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The Mutual Repulsive Potential of Closed Shells¹

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A method is developed for representing, in terms of a small number of integrals, the mutual potential of two ions or atoms having a rare gas electron configuration. The accuracy is the usual first approximation of the Heitler-London method. The integrals are evaluated for two like atoms, and numerical calculations made for two neon atoms. The total (repulsive) potential at $R = 1.8 \times 10^{-8}$ cm is 344×10^{-14} erg; at $R = 2.3 \times 10^{-8}$ cm, 35×10^{-14} erg; and at $R = 3.2 \times 10^{-8}$ cm, 0.4×10^{-14} erg.

INTRODUCTION

THE calculation of the potential between two rare gas atoms by a generalized Heitler-London³ method is a problem which in some respects is unique. First, the absence of degeneracy makes the solution comparatively simple in spite of the large numbers of electrons. Secondly the results are, almost without alteration, applicable to the repulsive potential between ions having a rare gas electron configuration, and so refer to a large number of chemical compounds. Thirdly, the experimental conditions under which this potential is observed: comparatively large distance between the ions and consequently low values of the potential, and in crystals symmetric surroundings for the ions leading to a minimum of distortion; lead one to believe that the theoretical calculations should give fairly accurate agreement with observed potentials.

The mutual potential of two helium atoms has been calculated by Slater⁴ and others, but no adequate treatment has been given for the case of eight electrons.

In this paper the potential for two atoms or ions having closed shell configurations of eight

electrons is represented in terms of a comparatively small number of integrals. The evaluation and numerical calculations are carried out for the case of two neon atoms. In a subsequent paper semi-empirical approximations of the integrals will be given which enable a simple and moderately accurate functional representation of the repulsive potential of two (rare gas shell) ions with known outer electron distribution.

THE INTEGRALS

The potential is determined as a perturbation energy of two atoms in a manner exactly analogous to the method of Heitler and London.³ Two atoms a and b of core charge z_a and z_b , assumed to be point charges, have a nuclear separation R . There are sixteen electrons (twelve p and four s electrons) numbered from 1 to 16.⁵ r_{ak} and r_{bk} are used as symbols for the distances from the nuclei a and b respectively to the electron k . The zeroth order wave function is a linear combination of permutations of the product of one-electron hydrogen-like functions,

¹ From a dissertation submitted by W. E. Bleick to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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³ W. Heitler and F. London, *Zeits. f. Physik* **44**, 455 (1927).

⁴ J. C. Slater, *Phys. Rev.* **32**, 349 (1928).

⁵ In order not to make the succeeding mathematical presentation too cumbersome 8 electrons and a core charge (+8 for neutral atoms) are used instead of the more exact treatment with all electrons. The final results are so simple that the exact equations can be written readily. The extra integrals which would be introduced by the inclusion of the electrons underlying the closed shells can be seen to be negligible. The integrals which are evaluated, however, are modified to allow for the existence of the inner electrons.

$$\Psi_0 = (1/16!) \sum_P^{16! \text{ terms}} c_P \Psi_P, \quad \Psi_P = P(\Psi_1), \quad (1)$$

$$\Psi_1 = \psi_{a0s}\alpha(1) \cdot \psi_{a0s}\beta(2) \cdot \psi_{a-\alpha}(3) \cdot \psi_{a-\beta}(4) \cdot \psi_{a0p}\alpha(5) \cdots \psi_{a+\beta}(8) \cdot \psi_{b0s}\alpha(9) \cdots \psi_{b+\beta}(16),$$

where ψ_{a0s} , ψ_{a-} , ψ_{a0p} and ψ_{a+} are the ns and np one-electron (Hartree) functions of atom a with $m_l = 0, -1, 0, +1$, respectively, and α and β represent the two possible spin functions. The zero m_l 's are given the subscript s or p according as the m_l refers to an s or p state.

P is a permutation operator, operating on the product of the 16 different functions of the sixteen electrons; 16! different permutations of the 16 electrons among the 16 functions are possible.

c_P has the value $+1$ when the permutation P is even, and -1 when P is odd. The symbol Ψ_1 is used for the identical permutation of the product, written out as in Eq. (1), with electrons 1 to 8 on atom a , and 9 to 16 on atom b . Ψ_P is used for this product operated on by the permutation P .

