configurations. The correlation of antibonding electrons is accounted by ψ_{10} ($1s, 1s'$) function whereas correlation of bonding electrons arises from inclusion of $2p\sigma$ and $2p\pi$ orbitals. A comparison of repulsive energies at various interatomic distances obtained by various investigators is shown in Fig. 7.

Some important results are given in Table 1. It is observed that superposition of configurations yields repulsive energies in the region $0.5A < R < 1A$ which differs but little from those obtained by the use of $MO-\zeta$ method. It may also be seen that experimental results differ grossly from the theoretical repulsive energies. The variation of repulsive energy with distance derived from ψ_{64} ($1s, 1s', 2p\sigma, 2p\pi$) function may be represented by the expression¹².

$$V(R) = 191.47 e^{-3.849R} \quad (\text{ev}) \quad (0.5 < R < 1A) \quad (18)$$

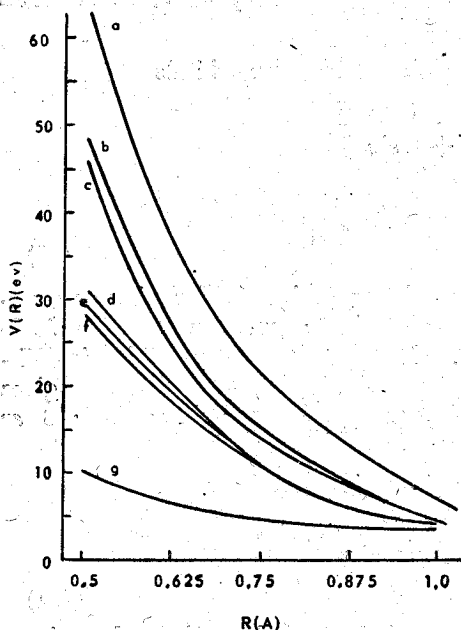


Fig. 7—Repulsion energy curves: (a) Rosen (b) Slater (c) G-W (d) Ransil (e) $MO-\zeta$ (f) $\psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$ (g) Scattering-data

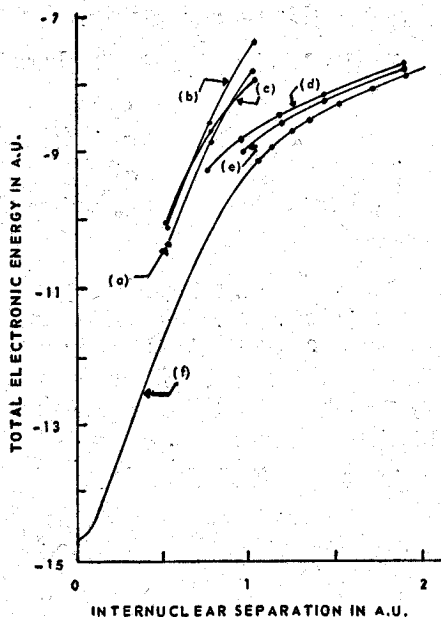


Fig. 8—Total electronic energy vs internuclear distance (both in atomic units) (a) the united atom configuration mixture $1s^2.2s^2 + 1s 3d .2s^2$ (b) the united atom configuration $1s^2 2s^2$ (c) The united atom configuration $1s^2 2p\sigma^2$ (d) Ransil's two-centre calculation. (e) Philipson's two centre calculation with 64 configurations (f) Amdur—Bertrand experimental results fitted with a Buckingham interpolation curve.

The energies of separated atoms and united atom for various functions are shown in Table 2.

Repulsive energy of two helium atoms can also be calculated in terms of one centre wave functions. The origin is supposed to be at the mass centre M of the charges on two nuclei. The potential energy U due to two nuclei can be expressed in terms of distance r from the mass centre

$$U(r, \theta, \phi) = -\frac{2\zeta}{r} \left[1 + \sum_{s=1}^{\infty} \left(\frac{R}{2r} \right)^{2s} P_{2s}(\cos \theta) \right] \quad (19)$$

where $P_{2s}(\cos \theta)$ is Legendre polynomial. The coordinate system is shown in Fig. 1.

For the calculation of energy the two out of the four electrons may be assigned to one centre inner molecular orbital ϕ_i .

$$\phi_i = 0.68(1s\sigma) + 0.32(4s\sigma) + 0.17(4d\sigma) \quad (20)$$

where

$$(1s\sigma) = \frac{(2\zeta_1)^{3/2}}{2^{1/2}} \exp(-\zeta_1 r) Y_{00}, \quad \zeta_1 = 1.75$$

$$(4s\sigma) = \frac{(2\zeta_2)^{9/2}}{(8!)^{1/2}} r^3 \exp(-\zeta_2 r) Y_{00}, \quad \zeta_2 = 6.25$$

$$(4d\sigma) = \frac{(2\zeta_2)^{9/2}}{(8!)^{1/2}} r^3 \exp(-\zeta_2 r) Y_{20}$$

Y 's being spherical harmonics.

