

CALCULATION OF INTERACTION BETWEEN ATOMS  
WITH *s*-ELECTRONS

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## ABSTRACT

An attempt is made to systematize the general calculation of the interaction energy of a pair of atoms each of which has one or two equivalent *s*-electrons outside of closed shells. General expressions for this energy are set up in terms of certain integrals and these integrals are evaluated for wave functions of Slater's type in terms of functions which are either tabulated or derivable from those in the accompanying tables. The method is applied to the calculation of some of the constants of a normal Na<sub>2</sub> molecule (which show fair agreement with the experimental values) and the repulsion energy of two normal helium atoms.

## I. INTRODUCTION

THE interaction between two hydrogen atoms insofar as it is obtainable from a first-order calculation of the perturbation energy was determined by Heitler and London in their paper<sup>1</sup> which opened the way to molecular calculations. The investigation of the interaction between two atoms other than hydrogen is considerably more complicated due to the greater number of electrons and the increased number and complexity of the wave functions. In this paper an effort is made to systematize such calculations for the case of two atoms each of which has one or two equivalent *s*-electrons in its outermost shell. While the calculations are long in some cases they are not particularly difficult; and to judge from the examples worked out, the results are fairly good.

## II. THEORY

The theory for the type of interaction considered in this paper was first set forth by Heitler and London. However, it may be of some interest to develop it again at this time using the method of J. C. Slater in his paper on "Theory of Complex Spectra."<sup>2</sup>

## 1. Assumptions.

In the first place it is assumed that the functions of the atoms can be represented by products (or sums of products) of wave functions of the individual electrons, each such function being formed of one factor depending on the space quantum numbers and the electron coordinates and one factor on the spin quantum number and the spin coordinate, the latter being the component of the spin vector along the line joining the nuclei of the two atoms

<sup>1</sup> Heitler and London, *Zeits. f. Physik* **44**, 455 (1927)

<sup>2</sup> Slater, *Phys. Rev.* **34**, 1293 (1929).

involved. In accordance with the Pauli principle the complete wave function for each atom is taken as a determinant the elements of which are the individual wave functions with all possible permutations of electron coordinates. This wave function is assumed to satisfy the wave equation for the given atom. Similarly the wave function for the system of two atoms is taken as a determinant involving the individual wave functions of both atoms (zero'th order approximation). The electron spin serves only to determine the symmetry but does not affect the energy in this approximation. Questions of nuclear symmetry or spin are not considered here.

Another assumption made is that closed shells contribute nothing to the interaction. Strictly speaking, closed shells cause a repulsion through the interaction of each with the outer electrons of the other atoms and—a much smaller force—through their interaction with each other. The repulsive effect becomes rapidly smaller the deeper the shells in question are located within the atoms. For ordinary molecular distances this repulsion is small compared to the forces between the outer electrons.

The attraction between the atoms due to their mutual polarization (Van der Waals force) is not treated in this paper. It is known<sup>3</sup> that this polarization force varies practically as  $1/R^6$  ( $R$  the distance between centers of atoms) whereas the “exchange” force considered here varies exponentially. Consequently for large distances the polarization force predominates and causes an attraction. For small distances it becomes relatively unimportant. For this reason it can be left out in calculations involving atoms in an “attractive” state where the equilibrium distance is small. In this case there is moreover a cancellation between the polarization force and the repulsion due to inner shells which may cause calculated results to be fairly accurate for the heavier atoms. But for “repulsive” states the distance between atoms is larger and the Van der Waals force must be taken into account; in fact there could be no equilibrium without it. If wanted it can be obtained by a separate calculation and added to the results obtained by the calculation treated here.

Finally, it is assumed that closed shells completely shield the nucleus insofar as effects on another atom are concerned. That is, the effective charge (which is to be understood hereafter whenever charge is mentioned) is the nuclear charge less the charge of all the electrons in closed shells. For the usual molecular distances this is certainly valid. In cases where the atoms are exceptionally close together, the effective charge may have to be corrected for incomplete shielding; but the formal results obtained below remain unchanged.

## 2. Notation.

We consider two atoms  $A$  and  $B$  with nuclei  $a$  and  $b$  and effective nuclear charges  $Z_a$  and  $Z_b$ . The two possible orientations of each electron spin vector will be denoted by  $\bar{\alpha}$  and  $\bar{\beta}$  (corresponding to  $m_s = +1/2$ ,  $m_s = -1/2$ ). The coordinates of the various electrons will be specified by numbers. The individual space wave-functions will be designated by  $u(a)$  and  $u(b)$ ; if the spin

<sup>3</sup> Eisenschitz and London, *Zeits. f. Physik* **60**, 491 (1930).

and the electron are to be distinguished, by  $u(a\bar{\alpha}1)$  for example. Combined wave functions will be indicated by  $u$  with subscripts. The internuclear distance will be denoted by  $R$ , other distances by  $r$  with appropriate subscripts. In integrations the element of volume in the total coordinate space will be denoted by  $d\tau$  and that in the coordinate space of a single electron by  $dv$  (with a subscript if necessary). Then

$$d\tau = dv_1 dv_2 \dots$$

Furthermore, let

$$I = \int u(a)u(b)dv, \tag{1}$$

$$K_1(a) = \int \frac{[u(b)]^2}{r_a} dv, \text{ etc.}, \tag{2}$$

$$K_2 = \int \frac{[u(a1)]^2 [u(b2)]^2}{r_{12}} d\tau, \tag{3}$$

$$J_1(a) = \int \frac{u(a)u(b)}{r_a} dv, \text{ etc.}, \tag{4}$$

$$J_2 = \int \frac{u(a1)u(b1)u(a2)u(b2)}{r_{12}} d\tau \tag{5}$$

$$J_3(a) = \int \frac{[u(a1)]^2 u(a2)u(b2)}{r_{12}} d\tau, \text{ etc.} \tag{6}$$

Other symbols or quantities will be defined as needed.