The Schrödinger equation may be written

$$H(\Psi_0) = (T + V)(\Psi_0) = E\Psi_0. \quad (2)$$

The potential energy V has the form,

$$V = e^2 \left[\sum_{k=1}^{k=16} \sum_{l=1}^{l=16} \frac{1}{r_{kl}} - \sum_{k=1}^{k=16} \left(\frac{z_a}{r_{ak}} + \frac{z_b}{r_{bk}} \right) + \frac{z_a z_b}{R} \right]. \quad (3)$$

If this value for V is substituted in (2) we may follow Heitler and London and cancel, in every permutation occurring additively in Ψ_0 , the kinetic energy term plus that part of the potential energy which for the particular permutation occurs in the isolated atoms, operating on the permuted product Ψ_P with the sum of the energies of the two atoms $E_{0a} + E_{0b}$ multiplied by Ψ_P . There remains an equation in which the perturbation energy, and what may be termed a perturbation potential, occur. The form of the perturbation potential depends, however, on the permutation of the term Ψ_P which follows it. Calling ΔV_1 the perturbation potential for the identical permutation term Ψ_1 , the perturbation potential ΔV_P for the term Ψ_P is obtained by operating on ΔV_1 with P .

$$\Delta V_1 = e^2 \left[\sum_{k=1}^{k=8} \sum_{l=9}^{l=16} \frac{1}{r_{kl}} - \sum_{k=1}^{k=8} \frac{z_b}{r_{bk}} - \sum_{l=9}^{l=16} \frac{z_a}{r_{al}} + \frac{z_a z_b}{R} \right], \quad (4)$$

$$\Delta V_P = P(\Delta V_1). \quad (5)$$

The procedure outlined above leads to the equation,

$$(1/16!) \sum_P^{16! \text{ terms}} c_P \Delta V_P \Psi_P = \Delta E \Psi_0. \quad (6)$$

Multiplication by Ψ_0^* and integration over the whole space τ gives

$$(1/16!) \sum_P^{16! \text{ terms}} \sum_{P'}^{16! \text{ terms}} c_P c_{P'} \int \Psi_P^* \Delta V_{P'} \Psi_{P'} d\tau = \Delta E \int \Psi_0^* \Psi_0 d\tau = \Delta E (1 - S). \quad (7)$$

S corresponds to the S of Heitler and London and has a small value (~ 0.01).

$$-S = (1/16!) \sum_P^{16! \text{ terms}} \sum_{P'}^{16! \text{ terms}} c_P c_{P'} \int \Psi_P^* \Psi_{P'} d\tau \quad (8)$$

in which \sum' indicates that P and P' never take identical values. As will become evident later only permutations of one pair need be considered and the alternate Eq. (9) may be used,

$$S = 2 \sum_i \sum_j S_{ij}, \quad \left(\begin{matrix} i \\ j \end{matrix} \right) = 0_s, -1, 0_p, +1 \quad (9)$$

$$S_{ij} = |s_{ij}|^2$$

$$s_{ij} = \int \psi_{ai}^* \psi_{bj} d\tau,$$

i and j being indices that in this case indicate the value of the quantum number m_l .

The sum on the left of Eq. (7) contains $(16!)^2$ terms. After integration the numerical value of any term is, of course, independent of the numbers assigned to the electrons. We, therefore, change the notation of the electrons in each term taken as a whole, so that $\Psi_{P'}$ and $\Delta V_{P'}$ become Ψ_1 and ΔV_1 , operating on the term with $(P')^{-1}$, obtaining $16!$ different terms each occurring $16!$ times. This gives

$$\sum_P^{16! \text{ terms}} c_P \int \Psi_P^* \Delta V_1 \Psi_1 d\tau = \Delta E(1 - S). \quad (10)$$

Of the $16!$ terms in Eq. (10) less than seventeen are different from each other and appreciably different from zero.

First since ΔV_1 is not a function of the spin coordinates and since α and β are orthogonal, $\int \alpha^* \beta = 0$, terms in which any electron in Ψ_P^* has a different spin than in Ψ_1 are zero.

Secondly, since the perturbation potential contains no terms with the coordinates of more than one electron on the same atom in Ψ_1 , and since $\int \psi_{ai}^* \psi_{aj} d\tau = 0$ when $i \neq j$ all terms in which any electron has a different place (different ψ) on the same atom in Ψ_P^* and Ψ_1 are zero.