The other two electrons may be assumed to be present in the molecular orbital

$$\phi_2(2\rho\sigma) = \frac{(2\zeta_3)^{5/2}}{(4!)^{1/2}} r \exp(-\zeta_3 r) Y_{10}, \quad \zeta_3 = 1.5 \quad (21)$$

Various parameters in ϕ_1 & ϕ_2 may be optimised by variation technique. The wave function built up from ϕ_1 & ϕ_2 , which depends upon distance from the M centre, may be used in calculation of E . This method¹³ gives repulsive energy of 34.7 *ev* at $R=0.5A$ which is 3.7 *ev* lower than the value given by Sakamoto and Ishiguro⁷.

Miller & Present¹⁴ have also calculated the interaction energy between two helium atoms by one centre method. The repulsive energy at $R < 0.56A$ is found to be lower for configuration $1s^2 2s^2$ than for the configuration $(1s)^2 (2p\sigma)^2$. At distances greater than $0.56A$ contribution of configuration $(1s)^2 (2p\sigma)^2$ is large. Admixture of excited configurations $(1s')(3d')(2s)^2$ with basic configuration $(1s)^2 (2s)^2$ gives significant improvement in energy. The one centre method involving configuration interaction is, to some extent, superior in performance at $R \leq 0.6A$ to two centre method. A comparison of results of Miller & Present with those of other investigators is given in Fig. 8. It is possible to extend the range of one centre method beyond $0.75A$ by inclusion of other configurations.

TABLE 1

IMPORTANT RESULTS OBTAINED BY VARIOUS INVESTIGATORS ON THE COMPARISON OF REPULSIVE ENERGIES AT VARIOUS INTERATOMIC DISTANCES

	$V(R) = \frac{-bR}{ae}$ in ev		$V(R)$ in ev at $R =$			E at $R = \infty$ atomic units
	a	b	0.50	0.625	0.75	
$\phi_{He} = 1.392e^{-2(r_1 + r_2) + 0.5r_{12}}$	481.0	4.60	48.23	27.14	15.27	4.835
$\times e^{(0.010)(r_1^2 + r_2^2)}$ for $r_1, r_2 < 3$						
Slater ²⁰ $\phi_{He} = 1.241e^{-2r_1 - 1.344r_2}$						
$\times r_2^{-0.255(1 + 0.0707/r_2)}$ $r_1 < r_2$ $r_2 > 3$						
Rosen $\phi_{He} = \left(\frac{\zeta_1^3}{\pi}\right)^{\frac{1}{2}} e^{-\zeta_1 r_1}$ $\times \left(\frac{\zeta_2^3}{\pi}\right)^{\frac{1}{2}} e^{-\zeta_2 r_2}$ $\zeta_1 = 2.15; \zeta_2 = 1.19$	577.0	4.40	63.93	36.89	21.28	7.084
						-5.7508
Griffing and Wehner $\phi = N(\chi_a \pm \chi_b)$ $\chi_a = \left(\frac{\zeta a^3}{\pi}\right)^{\frac{1}{2}} e^{-\zeta a r}$ $\zeta = 1.6875$	234.0	4.09	44.90	25.08	14.32	4.790
						-5.6953
Sakamoto and Ishiguro $\phi = N_a e^{-(\alpha + \beta)(r_{ai}/R)}$ $\times N_b e^{-(\alpha - \beta)(r_{bi}/R)}$						-5.6953
Huzinaga $\phi_g = \sigma_g(1s), \phi_u = \sigma_u(1s')$			30.27	18.16	10.89	3.917
Hashino and Huzinaga $\phi_1 = \sigma_g(1s) + \lambda_g \cdot \sigma_g(2p)$ $\phi_2 = \sigma_u(1s) + \lambda_u \cdot \sigma_u(2p)$ $\zeta = 1.6875$ λ_g & λ_u are varied to minimize energy				21.65		

TABLE 1—(contd.)