### 3. Development.

It is convenient to break up the general problem into three cases that may arise depending on the number of electrons involved (outside of closed shells).

(a) *One electron on each atom.* The spin vectors of the two electrons may be either parallel or anti-parallel. In the first case the resultant vector  $S$  will be of one unit magnitude and hence will give three possible spin components,  $M_s = 1, 0, -1$ , according to its orientation, resulting in a triplet term ( $^3\Sigma$ ). In the second case  $S=0$  and hence  $M_s=0$ , giving a singlet term ( $^1\Sigma$ ). Hence wave functions for  $M_s = \Sigma m_s = \pm 1$  correspond to the triplet. But those for  $\Sigma m_s = 0$  may belong to either the triplet or singlet. The possible wave functions are

| Wave Function   | $m_s(a)$       | $m_s(b)$       | $\Sigma m_s$ | Multiplicity |
|---|----------------|----------------|--------------|--------------|
| $u_1 = u(a\bar{\alpha}1)u(b\bar{\alpha}2) - u(a\bar{\alpha}2)u(b\bar{\alpha}1)$ | $\frac{1}{2}$  | $\frac{1}{2}$  | 1            | 3            |
| $u_2 = u(a\bar{\alpha}1)u(b\bar{\beta}2) - u(a\bar{\alpha}2)u(b\bar{\beta}1)$   | $\frac{1}{2}$  | $-\frac{1}{2}$ | 0            |              |
| $u_3 = u(a\bar{\beta}1)u(b\bar{\alpha}2) - u(a\bar{\beta}2)u(b\bar{\alpha}1)$   | $-\frac{1}{2}$ | $\frac{1}{2}$  | 0            | 1 or 3       |
| $u_4 = u(a\bar{\beta}1)u(b\bar{\beta}2) - u(a\bar{\beta}2)u(b\bar{\beta}1)$     | $-\frac{1}{2}$ | $-\frac{1}{2}$ | -1           |              |

We can now set up the secular equation to determine the energy levels. In doing this, we note first that as Slater showed,<sup>2</sup> the energy operator will have no components (to the degree of approximation considered here) between states of different  $\Sigma m_s$ . Secondly we see that  $u_2$  and  $u_3$  are not orthogonal to each other. The secular equation becomes

$$\begin{vmatrix} W - H_{11} & 0 & 0 & 0 \\ 0 & W - H_{22} & W\delta_{23} - H_{23} & 0 \\ 0 & W\delta_{32} - H_{32} & W - H_{33} & 0 \\ 0 & 0 & 0 & W - H_{44} \end{vmatrix} = 0$$

where

$$H_{ij} = \int u_i H u_j d\tau / \left( \int u_i^2 d\tau \int u_j^2 d\tau \right)^{1/2}$$

$$\delta_{ij} = \int u_i u_j d\tau / \left( \int u_i^2 d\tau \int u_j^2 d\tau \right)^{1/2}$$

The Hamiltonian operator H is given by

$$H = -\frac{\hbar^2}{8\pi^2m}(\nabla_1^2 + \nabla_2^2) + e^2 \left( \frac{Z_a Z_b}{R} - \frac{Z_a}{r_{a1}} - \frac{Z_a}{r_{a2}} - \frac{Z_b}{r_{b1}} - \frac{Z_b}{r_{b2}} + \frac{1}{r_{12}} \right). \quad (7)$$

In this expression each nuclear charge is to be considered as a function of the electron coordinates in the sense that it has two values: one for the case where the electron in question is in the same atom (when the shielding by the inner electrons is incomplete), the second when the electron is in the other atom (when the shielding by the inner electrons is practically complete).

Now the individual wave functions satisfy equations involving the atomic Hamiltonians. For example

$$H_{a1}u(a1) = E_{0a}u(a1), \quad (8)$$

where

$$H_{a1} = -\frac{\hbar^2}{8\pi^2m}\nabla_1^2 - \frac{Z_a e^2}{r_{a1}}.$$

Using the fact that individual wave functions with opposite spins are orthogonal, one gets by a simple calculation

$$H_{11} = H_{44} = E_{0a} + E_{0b} + e^2 \left\{ \frac{Z_a Z_b}{R} + \frac{K_2 - [Z_a K_1(a) + Z_b K_1(b)] - [J_2 - I(Z_a J_1(a) + Z_b J_1(b))]}{1 - I^2} \right\} \quad (9)$$

$$H_{22} = H_{33} = E_{0a} + E_{0b} + e^2 \left\{ \frac{Z_a Z_b}{R} + K_2 - [Z_a K_1(a) + Z_b K_1(b)] \right\} \quad (10)$$

$$H_{23} = H_{32} = -I^2 \left[ E_{0a} + E_{0b} + e^2 \frac{Z_a Z_b}{R} \right] - e^2 [J_2 - I(Z_a J_1(a) + Z_b J_1(b))] \quad (11)$$

$$\delta_{23} = \delta_{32} = -I^2. \quad (12)$$

The roots of the secular equation are given by

$$W_1 = H_{11}, \quad (13)$$

$$W_2 = H_{44} = H_{11}, \quad (14)$$

and by the roots of

$$\begin{vmatrix} W - H_{22} & W\delta_{23} - H_{23} \\ W\delta_{32} - H_{32} & W - H_{33} \end{vmatrix} = 0,$$

which are

$$W_3 = \frac{H_{22} + H_{23}}{1 + \delta_{23}} = H_{11}, \quad (15)$$

and

$$W_4 = \frac{H_{22} - H_{23}}{1 - \delta_{23}} = E_{0a} + E_{0b} + e^2 \left\{ \frac{Z_a Z_b}{R} + \frac{K_2 - [Z_a K_1(a) + Z_b K_1(b)] + J_2 - I[Z_a J_1(a) + Z_b J_1(b)]}{1 + I^2} \right\}. \quad (16)$$

The energy given by the roots  $W_1 = W_2 = W_3$  is that of the triplet, the three levels having the same energy because the spin is not present in the Hamiltonian. The root  $W_4$  gives the energy of the singlet.