Thirdly, since the perturbation potential contains no terms with the coordinates of more than two electrons, and since $\int \psi_{ai}^* \psi_{bj} d\tau = s_{ij} \ll 1$ we may neglect terms in which more than one pair of electrons has different positions in Ψ_P^* and Ψ_1 , because these will all be multiplied by factors $S_{ij} = |s_{ij}|^2 \ll 1$.

Odd numbered electrons (spin α) may only be permuted with odd numbered electrons, and even with even. Fourthly, for every permutation

of one pair of odd numbered electrons there will be a corresponding permutation of even numbered electrons in which electrons the same pair of functions ψ_{ai} and ψ_{bj} are permuted. The two terms will be numerically the same.

Of the $16!$ different terms Ψ_P^* we need now only consider the identical permutation Ψ_1^* and sixteen others. These sixteen others are those in which one of the four odd electrons (spin α) on atom a in Ψ_1 (electrons 1, 3, 5 or 7) is exchanged with one of the four odd electrons (spin α) on atom b in Ψ_1 (electrons 9, 11, 13 or 15). Each of these sixteen terms must be multiplied by a factor 2 to allow for the corresponding numerically identical term of electrons with spin β (even). The term of the identical permutation will have the plus sign for c_P ; the other sixteen terms will have the minus sign.

Due to the analytical form of the functions ψ several of the sixteen terms will be numerically identical. For instance if the atoms a and b are the same, there are only seven different terms. If the permuted pair of electrons had both m_l 's $= 0_p$ one term results; and similarly if both m_l 's $= 0_s$. Two terms with the m_l 's $= 0_p$ and 0_s are identical. Four terms with the m_l 's $= 0_p$ and $+1$ or 0_p and -1 are identical; and similarly if the m_l 's $= 0_s$ and $+1$ or 0_s and -1 . If both m_l 's were $+1$ or both -1 the two terms are identical. Finally two terms with the m_l 's $= +1$ and -1 are identical.

In order to further simplify the integrals it is necessary to introduce twelve new functions, six of the coordinate r_a the distance from the nucleus a , and six functions of the coordinate r_b . The functions are ρ_a , ρ_b , ρ_{ai}' , ρ_{bi}' , U_a , U_b , U_{ai}' and U_{bi}' .

ρ_a is the density of electric charge (in units of e) in the atom a . ρ_{ai}' is the density of charge in the atom a with the i 'th electron of the closed shell missing. U_a is the potential due to atom a . U_{ai}' is the potential due to a when the i 'th electron of the closed shell is missing. ρ_{ai}' and U_{ai}' are not to be confused with the corresponding functions of a singly charged ion of the element a , where the electron distribution has altered due to the altered field. They are calculated assuming the electron distribution of the atomic functions, neglecting one electron of the closed shell. Strictly speaking in the case of the

np electrons ρ_{ai}' and U_{ai}' are not functions of r_a alone, but also of θ_a and ϕ_a . They depend on the quantum number m_l of the missing electron. This neglect of the angular part of the function in the field is the same assumption that is made in the calculation of the Hartree functions which will be used in the evaluations.

The equations for ρ_a and ρ_{ai}' are the following:

$$\rho_a(r_a) = - \sum_{\text{all electrons}} |\psi_{ai}|^2 + z_a(\delta(r_a)/4\pi r_a^2), \quad (11)$$

$$\rho_{ai}'(r_a) = \rho_a + |R_{ai}(r_a)|^2/4\pi,$$

where $\delta(r_a)$ is Dirac's delta-function,⁶ and $R_{ai}(r_a)$ is the radial function (normalized) of the i 'th electron of the closed shell.

The potential $U_a(r_a)$ is given by

$$U_a(r_a) = - \int_{r_a}^{\infty} 4\pi r^2 \rho_a(r) dr + \int_{r_a}^{\infty} 4\pi r \rho_a(r) dr, \quad (12)$$

which is identical with

$$U_a(r_a) = z_a/r_a - \sum_{\text{all electrons}} \int \psi_{ai}^*(r_i)^{-1} \psi_{ai} d\tau_i, \quad (13)$$

where r_i is the distance from some point with the coordinate r_a to the i 'th electron, and $d\tau_i$ is the volume element of the i 'th electron.