	Diagonal term:	24.77			
	$w = \chi_a(1) \alpha(1) \chi_a(2) \beta(2)$				
	$\chi_b(3) \alpha(3) \chi_b(4) \beta(4)$				
Moore	$\chi [1 + r \zeta^2 (x_{a_1} x_{b_2} + x_{a_1} x_{b_4}$ $+ x_{a_2} x_{b_3} + x_{a_2} x_{b_4})$ $+ r \zeta^2 (y_{a_2} y_{b_3} + \dots)$ $+ 8 \zeta^2 (z_{a_1} z_{b_3} + \dots)$				
	$\phi_1 = C_{1s} \sigma_g(1s) + C_{2s} \sigma_g(2s)$ $+ C_{2p} 2p\sigma$	30.84	..	11.34	4.104
Ransil	$\phi_2 = C_{1s} \sigma_u(1s) + C_{2s} \sigma_u(2s)$ $+ C_{2p} \sigma_u(2p)$				
	ζ is common to all coefficients & ζ is determined by minimising energy.				
Phillipson	$\psi_{s4}(1s, 1s', 2p\sigma, 2p\pi)$	191.47	3.8486	27.76	17.33 10.78 4.059

TABLE 2

ENERGIES OF SEPARATED ATOMS AND UNITED ATOMS BY VARIOUS FUNCTIONS

He ₂ separated atom energies and united atom energies					
MO— ζ	He ₂ separated atom energies 2E(He) Energy in a.u.	Difference from Hartree Fock in e.v.	He ₂ united atom energies Be atom wave function	Energy in a.u.	Difference from H.F. in e.v.
Hartree=Fock	-5.723	0	1s ² 2p ²	-14.387	+5.06
$\psi_{10}(1s, 1s')$	-5.740	-0.453	1s ² 1s' ²	-14.506	+1.82
$\sigma_u 1s(1s')$	-5.751	-0.761	1s ² 2s ²	-14.557	+0.435
$\psi_{s4}(1s, 1s', 2p\sigma, 2p\pi)^{64}$	-5.755	-0.861	Hartree Fock	-14.573	0.0
Exact	-5.807	-2.27	1s ² 2s ² (exact)	-14.667	-2.56

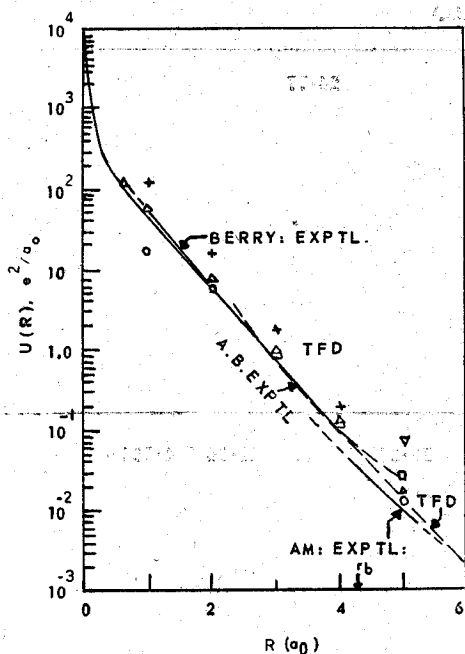


Fig. 9—Repulsive interaction potentials for the $Ar-Ar$ system. A—A.B.; Amdur Bertrand, +—Chakraborti (Born-Meyer); □—Sexana (12.6) O—Sexana (Exp-6) and Δ —Repulsive part of Exp.—6

The review of quantum mechanical calculations given above suggests that results derived from scattering¹⁵ data are too low by about 18 ev at $0.5A$. This discrepancy may provide further impetus to theoretical and experimental investigations.

The difficulties of calculations of potential function increase as the number of electrons in the system increases. Thomas—Fermi—Dirac statistical model of the atom has been found to be useful when the number of electrons is large. In this TFD model of atom, electrons are regarded as forming a perfect gas satisfying Fermi statistics and occupying region of phase space of lowest energy. Two electrons are assumed to reside in each element of phase space of volume $(2\pi\hbar)^3$. The electrons density surrounding the nucleus of an atom rises steeply and then falls down gradually. There is a sharp cut off in electron density at the spherical surface with $r=r_b$. Based upon this treatment Abrahamson¹⁶ has derived the following expression for the potential between rare gas atoms.

$$V = \frac{1}{2} \left(\frac{Z_1 Z_2 e^2}{r} \right) \left[f_1 \left(Z_1 \frac{1/3 R}{a} \right) + f_2 \left(Z_2 \frac{1/3 R}{a} \right) \right] + \bar{\Delta} \quad (22)$$

where Z_1 and Z_2 are atomic numbers of interacting atoms, f_1 and f_2 are screening functions, $a=0.8853a_0$ and $a_0=0.529$. The term $\bar{\Delta}$ is given by the expression

$$\bar{\Delta} = \frac{1}{6} \int_{D_{12}} \left\{ K_1 \left[(\rho_{01} + \rho_{02})^{5/2} - (\rho_{01} + \rho_{02})^{5/3} \right] - 2 K_2 \left[(\rho_{01} + \rho_{02})^{4/3} - (\rho_{01} + \rho_{02})^{4/3} \right] \right\} d\tau_1 \quad (23)$$