If one determines the wave functions corresponding to  $W_3$  and  $W_4$  one finds by the usual theory that they are given (to within an arbitrary factor) by

$$\bar{u}_2 = u_2 + u_3, \quad (17)$$

$$\bar{u}_3 = u_2 - u_3, \quad (18)$$

where  $\bar{u}_2$  is the wave function belonging to the triplet and  $\bar{u}_3$  to the singlet.

Heitler and London<sup>1</sup> pointed out that the functions of the triplet were all antisymmetric in the two nuclei and hence would have a node in the region between the nuclei, whereas the singlet function was symmetrical and would not, and hence concluded that the singlet would have a lower energy than the triplet. This means that

$$J_2 - I(Z_a J_1(a) + Z_b J_1(b)) < 0 \quad (19)$$

and this has been verified in a number of calculations for typical cases involving neutral atoms, i.e. those for which

$$Z_a = Z_b = 1.$$

It is found in general that for neutral atoms the triplet energy rises monotonically as the atoms approach each other and hence there is repulsion between them. The singlet energy, it turns out, has a minimum for some particular distance between the atoms, and thus a pair of atoms with electron spins anti-parallel will attract each other until they arrive to within this distance.

(b) *One atom with one electron, the other with two.* For this case the only energy level is a doublet because of the two possible spin orientations of the single electron; since in the two-electron atom the spins must be opposite because the space wave functions are the same. Hence there are only two functions possible. If  $A$  is the atom with one electron these functions are

$$u_1 = \begin{vmatrix} u(a\bar{\alpha}1) & u(a\bar{\alpha}2) & u(a\bar{\alpha}3) \\ u(b\bar{\alpha}1) & u(b\bar{\alpha}2) & u(b\bar{\alpha}3) \\ u(b\bar{\beta}1) & u(b\bar{\beta}2) & u(b\bar{\beta}3) \end{vmatrix} \quad (20)$$

and

$$u_2 = \begin{vmatrix} u(a\bar{\beta}1) & u(a\bar{\beta}2) & u(a\bar{\beta}3) \\ u(b\bar{\alpha}1) & u(b\bar{\alpha}2) & u(b\bar{\alpha}3) \\ u(b\bar{\beta}1) & u(b\bar{\beta}2) & u(b\bar{\beta}3) \end{vmatrix}.$$

The energy is given by

$$W = \int u_1 H u_1 d\tau / \int u_1^2 d\tau = \int u_2 H u_2 d\tau / \int u_2^2 d\tau \quad (22)$$

where

$$H = -\frac{\hbar^2}{8\pi^2m} \sum_{i=1}^3 \nabla_i^2 + e^2 \left\{ \frac{Z_a Z_b}{R} - Z_b \sum_{i=1}^3 \frac{1}{r_{ai}} - \sum_{i=1}^3 \frac{1}{r_{bi}} + \sum_{i>j=1}^3 \frac{1}{r_{ij}} \right\}. \quad (23)$$

Making use of the facts that matrix components of  $H$  between functions with opposite spins are zero, and that the integrals are independent of the electron labels, it follows readily that

$$\begin{aligned} \int u_1 H u_1 d\tau &= 3! \left\{ \int u(a1)u(b2)u(b3) H u(a1)u(b2)u(b3) d\tau \right. \\ &\quad \left. - \int u(a2)u(b1)u(b3) H u(a1)u(b2)u(b3) d\tau \right\} \\ \int u_1^2 d\tau &= 3! \left\{ \int [u(a1)u(b2)u(b3)]^2 d\tau \right. \\ &\quad \left. - \int u(a1)u(b1)u(a2)u(b2)[u(b3)]^2 d\tau \right\}. \end{aligned}$$

By means of the relation

$$Hu(a1)u(b2)u(b3) = \left\{ E_{0a} + E_{0b} + e^2 \left[ \frac{Z_a Z_b}{R} - \frac{Z_a}{r_{a2}} - \frac{Z_a}{r_{a3}} - \frac{Z_b}{r_{b1}} + \frac{1}{r_{12}} + \frac{1}{r_{13}} \right] \right\} u(a1)u(b2)u(b3)$$

one obtains

$$W = E_{0a} + E_{0b} + e^2 \left\{ \frac{Z_a Z_b}{R} + \frac{2K_2 - Z_a K_1(a)(2 - I^2) - Z_b K_1(b) - [J_2 + I(J_3(b) - Z_a J_1(a) - Z_b J_1(b))]}{1 - I^2} \right\}. \quad (24)$$

Because of the fact that the two atoms can behave in only one way, that is, because there is nothing in the atom  $B$  to distinguish the two possible spin orientations of the electron in atom  $A$ , the force between the atoms must be repulsive.<sup>1</sup> Another way of putting it is that an atom with a closed shell will exert a repulsion on any other whatever the state of the latter may be.

(c) *Each atom with two electrons.* For this case there is only one possible wave function corresponding to a singlet ( $^1\Sigma$ ) state

$$u = \begin{vmatrix} u(a\bar{\alpha}1) & u(a\bar{\alpha}2) & u(a\bar{\alpha}3) & u(a\bar{\alpha}4) \\ u(a\bar{\beta}1) & u(a\bar{\beta}2) & u(a\bar{\beta}3) & u(a\bar{\beta}4) \\ u(b\bar{\alpha}1) & u(b\bar{\alpha}2) & u(b\bar{\alpha}3) & u(b\bar{\alpha}4) \\ u(b\bar{\beta}1) & u(b\bar{\beta}2) & u(b\bar{\beta}3) & u(b\bar{\beta}4) \end{vmatrix}. \quad (25)$$

The energy is given by

$$W = \int uHu d\tau / \int u^2 d\tau$$

where  $H$  has a form similar to (23).