The potential $U_{ai}'(r_a)$ is given by an equation identical with (12) in which ρ_{ai}' is substituted for ρ_a . This equation is identical with Eq. (13) in which the sum goes over all but one electron.

With the help of these functions, which it should be noted are easily calculated when the Hartree functions of the atom are available, we consider the seventeen terms of the sum on the left-hand side of Eq. (10).

The first term, in which the two identical permutations occur, is the classical Coulomb

interaction, $e^2 \int U_a \rho_b d\tau = e^2 \int U_b \rho_a d\tau$. We may designate, in accordance with Heitler and London, this as W_{11} . It has a negative value in the range of R we are considering, occurs with a positive coefficient, and so leads to attraction.

The remaining exchange energy terms are not so trivially evaluated. Let us consider the term Ψ_{p^*} in which the electron pair $1 \leq i \leq 8$ and $9 \leq j \leq 16$ have exchanged the places they have in Ψ_1 . All other electrons have the same positions (same ψ 's) as in Ψ_1 .

In this term we consider first those (additive) terms in ΔV_1 , Eq. (4), which contain neither i nor j , that is where $k \neq i$, $l \neq j$. The partial integration of these terms gives

$$S_{ij} e^2 \int U_{ai}' \rho_{bj}' d\tau = S_{ij} e^2 \int U_{bj}' \rho_{ai}' d\tau.$$

The summation over all possible exchanges i and j gives $2e^2 \sum_i \sum_j S_{ij} \int U_{ai}' \rho_{bj}' d\tau$. Since U_{ai}' and ρ_{bj}' do not differ greatly from U_a and ρ_b , and S is very small we introduce no great error by writing this SW_{11} . The terms all occur with a negative coefficient.

In the perturbation potential we have left the following terms: first $\sum_i' (r_{il})^{-1} - z_b/r_{bi}$, secondly $\sum_k' (r_{jk})^{-1} - z_a/r_{aj}$, and thirdly $(r_{ij})^{-1}$, where the symbol \sum' is used to indicate that the sum over l does not include j , and the sum over k does not include i . The partial integration of the first of these terms gives $-s_{ij} e^2 \int U_{bj}' \psi_{bi}^* \psi_{ai} d\tau$, and of the second $-s_{ji} e^2 \int U_{ai}' \psi_{ai}^* \psi_{bj} d\tau$. The third term cannot be further simplified. All these terms occur with negative coefficient. ψ_{ai} and ψ_{bj} are the functions in which the electrons i and j occur in Ψ_1 .

The results of these considerations are summed up in Eq. (14).

$$\Delta E = W_{11} - [2/(1-S)] \sum_i \sum_j (s_{ji} U_{ij}' + R_{ij}^{-1}), \quad \left(\begin{matrix} i \\ j \end{matrix} \right) = 0, -1, 0, +1, \quad (14)$$

$$W_{11} = e^2 \int U_a \rho_b d\tau = e^2 \int U_b \rho_a d\tau,$$

$$U_{ij}' = -e^2 \int (U_{ai}' + U_{bj}') \psi_{ai}^* \psi_{bj} d\tau,$$

$$R_{ij}^{-1} = e^2 \int \int \psi_{ai}^* \psi_{bj}(1) (r_{12})^{-1} \psi_{bj}^* \psi_{ai}(2) d\tau_1 d\tau_2.$$

⁶ P. A. M. Dirac, *The Principles of Quantum Mechanics*, p. 63, Oxford (1930).

The symbol $d\tau$ is used as elsewhere to indicate the volume element, and all integrations are to be carried out over all space. s_{ij} and S are defined in Eq. (9), and the U 's and ρ 's in (11), (12), (13).

To proceed further it is necessary to have analytical one-electron functions for the atoms a and b . That is, functions whose product satisfies the radial part of the Schrödinger Eq. (2) for the single atoms a and b , and which are orthogonal and normalized. Slater⁷ has given such analytical approximations for the Hartree⁸ functions. It is obvious that if the summation over i and j in (14) includes the inner electrons the expression is that which would be obtained if these electrons were not neglected. The expressions (11), (12) and (13) for ρ and U are taken to include all electrons. Actually it is here advisable, particularly in calculating U_{ai}' and U_{bj}' , to include the inner electrons, and this does not add appreciably to the work of evaluation. It is, however, numerically unnecessary to include the inner electrons in the summation of (14). By the use of elliptic coordinates the calculation of W_{11} and U_{ij}' is straightforward and simple, although

somewhat long. The calculation of R_{ij}^{-1} is difficult.