where $K_1 = 2.871 (e^2/a_0)$, $K_2 = 0.7386e^2$, $\rho_{0i}(r_i)$ is exact undistorted TFD electron density distance r_i from atom i and D_{12} is overlap region shared by both clouds and τ_1 is volume of overlap region. The screening function is expressed in the form

$$f = \left(\frac{r}{Z_e} \right) (u - u_0 + \tau_0^2) \quad (24)$$

where u is electric potential at any point, $u_0 = \frac{(Z-n)e}{r_0} + \frac{15}{6} \tau_0^2$

$$\text{and } \tau_0 = 0.2251 \left(\frac{e}{a_0} \right)^{\frac{1}{2}}$$

n , being the number of electrons per atom and r_0 , the radius of *TFD* atom. This function is evaluated by making use of the expression

$$\frac{d^2 f}{dx^2} = x \left[\left(\frac{f}{x} \right)^{\frac{1}{2}} + \beta_0 \right]^3$$

where $x = \frac{r}{\mu}$, $\mu = 0.8853 a_0 Z^{-1/3}$, $\beta_0 = 0.2118 Z^{-2/3}$.

The potential function V derived from expression (22) and experimental results¹⁵ for argon are shown in Fig. 9.

At short interatomic distances this function approaches Bohr's Screened Coulomb potential^{17, 18}

$$V = \frac{\rho_1 \rho_2}{R} \exp \left(- \frac{R}{a_1} \right) \quad (25)$$

where $a_1 = a_0 / (\rho_1^{2/3} + \rho_2^{2/3})^{1/2}$. At appreciable distances the agreement between the calculated results and experimental data of Amdur¹⁹ *et al* is close.

For practical applications Singh's²¹ four parameter potential

$$V = \frac{\epsilon r_0 \cos \beta x}{r} \left[e^{2\alpha \sinh \beta x} - 2 e^{\alpha \sinh \beta x} \right] \quad (26)$$

where $x = (r_0 - r)$ and ϵ , α , β & r_0 are constants, is found to be useful to describe the behaviour of gases with large number of electrons.

REFERENCES

1. ROSEN, P., *J. Chem. Phys.*, **18** (1950), 1182.
2. GRIFFING, V. & WEHNER, F., *ibid.*, **23** (1955), 1024.
3. HASHINO, T. & HUZINAGA, S., *Progr. Theoret. Phys. (Kyoto)*, **18** (1957), 139; *ibid.*, **20** (1958), 631.
4. DOOLING, J. S. & PIPEB, P., *Bull. Amer. Phys. Soc.*, **5** (1960), 339.
5. MOORE, N., *J. Chem. Phys.*, **33** (1960), 471.
6. RANSIL, B. J. *ibid.*, **34** (1961), 2109.
7. SAKAMOTO, M. & ISHIGURO, E., *Progr. Theoret. Phys. (Kyoto)*, **15** (1956), 37.
8. STATEB, J. C., "Quantum Theory of Molecules and Solids" (McGraw Hill Book Co., New York) 1963, p. 115.
9. HUZINAGA, S., *Progr. Theoret. Phys. (Kyoto)*, **18** (1957), 140.
10. BUCKINGHAM, R. A., *Trans. Faraday. Soc.*, **54** (1958), 453.
11. COULSON, C. A. & NEILSON, A. H., *Proc. Phys. Soc.*, **78** (1961), 831.
12. PHILLIPSON, P. E., *Phys. Rev.*, **125** (1962), 1981.

13. HUZINAGA, S., *Progr. Theoret. Phys. (Kyoto)*, **17** (1957), 169.
14. MILLER, E. V. & PRESENT, R. D., *J. Chem. Phys.*, **38** (1953), 1179.
15. AMDUR, I., *ibid.*, **17** (1949), 844.
AMDUR, I. & HARKNESS, A. L., *ibid.*, **22** (1954), 664.
AMDUR, I., JORDAN, J. E. & COLGATE, S. O., *ibid.*, **34** (1961), 1525.
16. ABRAHAMSON, A. A., *Phys. Rev.*, **130** (1963), 693.
17. GIBSON, J. R., GOLAND, A. N., MILGRAM, M. & VINEYARD, G. H., *ibid.*, **120** (1960), 1229.
18. HOLMES, D. K. & LEIBFRIED, G., *J. Appl. Phys.*, **31** (1960), 1046.
19. AMDUR, I., DAVENPORT, D. E. & KELLS, M. C., *J. Chem. Phys.*, **18** (1950), 525.
AMDUR, I. & MASON, E. A., *ibid.*, **22** (1954), 670.
AMDUR, I. & BERTRAND, R. R., *ibid.*, **36** (1962), 1078.
20. SLATER, J. C., *Phys. Rev.*, **32** (1928), 349.
21. SINGH, K., *J. Chem. Soc.*, (1964), 4551.