Expanding gives

$$\begin{aligned} \int uHu d\tau &= 4! \left\{ \int u(a1)u(a2)u(b3)u(b4)Hu(a1)u(a2)u(b3)u(b4) d\tau \right. \\ &\quad - 2 \int u(a3)u(a2)u(b1)u(b4)Hu(a1)u(a2)u(b3)u(b4) d\tau \\ &\quad \left. + \int u(a3)u(a4)u(b1)u(b2)Hu(a1)u(a2)u(b3)u(b4) d\tau \right\}, \\ \int u^2 d\tau &= 4! \left\{ \int [u(a1)u(a2)u(b3)u(b4)]^2 d\tau \right. \\ &\quad - 2 \int u(a1)u(b1)u(a3)u(b3) [u(a2)u(b4)]^2 d\tau \\ &\quad \left. + \int u(a1)u(b1)u(a2)u(b2)u(a3)u(b3)u(a4)u(b4) d\tau \right\}. \end{aligned}$$

Proceeding as before one gets

$$W = E_{0a} + E_{0b} + e^2 \left\{ Z_a Z_b / R + (K_2(4 - 2I^2) - 2(1 - I^2)(Z_a K_1(a) + Z_b K_1(b)) + 2I[(1 - I^2)(Z_a J_1(a) + Z_b J_1(b)) - (J_3(a) + J_3(b)) - J_2(2 - 4I^2)]) / (1 - I^2)^2 \right\}. \quad (26)$$

This can be written also in the form

$$W = E_{0a} + E_{0b} + e^2 \left\{ \frac{Z_a Z_b}{R} + 4 \frac{K_2 - [(Z_a/2)K_1(a) + (Z_b/2)K_1(b)] - J_2 - I[(Z_a/2)J_1(a) + (Z_b/2)J_1(b)]}{1 - I^2} + \frac{I^2 K_2 + J_2 - I[J_3(a) + J_3(b)]}{(1 - I^2)^2} \right\}. \quad (27)$$

The term in braces is analogous to the perturbation energy obtained for the case of two one-electron atoms. For two neutral atoms ( $Z_a = Z_b = 2$ ) it is in fact 4 times this corresponding energy. The last term is a correction term of the same order of magnitude as the preceding.

The force between the atoms in this case is repulsive just as in the previous case.

### III. INTEGRALS

We now come to the question of determining the numerical values of the expressions set up in the preceding section. For this purpose it is necessary first of all to choose atomic wave functions which are simple enough in form so as not to complicate the calculations excessively and yet have sufficient accuracy for the purpose. In general the accuracy required in molecular problems is less than that for atomic problems because the theory itself is less accurate.

The best form of wave function for the present purpose is that given by Slater,<sup>4</sup> of the form  $r^{n-1} e^{-(Z-s)/na_0 r}$  where  $a_0 = 0.529 \text{ \AA}$ ,  $n$  is the effective quantum number and  $s$  is a shielding constant, both of the latter being assigned by rules proposed by him. In the case of a stable molecule, i.e. for a pair of atoms in an attractive state, these wave functions are to be used as given by Slater with one exception, namely that  $n$  is to have only integral values. In those cases for which Slater's  $n$  is not an integer there are two ways of proceeding. Either one can calculate the quantities for the two nearest values of  $n$  and interpolate or—and this is the better procedure—one can approximate the wave function in the important region, i.e. where there is most overlapping, by using the nearest integral value of  $n$  and then readjusting the shielding constant to get a good fit.

In the case of "repulsive" states, Slater's rules for setting up wave functions are not accurate for the larger distances involved. One can either use the real quantum number for  $n$  and take for  $s$  one less than the total number of electrons in the atom; or one can determine the wave function by some

<sup>4</sup> Slater, Phys. Rev. **36**, 57 (1930).

other method, for example that of Hartree, and having determined, fit to it a wave function of the form given above by choosing suitable values of  $n$  and  $s$ . This will be made clearer in an example to follow.

In any case one can write the wave function in the form  $r^{n-1}e^{-\alpha r}$  where  $\alpha$  is a known constant. In the molecular problem the wave function is then normalized. For the repulsion problem this is not advisable, it being better to adjust the multiplying constant to get the best approximation to the true wave function *in the important region*. In the latter case one can then assume that enough of the electron charge (either positive or negative) is concentrated at the center of the atom to make up one electron. In what follows the multiplying factor will be denoted by  $N$  if the wave function is normalized, otherwise by  $C$ .

For the problem on hand we consider two wave functions, one for each atom

$$\begin{aligned} u(a) &= N_a r^{m-1} e^{-\alpha r} \\ u(b) &= N_b r^{n-1} e^{-\beta r}. \end{aligned} \tag{28}$$

From the condition

$$\int [u(a)]^2 dv = 4\pi N_a^2 \int_0^\infty r^{2m} e^{-2\alpha r} dr = 1$$

it follows that

$$N_a = \left( \frac{(2\alpha)^{2m+1}}{4\pi(2m)!} \right)^{1/2}, \tag{29}$$

and an analogous expression holds for  $N_b$ .

The integrals defined in the previous section can be calculated by a few simple devices, such as the use of elliptic coordinates, the fact that the potential of a spherical shell is constant inside the shell and outside is the same as if concentrated at the center, and the Neumann expansion of  $1/r_{12}$  in terms of Legendre functions.<sup>5</sup> The integrals can be separated into two groups according as to whether  $\alpha = \beta$  or  $\alpha \neq \beta$ .