NEON ATOM FUNCTIONS

The Hartree field used for neon is that of Brown.⁹ The following analytical representations of the $2p$ and $2s$ radial functions were employed:

$$R_{2p}(r) = r(17.9e^{-3.80r} + 2.30e^{-1.69r}), \quad (15)$$

$$R_{2s}(r) = 13.6e^{-8.22r} - r(14.7e^{-3.69r} + 4.76e^{-2.15r}). \quad (16)$$

The $2p$ representation differs slightly from that given by Brown and is a better approximation to his calculated field for large radii. The unit of length in these and the following functions is the Bohr atomic unit, i.e., 0.528×10^{-8} cm.

Brown tabulates values of the charge density ρ and of the $2p$ and $2s$ radial functions. It is easy by subtraction of $(2p)^2$ and $(2s)^2$, respectively, from ρ to calculate the modified charge densities ρ_{2p}' and ρ_{2s}' of (11). Approximate analytical representations of these densities are

$$\rho(r) = 10(\delta(r)/4\pi r^2) - 595e^{-19.3r} - r^2(155e^{-6.05r} + 3.56e^{-3.47r}), \quad (17)$$

$$\rho_{2p}'(r) = 10(\delta(r)/4\pi r^2) - 613e^{-19.5r} - r^2(132e^{-5.99r} + 2.88e^{-3.45r}), \quad (18)$$

$$\rho_{2s}'(r) = 10(\delta(r)/4\pi r^2) - 595e^{-19.3r} - r^2(134e^{-6.04r} + 2.89e^{-3.41r}). \quad (19)$$

The integrations of ρ , ρ_{2p}' and ρ_{2s}' according to (12) and (13), yield the following potentials:

$$U(r) = (20.0 + 2.08r^{-1})e^{-19.3r} + (53.2r^2 + 52.8r + 26.2 + 5.77r^{-1})e^{-6.05r} + (3.73r^2 + 6.46r + 5.59 + 2.15r^{-1})e^{-3.47r}, \quad (20)$$

$$U_{2p}'(r) = 1/r + (20.2 + 2.07r^{-1})e^{-19.5r} + (46.1r^2 + 46.2r + 23.1 + 5.15r^{-1})e^{-5.99r} + (3.04r^2 + 5.29r + 4.60 + 1.78r^{-1})e^{-3.45r}, \quad (21)$$

$$U_{2s}'(r) = 1/r + (20.1 + 2.08r^{-1})e^{-19.3r} + (46.1r^2 + 45.8r + 22.8 + 5.02r^{-1})e^{-6.04r} + (3.13r^2 + 5.50r + 4.84 + 1.89r^{-1})e^{-3.41r}. \quad (22)$$

CALCULATIONS

In the calculation of the integrals it is convenient to introduce the elliptic coordinates p , q defined by

$$p = (r_a + r_b)/R, \quad q = (r_a - r_b)/R.$$

⁷ J. C. Slater, Phys. Rev. **42**, 33 (1932).

⁸ D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89, 111 (1928).

As the third coordinate the azimuth ϕ about the line of nuclei is taken. The volume element is $(R/2)^3(p^2 - q^2)dpdq d\phi$. It is assumed that the polar axis of each atom is directed toward the other atom along the line of nuclei. Then θ_a and θ_b , the angles between the radius vectors r_a and r_b respectively and the line of nuclei, are given by

⁹ F. W. Brown, Phys. Rev. **44**, 214 (1933).

$$\begin{aligned}\sin \theta_a &= [(p^2 - 1)(1 - q^2)]^{1/2} / (p + q), \\ \sin \theta_b &= [(p^2 - 1)(1 - q^2)]^{1/2} / (p - q), \\ \cos \theta_a &= (1 + pq) / (p + q), \\ \cos \theta_b &= (1 - pq) / (p - q).\end{aligned}$$

In these coordinates all of the integrals except R_{ij}^{-1} reduce to a sum of terms of the type

$$\begin{aligned}\int_{p=-1}^{p=\infty} \int_{q=-1}^{q=+1} p^n q^m e^{-\alpha p - \beta q} dp dq \\ = (-1)^m (e^{\beta - \alpha} / \beta \alpha) A_n(\alpha) B_m(\beta), \\ (n, m \geq 0; \alpha > 0),\end{aligned}$$

where

$$A_n(\alpha) = \sum_{i=0}^n n! \alpha^{-i} / (n-i)!, \quad (23)$$

$$B_m(\beta) = A_m(-\beta) + (-1)^{m+1} e^{-2\beta} A_m(\beta),$$

$$B_m(-\beta) = (-1)^{m+1} e^{2\beta} B_m(\beta),$$

and α and β are proportional to R . The polynomials $A_n(\alpha)$ are conveniently calculated from the recursion formula

$$A_n(\alpha) = 1 + n A_{n-1}(\alpha) / \alpha. \quad (24)$$

The integrals R_{ij}^{-1} have been evaluated for the $2p$ electrons of like atoms and are given in an appendix.

NUMERICAL RESULTS

The numerical values of the integrals (9) and (14) for two neon atoms are tabulated in Tables I and II. The nuclear separation of 3.2×10^{-8} cm corresponds to the equilibrium separation of atoms in the neon lattice at the temperature of liquid helium. The separation of 2.3×10^{-8} cm is the same as the distance of closest approach of unlike ions in the sodium fluoride lattice at room temperature.

DISCUSSION OF THE RESULTS

Lennard-Jones¹⁰ gives several choices of values for the three constants A , B and n of an empirical equation $\phi = -A/R^6 + B/R^n$ for the total potential between two neon atoms as deduced from

TABLE I. Numerical values of the integrals for two neon atoms.

R (cm $\times 10^8$)	i	j	S_{ij} ($\times 10^3$)	S_{ij} ($\times 10^4$)	$-U_{ij}/e^2$ (cm^{-1}) $\times 10^{-4}$	$-s_{ij}U_{ij}/e^2$ (cm^{-1}) $\times 10^{-4}$	R_{ij}^{-1}/e^2 (cm^{-1}) $\times 10^{-4}$
1.8	0_p	0_p	11.6	133	4184	483	203
	0_p	0_s	9.73	94.7	4174	406	116
	0_s	0_s	5.02	25.2	2069	104	30.8
	± 1	± 1	3.87	15.0	1083	41.9	13.1
	0_p	± 1	0	0	0	0	14.2
	± 1	0_s	0	0	0	0	6.15
	± 1	∓ 1	0	0	0	0	1.41
	0_p	0_p	5.43	29.4	1502	81.5	37.5
2.3	0_p	0_s	3.42	11.7	1166	39.9	13.1
	0_s	0_s	1.31	1.71	412	5.39	1.91
	± 1	± 1	1.24	1.54	263	3.26	1.23
	0_p	± 1	0	0	0	0	1.67
	± 1	0_s	0	0	0	0	0.403
	± 1	∓ 1	0	0	0	0	0.129
	0_p	0_p	0.984	0.968	173	1.70	0.982
	0_p	0_s	0.410	0.168	102	0.418	0.162
3.2	0_s	0_s	0.0930	0.00865	19.7	0.0183	0.00832
	± 1	± 1	0.141	0.0200	21.4	0.0302	0.0138
	0_p	± 1	0	0	0	0	0.0259
	± 1	0_s	0	0	0	0	0.00245
	± 1	∓ 1	0	0	0	0	0.00143
	0_p	0_p	0.984	0.968	173	1.70	0.982
	0_p	0_s	0.410	0.168	102	0.418	0.162
	0_s	0_s	0.0930	0.00865	19.7	0.0183	0.00832

various experimental measurements. Two sets, $n = 9$, $A = 13.7 \times 10^{-60}$, $B = 3.27 \times 10^{-82}$ and $n = 12$, $A = 8.45 \times 10^{-60}$, $B = 36.3 \times 10^{-106}$, have been used to calculate the "experimental" values of the potential given in the first two columns of Table III. Needless to say the extrapolation of these equations to $R = 1.8 \times 10^{-8}$ cm has not much value. In order to calculate the corresponding theoretical potential it is necessary to include a term which would be added by the second approximation of the method used here. At fairly large distances this term can be readily approximated, as shown by London,¹¹ using a development of the perturbation potential in R . The first term becomes $-A/R^6$, $A \cong 3\alpha^2 J/4$. α is the polarizability, and J an energy corresponding to the most intense absorption frequencies. Using $\alpha = 0.392 \times 10^{-24}$ cm³ and $J = 25$ volts, $A = 4.6 \times 10^{-60}$ erg cm⁶. By adding this term to our previously calculated repulsion the third column of Table III is obtained.