In evaluating the integrals use is made of certain functions given by Guillemin and Zener,<sup>6</sup> which are most conveniently defined as follows

$$A_n(\alpha) = A_n(1, \alpha) = \int_1^\infty x^n e^{-\alpha x} dx = \frac{n! e^{-\alpha}}{\alpha^{n+1}} \sum_{\nu=0}^n \frac{\alpha^\nu}{\nu!} \tag{30}$$

$$A_n(-1, \alpha) = \int_{-1}^\infty x^n e^{-\alpha x} dx = \frac{n! e^\alpha}{\alpha^{n+1}} \sum_{\nu=0}^n \frac{(-\alpha)^\nu}{\nu!} \tag{31}$$

$$B_n(\alpha) = \int_{-1}^1 x^n e^{-\alpha x} dx = A_n(-1, \alpha) - A_n(1, \alpha) \tag{32}$$

$$\begin{aligned} F_n(\alpha) &= \int_1^\infty x^n e^{-\alpha x} Q_0(x) dx = \frac{1}{2} \int_1^\infty x^n e^{-\alpha x} \ln \left( \frac{x+1}{x-1} \right) dx \\ &= \frac{1}{2} [(\ln 2\alpha + C)A_n(1, \alpha) - Ei(-2\alpha)A_n(-1, \alpha)] - \theta(n, \alpha) \end{aligned} \tag{33}$$

<sup>5</sup> Sugiura, Zeits. f. Physik **45**, 484 (1927).

<sup>6</sup> Zener and Guillemin, Phys. Rev. **34**, 999 (1929). Their notation has been changed slightly.

where

$$C = 0.577216 \cdots \text{ (Euler's constant)}$$

and

$$\theta(n, \alpha) = \frac{e^{-\alpha}}{\alpha} \sum_{\nu=0}^n C_{\nu}^n \alpha^{-\nu}, \quad (34)$$

the coefficients  $C_{\nu}^n$  being defined by the relations

$$C_{\nu}^{n+1} = C_{\nu}^n + \nu C_{\nu-1}^n + \frac{[1 + (-1)^{n-\nu}]}{2} \frac{n!}{(n-\nu+1)!}, \quad 0 < \nu \leq n \quad (35)$$

$$C_0^n = 0.$$

In addition to these we define the coefficients  $p_{\tau}^i$  and  $q_{\tau}^i$  by means of the identities

$$P_{\tau}(x) = \sum_{i=0}^{\tau} p_{\tau}^i x^i, \quad (36)$$

$$Q_{\tau}(x) = Q_0 \sum_{i=0}^{\tau} p_{\tau}^i x^i + \sum_{i=0}^{\tau} q_{\tau}^i x^i, \quad (37)$$

where  $P_{\tau}(x)$  and  $Q_{\tau}(x)$  are Legendre functions of the first and second kind respectively of order  $\tau$  ( $Q_0(x) = 1/2 \ln(x+1)/(x-1)$ ).

These coefficients satisfy recursion formulae which follow from the relations between Legendre functions

$$p_{\tau}^j = \left(\frac{2\tau-1}{\tau}\right) p_{\tau-1}^{j-1} - \left(\frac{\tau-1}{\tau}\right) p_{\tau-2}^j, \quad (0 < j \leq \tau, \tau > 1) \quad (38)$$

$$p_{\tau}^0 = -\left(\frac{\tau-1}{\tau}\right) p_{\tau-2}^0, \quad (\tau > 1)$$

$$p_0^0 = p_1^1 = 1,$$

and

$$q_{\tau}^j = \left(\frac{2\tau-1}{\tau}\right) q_{\tau-1}^{j-1} - \left(\frac{\tau-1}{\tau}\right) q_{\tau-2}^j, \quad (0 < j \leq \tau, \tau > 1) \quad (39)$$

$$q_{\tau}^0 = -\left(\frac{\tau-1}{\tau}\right) q_{\tau-2}^0, \quad (\tau > 1)$$

$$q_0^0 = 0, \quad q_1^1 = -1.$$

The coefficients  $D_p^{mn}$  are defined by the identity

$$(x+y)^m (x-y)^n = \sum_{p=0}^{m+n} D_p^{mn} x^{m+n-p} y^p,$$

so that

$$D_p^{mn} = \sum_k (-1)^k \binom{m}{p-k} \binom{n}{k}. \tag{40}$$

They satisfy the following relations

$$\begin{aligned} D_p^{mn} &= D_p^{m-1,n} + D_{p-1}^{m-1,n} = D_p^{m,n-1} - D_{p-1}^{m,n-1}, \quad (0 < p \leq m+n) \tag{41} \\ D_p^{mn} &= (-1)^p D_p^{nm}, \quad D_{m+n-p}^{mn} = (-1)^n D_p^{mn}, \\ D_{2k+1}^{mm} &= 0, \quad D_{2k}^{mm} = (-1)^k \binom{m}{k}, \\ D_p^{m,0} &= \binom{m}{p}, \\ D_0^{mn} &= 1. \end{aligned}$$

Finally we require several more quantities, as follows

$$\begin{aligned} R_\tau^n &= \int_{-1}^1 x^\tau P_\tau(x) dx, \tag{42} \\ &= \frac{2^{\tau+1} n! \left(\frac{n+\tau}{2}\right)!}{\left(\frac{n-\tau}{2}\right)! (n+\tau+1)!}, \quad \text{if } n-\tau \geq 0 \text{ and even,} \\ &= 0, \quad \text{if } n-\tau < 0 \text{ or odd,} \end{aligned}$$

$$\begin{aligned} G_\tau^n(\alpha) &= \int_{-1}^1 x^\tau e^{-\alpha x} P_\tau(x) dx, \tag{43} \\ &= \sum_{i=0}^\tau p_\tau^i B_{n+i}(\alpha), \end{aligned}$$

$$A_n^m(\alpha) = \sum_{\nu=0}^m \frac{\alpha^\nu}{\nu!} A_{n+\nu}(\alpha) \tag{44}$$

$$F_n^m(\alpha) = \sum_{\nu=0}^m \frac{\alpha^\nu}{\nu!} F_{n+\nu}(\alpha). \tag{45}$$