The certainty of the experimental values of the potential is somewhat less than that indicated by the agreement between the two columns of Table III. Obviously the attractive potential is actually greater than that used to calculate the column marked "theoretical." This is due partly to the rough approximation used to obtain the constant A , and partly to the neglect of higher order terms. Table III indicates, however, that the values of the repulsive potential calculated

¹⁰ J. E. Lennard-Jones, Proc. Phys. Soc. **43**, 461 (1931).

¹¹ F. London, Zeits. f. physik. Chemie **11**, 222 (1930).

TABLE II. Sums.

R (cm $\times 10^8$)	S ($\times 10^3$)	$\frac{-2}{1-S} \sum_i \sum_j s_{ji} U'_{ij}$	$\frac{2}{1-S} \sum_i \sum_j R_{ij}^{-1}$	$\frac{-2}{1-S} \sum_i \sum_j (s_{ji} U_{ij} + R_{ij}^{-1})$ (ergs $\times 10^{14}$)	$-W_{11}$	ΔE
1.8	75.6	729	283	446	102	344
2.3	11.5	79.7	35.3	44.4	9.45	34.9
3.2	0.271	1.19	0.663	0.526	0.101	0.426

in this paper are not in definite disagreement with experiment. A much better comparison with experiment could, of course, be carried out if the repulsive potential between an alkali and a halide ion were calculated.

It is interesting to attempt to fit the values of Table II to a simple two constant equation. This has been done using the two extreme values to calculate the constants and comparing the equation with the value of Table II at $R=2.3A$. The equation $\varphi(R) = B/R^n$; $B = 2.71 \times 10^{-102}$ in ergs and cm, $n=11.63$, fits the two values at $R=1.8A$ and $3.2A$ but gives 19.8×10^{-14} erg at $2.3A$ instead of 34.9×10^{-14} , a deviation of 40 percent. The equation $\varphi(R) = b \exp(2r_0 - R)/\rho$, b arbitrarily chosen as 10^{-12} erg, $r_0 = 1.029 \times 10^{-8}$ cm and $\rho = 0.2091 \times 10^{-8}$ cm fits the two values at 1.8 and 3.2A and gives 31.5×10^{-14} erg at 2.3A, an agreement to within 10 percent. Obviously the exponential equation gives a better fit than the inverse power.

TABLE III. The total potential between two neon atoms.

$R \times 10^8$ cm	Potential, ergs $\times 10^{14}$		Theoretical
	Experimental $n=9$	$n=12$	
1.8	124	289	331
2.3	8.9	10.9	31.9
3.2	-0.35	-0.47	0.00
3.5	-0.33	-0.35	-0.2
4.0	-0.21	-0.18	-0.1

The exponential equation above is of the form proposed by Born and Mayer¹² for the repulsion between alkali and halide ions, the value of ρ for all the alkali halides being 0.345×10^{-8} cm, and the comparable r_0 values for Na^+ ion and F^- ion being respectively 0.875×10^{-8} cm and 1.110×10^{-8} cm.¹³ Presumably the more diffuse electron distribution function of the negative ion determines the steepness (the value of ρ) in the repulsion between the ions.

APPENDIX

The analytical expressions of the R_{ij}^{-1} integrals for the $2p$ electrons of like atoms are given here since they have not appeared previously in the literature in closed form. It is assumed that the normalized $2p$ radial function of both atoms is mre^{-kr} where m and k are constants. The integrals were calculated by using Neumann's¹⁴ expansion in elliptic coordinates of the reciprocal distance $1/r_{12}$ between two points (p_1, q_1, ϕ_1) and (p_2, q_2, ϕ_2) . This formula for the case $p_1 > p_2$ is

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{\tau=0}^{\infty} \sum_{\nu=-\tau}^{\nu=+\tau} (-1)^\nu (2\tau+1) \left[\frac{(\tau-|\nu|)!}{(\tau+|\nu|)!} \right]^2 P_{\tau\nu}(p_2) Q_{\tau\nu}(p_1) P_{\tau\nu}(q_1) P_{\tau\nu}(q_2) e^{i\nu(\phi_2-\phi_1)},$$

where $P_{\tau\nu}$ and $Q_{\tau\nu}$ are the associated Legendre polynomials of the first and second kinds, respectively. For the case $p_1 < p_2$ exchange the rôles of p_1 and p_2 .