In Tables I-VII<sup>7</sup> are given some of the values of

$$A_n(1, \alpha), A_n(-1, \alpha), C_\nu^n, R_\tau^i, p_\tau^i, q_\tau^i, \text{ and } D_p^{mn}.$$

By means of the defining equations and recursion formulae the tables can be extended if necessary. Although it would be convenient to have tables of the

<sup>7</sup> Tables I and II were prepared by Dr. S. Ikehara to whom I am indebted. Bartlett (Phys. Rev. 37, 507 (1931)) has given a smaller table of  $A_n(1, \alpha)$ . Part of Table III is given in reference (6).

TABLE I.  $A_n(1, \alpha)$

| $\alpha$ | 0                        | 1                        | 2                        | 3                        | 4                        | 5                        | 6                        | 7                        | 8                        |
|----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 1.5      | 1.48753·10 <sup>-1</sup> | 2.47922·10 <sup>-1</sup> | 4.79317·10 <sup>-1</sup> | 1.10739                  | 3.10178                  | 1.04880·10               | 4.21009·10               | 1.96620·10 <sup>3</sup>  | 1.04879·10 <sup>3</sup>  |
| 2.0      | 6.76676·10 <sup>-2</sup> | 1.01501                  | 1.69169                  | 3.21421·10 <sup>-1</sup> | 7.10510·10 <sup>-1</sup> | 1.84394·1                | 5.59950·1                | 1.96660·10               | 7.87313·10 <sup>3</sup>  |
| 2.5      | 3.28340                  | 4.59676·10 <sup>-2</sup> | 6.96081·10 <sup>-2</sup> | 1.16364                  | 2.19016                  | 4.70866·10 <sup>-1</sup> | 1.16291                  | 3.28899·1                | 1.05576·10               |
| 3.0      | 2.32465                  | 3.16998                  | 4.63009                  | 7.37565·10 <sup>-3</sup> | 1.30529                  | 2.60571                  | 5.91766·10 <sup>-1</sup> | 1.52957                  | 4.47288·1                |
| 3.5      | 1.65957                  | 2.21276                  | 3.13474                  | 4.79431                  | 8.05198·10 <sup>-3</sup> | 1.50795                  | 3.18186                  | 7.59031·10 <sup>-1</sup> | 2.04068                  |
| 4.0      | 1.19305                  | 1.56015                  | 2.15314                  | 3.18057                  | 5.10760                  | 1.50795                  | 1.79024                  | 3.97521                  | 9.90443·10 <sup>-1</sup> |
| 4.5      | 8.62782·10 <sup>-3</sup> | 1.10929                  | 1.49666                  | 2.14564                  | 3.31494                  | 5.59841                  | 1.04601                  | 2.17829                  | 5.05553                  |
| 5.0      | 6.27140                  | 7.94377·10 <sup>-3</sup> | 1.05081                  | 1.46779                  | 2.19278                  | 3.50884                  | 6.30849·10 <sup>-2</sup> | 1.24030                  | 2.70869                  |
| 5.5      | 4.57891                  | 5.72364                  | 7.44073·10 <sup>-3</sup> | 1.01595                  | 1.47384                  | 2.30019                  | 3.90817                  | 4.41571                  | 1.50523                  |
| 6.0      | 3.35629                  | 4.14601                  | 5.30735                  | 7.10266·10 <sup>-3</sup> | 1.00411                  | 1.51694                  | 2.47719                  | 4.41571                  | 8.64755·10 <sup>-2</sup> |
| 6.5      | 2.46867                  | 3.01726                  | 3.80967                  | 5.00845                  | 6.92062·10 <sup>-3</sup> | 1.01582                  | 1.60130                  | 2.73778                  | 5.11402                  |
| 7.0      | 1.34759                  | 1.61711                  | 1.99443                  | 2.54425                  | 3.38299                  | 4.73058·10 <sup>-3</sup> | 7.02428·10 <sup>-3</sup> | 1.11816                  | 1.92381                  |
| 7.5      | 4.13125·10 <sup>-4</sup> | 4.81980·10 <sup>-4</sup> | 5.73785·10 <sup>-4</sup> | 7.00018·10 <sup>-4</sup> | 8.79804·10 <sup>-4</sup> | 1.14630                  | 1.55942                  | 2.23245·10 <sup>-3</sup> | 3.38972·10 <sup>-3</sup> |
| 8.0      | 1.30269                  | 1.48879                  | 1.72806                  | 2.04328                  | 2.47028                  | 3.06717·10 <sup>-4</sup> | 3.93169·10 <sup>-4</sup> | 5.23438·10 <sup>-4</sup> | 7.28484·10 <sup>-4</sup> |
| 8.5      | 4.19328·10 <sup>-5</sup> | 4.71744·10 <sup>-5</sup> | 5.37264·10 <sup>-5</sup> | 6.20802·10 <sup>-5</sup> | 7.29729·10 <sup>-5</sup> | 8.75409·10 <sup>-5</sup> | 1.07589                  | 1.36073                  | 1.78006                  |
| 9.0      | 2.39375                  | 2.67536                  | 3.02324                  | 3.46077                  | 4.02234                  | 4.75983                  | 5.75363·10 <sup>-5</sup> | 7.13203·10 <sup>-5</sup> | 9.10624·10 <sup>-5</sup> |
| 9.5      | 1.37122                  | 1.52358                  | 1.70979                  | 1.94115                  | 2.23395                  | 2.61231                  | 3.11276                  | 3.79225                  | 4.74211                  |
| 10.0     | 4.53999·10 <sup>-6</sup> | 4.99399·10 <sup>-6</sup> | 5.53879·10 <sup>-6</sup> | 6.20163·10 <sup>-6</sup> | 7.02064·10 <sup>-6</sup> | 8.05032·10 <sup>-6</sup> | 9.37018·10 <sup>-6</sup> | 1.10991                  | 1.34193                  |
| 10.5     | 1.2018·10 <sup>-7</sup>  | 5.54686·10 <sup>-7</sup> | 6.04465·10 <sup>-7</sup> | 6.63134·10 <sup>-7</sup> | 7.33062·10 <sup>-7</sup> | 8.17460·10 <sup>-7</sup> | 9.20748·10 <sup>-7</sup> | 1.04912·10 <sup>-6</sup> | 1.21143·10 <sup>-6</sup> |
| 11.0     | 5.93949·10 <sup>-8</sup> | 6.36374·10 <sup>-8</sup> | 6.84860·10 <sup>-8</sup> | 7.40705·10 <sup>-8</sup> | 8.05579·10 <sup>-8</sup> | 8.81656·10 <sup>-8</sup> | 9.71802·10 <sup>-8</sup> | 1.07983·10 <sup>-7</sup> | 1.21101·10 <sup>-7</sup> |

TABLE I.  $A_n(1, \alpha)$

| $\alpha$ | 9                        | 10                       | 11                       | 12                       | 13                       | 14                       | 15                       | 16                       |
|----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 3.0      | 6.13863·1                | 2.04787·1                | 7.51051·10               | 3.00437·10 <sup>2</sup>  | 1.30191·10 <sup>3</sup>  | 6.07560·10 <sup>4</sup>  | 3.03780·10 <sup>4</sup>  | 1.62016·10 <sup>5</sup>  |
| 3.5      | 1.31111                  | 3.75467·1                | 1.18090                  | 4.04967·10               | 2.31957·10               | 8.11895·10               | 3.04465·10 <sup>2</sup>  | 1.21787·10 <sup>3</sup>  |
| 4.0      | 3.43235·10 <sup>-1</sup> | 8.62716·10 <sup>-1</sup> | 2.37705·1                | 7.13573·1                | 1.30191·10 <sup>3</sup>  | 6.07560·10 <sup>4</sup>  | 3.03780·10 <sup>4</sup>  | 1.62016·10 <sup>5</sup>  |
| 4.5      | 1.86481                  | 4.42135                  | 1.14771                  | 3.24394                  | 2.31957·10               | 8.11895·10               | 3.04465·10 <sup>2</sup>  | 1.21787·10 <sup>3</sup>  |
| 5.0      | 1.04749                  | 2.35245                  | 5.77511·10 <sup>-1</sup> | 1.54250                  | 4.45857·1                | 1.38736                  | 8.56938·1                | 2.74234·10               |
| 5.5      | 3.59762·10 <sup>-2</sup> | 7.33000·10 <sup>-2</sup> | 1.62608                  | 3.91606·10 <sup>-1</sup> | 1.01952                  | 2.85601·1                | 8.63296·10 <sup>-1</sup> | 1.23587·1                |
| 6.0      | 5.49771·10 <sup>-3</sup> | 9.57598·10 <sup>-3</sup> | 1.79691·10 <sup>-2</sup> | 3.63513·10 <sup>-2</sup> | 7.91743·10 <sup>-2</sup> | 1.85153·10 <sup>-1</sup> | 4.63296·10 <sup>-1</sup> | 1.23587·1                |
| 6.5      | 1.06689                  | 1.65440                  | 2.73904·10 <sup>-1</sup> | 4.81034·10 <sup>-1</sup> | 9.06375·10 <sup>-1</sup> | 1.82578·10 <sup>-1</sup> | 3.92541·10 <sup>-1</sup> | 8.98538·10 <sup>-2</sup> |
| 7.0      | 2.42189·10 <sup>-4</sup> | 3.44669·10 <sup>-4</sup> | 5.15853·10 <sup>-4</sup> | 8.15712·10 <sup>-4</sup> | 8.36747                  | 2.43500·10 <sup>-3</sup> | 4.60755·10 <sup>-3</sup> | 9.25704·10 <sup>-3</sup> |
| 7.5      | 1.20356                  | 1.65533                  | 2.38157                  | 3.60159                  | 5.74769·10 <sup>-4</sup> | 9.70616·10 <sup>-4</sup> | 1.73679                  | 3.27319                  |
| 8.0      | 6.11333·10 <sup>-5</sup> | 8.16381·10 <sup>-5</sup> | 1.13492                  | 1.65035                  | 2.52096                  | 4.05862                  | 6.90148·10 <sup>-4</sup> | 1.24064                  |
| 8.5      | 1.66174                  | 2.11573                  | 2.78131·10 <sup>-5</sup> | 3.79157·10 <sup>-5</sup> | 5.38304·10 <sup>-5</sup> | 7.99025·10 <sup>-5</sup> | 1.24394                  | 2.03570·10 <sup>-4</sup> |
| 9.0      | 1.42059·10 <sup>-6</sup> | 1.69584·10 <sup>-6</sup> | 2.06654·10 <sup>-6</sup> | 2.57856·10 <sup>-6</sup> | 3.30346·10 <sup>-6</sup> | 5.97250·10 <sup>-6</sup> | 1.07983·10 <sup>-7</sup> | 8.47353·10 <sup>-6</sup> |
| 9.5      | 1.37245·10 <sup>-7</sup> | 1.57427·10 <sup>-7</sup> | 1.83088·10 <sup>-7</sup> | 2.16327·10 <sup>-7</sup> | 2.60270·10 <sup>-7</sup> | 3.19665·10 <sup>-7</sup> | 4.01893·10 <sup>-7</sup> | 5.18701·10 <sup>-7</sup> |