¹² M. Born and J. E. Mayer, *Zeits. f. Physik* **75**, 1 (1932).

¹³ M. Huggins and J. E. Mayer, *J. Chem. Phys.* **1**, 643 (1933).

¹⁴ F. Neumann, *Vorlesungen über die Theorie des Potentials*, p. 341, Leipzig (1887).

The results are

$$R_{0p0p}^{-1} = 4g\{147W[1(0, 5, -18, 5); 0(\quad)] + 15W[1(21, -25, 27, -7); 6(7, -6, 7)] \\ + W[3(35, -30, 3, 0); 10(21, -11, 0)]\},$$

$$R_{\pm 1 \pm 1}^{-1} = g\{588W[1(0, 5, -6, 1); 0(\quad)] + 15W[1(21, -25, 3, 1); 6(7, -6, -1)] \\ + W[3(35, -65, 33, -3); 10(21, -32, 11)]\},$$

$$R_{0p\pm 1}^{-1} = -140g\{9W[1(0, 5, -6, 1); 2(0, 5, -2)] + W[3(7, -10, 3, 0); 2(21, -23, 5)]\},$$

$$R_{\pm 1 \mp 1}^{-1} = 70gW[3(7, -15, 9, -1); 2(21, -38, 9)],$$

where

$$g = 3R^9(m^2e^{-\alpha}/53,760\alpha)^2, \quad \alpha = kR,$$

$$W[c_1(a_6, a_4, a_2, a_0); c_2(b_5, b_3, b_1)] = c_1\{M^2(C + \ln \alpha) - 2LMe^{2\alpha}Ei(-2\alpha) + L^2e^{4\alpha}Ei(-4\alpha) \\ - (1/2\alpha) \sum_{j=0}^4 \sigma_j[2MA_j(\alpha) + \mu_j] + (1/2\alpha) \sum_{j=0}^5 s_jA_j(2\alpha)\} \\ - c_2\{MN + (1/2\alpha)[(5b_5\mu_4 + 3b_3\mu_2 + b_1\mu_0) - (6a_6\nu_5 + 4a_4\nu_3 + 2a_2\nu_1)]\}$$

and

$$L = a_6A_6(-\alpha) + a_4A_4(-\alpha) + a_2A_2(-\alpha) + a_0, \\ M = a_6A_6(\alpha) + a_4A_4(\alpha) + a_2A_2(\alpha) + a_0, \\ N = b_5A_5(\alpha) + b_3A_3(\alpha) + b_1A_1(\alpha), \\ M'_i = a_6A_{6+i}(2\alpha) + a_4A_{4+i}(2\alpha) + a_2A_{2+i}(2\alpha) + a_0A_i(2\alpha) \\ N'_i = b_5A_{5+i}(2\alpha) + b_3A_{3+i}(2\alpha) + b_1A_{1+i}(2\alpha), \\ \mu_i = M'_i + i\mu_{i-1}/\alpha, \quad \mu_0 = M'_0, \\ \nu_i = N'_i + i\nu_{i-1}/\alpha, \quad \nu_0 = N'_0, \\ A_{m, n}(\alpha) = A_m(\alpha) - m! \alpha^{n-m} A_n(\alpha)/n!, \quad (0 \leq n \leq m-1) \\ s_n = s_n(L, M) = \sum_{i=t}^3 a_{2i}[MA_{2i, n}(\alpha) + (-1)^{2i-n} LA_{2i, n}(-\alpha)], \quad t = (2n+3+(-1)^n)/4 \\ \sigma_n = s_n(1, 1).$$

The $A_j(\alpha)$ are the polynomials of Eq. (23) and $Ei(x)$ is the logarithmic-integral function.¹⁵ C denotes the Euler constant 0.5772157.

¹⁵ For definition and tables of this function see E. Jahnke and F. Emde, *Tables of Functions with Formulae and Curves*, Second edition, p. 78, B. G. Teubner, Leipzig (1933).