TABLE II  $A_n(-1, \alpha)$

| $\alpha$ | 0                       | 1                       | 2                       | 3                       | 4                       | 5                       | 6                       | 7                       | 8                       |
|----------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 1.5      | 2.98779                 | $9.95931 \cdot 10^{-1}$ | $1.65988$               | $3.31977 \cdot 10^{-1}$ | $3.87306$               | 9.92242                 | $4.26775 \cdot 10$      | $1.96174 \cdot 10^2$    | $1.04925 \cdot 10^3$    |
| 2.0      | 3.69453                 | $1.84726 \cdot 1$       | $1.84726$               | $9.23632 \cdot 10^{-1}$ | $1.84726$               | $1.84726 \cdot 10^{-1}$ | $6.46542 \cdot 1$       | $1.89345 \cdot 10$      | $7.94323 \cdot 10$      |
| 2.5      | 4.87300                 | 2.92380                 | 2.53396                 | $1.83225 \cdot 1$       | 1.94140                 | $9.90194 \cdot 10^{-1}$ | 2.49653                 | 2.11729·1               | 1.16483                 |
| 2.75     | 5.68823                 | 3.61978                 | 3.05566                 | 2.35478                 | 2.26309                 | $1.57352 \cdot 1$       | 2.25510                 | $5.20320 \cdot 10^{-2}$ | 5.83959·1               |
| 3.0      | 6.69518                 | 4.46345                 | 3.71954                 | 2.97564                 | 2.72767                 | 2.14907                 | 2.39704                 | 1.10209·1               | 3.75628                 |
| 3.25     | 7.93549                 | 5.49380                 | 4.55469                 | 3.73116                 | 3.34343                 | 2.79196                 | 2.78109                 | 1.94544                 | 3.14671                 |
| 3.5      | 9.46156                 | 6.75826                 | 5.59970                 | 4.66182                 | 4.13377                 | 3.55618                 | 3.36525                 | 2.73105                 | 3.21916                 |
| 3.75     | 1.13390·10              | 8.31523                 | 6.90416                 | 5.81562                 | 5.13562                 | 4.49146                 | 4.15262                 | 3.58739                 | 3.68585                 |
| 4.0      | 1.36495                 | 1.02372·10              | 8.53096                 | 7.25132                 | 6.39822                 | 5.65176                 | 5.17190                 | 4.59872                 | 4.45209                 |
| 4.25     | 1.64954                 | 1.26141                 | 1.05593·10              | 9.04174                 | 7.98851                 | 7.10067                 | 6.47092                 | 5.83741                 | 5.30733                 |
| 4.5      | 2.00038                 | 1.55585                 | 1.30889                 | 1.12779·10              | 9.97904                 | 8.91599                 | 8.11582                 | 7.37920                 | 6.88524                 |
| 5.0      | 2.96826                 | 2.37461                 | 2.01842                 | 1.17571                 | 1.56249·10              | 1.40577·10              | 1.28154·10              | 1.17439·10              | 1.08924·10              |
| 6.0      | 6.72381                 | 5.60318                 | 4.85609                 | 4.29577                 | 3.85997                 | 3.21554                 | 3.21664                 | 2.97107                 | 2.76239                 |
| 7.0      | 1.34282·10 <sup>2</sup> | 1.18296·10 <sup>2</sup> | 1.18296·10 <sup>2</sup> | 1.05964·10 <sup>2</sup> | 9.61112                 | 8.80110                 | 8.12238                 | 7.54380                 | 7.04470                 |
| 8.0      | 3.72620                 | 2.91109                 | 2.63453                 | 2.2062·10 <sup>2</sup>  | 4.0893·10 <sup>2</sup>  | 2.2062·10 <sup>2</sup>  | 2.06073·10 <sup>2</sup> | 1.92305·10 <sup>2</sup> | 1.80314·10 <sup>2</sup> |
| 8.5      | 5.78208                 | 5.10184                 | 4.16503                 | 4.16503                 | 3.82207                 | 3.53381                 | 3.28763                 | 3.07462                 | 2.88832                 |
| 9.0      | 9.00343                 | 8.00305                 | 6.99510                 | 6.99510                 | 6.07227                 | 5.62994                 | 5.25013                 | 4.91999                 | 4.63010                 |
| 10.      | 2.20265·10 <sup>3</sup> | 1.98238·10 <sup>3</sup> | 1.80617·10 <sup>3</sup> | 1.66080·10 <sup>3</sup> | 1.53833·10 <sup>3</sup> | 1.43348·10 <sup>3</sup> | 1.34256·10 <sup>3</sup> | 1.26286·10 <sup>3</sup> | 1.19236·10 <sup>3</sup> |
| 12.      | 1.35629·10 <sup>4</sup> | 1.24327·10 <sup>4</sup> | 1.14908·10 <sup>4</sup> | 1.06902·10 <sup>4</sup> | 9.99950                 | 9.39644                 | 8.86468                 | 8.39184                 | 7.96834                 |
| 14.      | 8.59003                 | 7.97646                 | 7.45054                 | 6.99349                 | 6.59189·10 <sup>4</sup> | 6.23578·10 <sup>4</sup> | 5.91755·10 <sup>4</sup> | 5.63125·10 <sup>4</sup> | 5.37217·10 <sup>4</sup> |

TABLE II  $A_n(-1, \alpha)$

| $\alpha$ | 9                       | 10                      | 11                      | 12                      | 13                      | 14                      | 15                      | 16                      |
|----------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 3.0      | 4.57366                 | 2.19407·10              | 7.37541·10              | $3.01712 \cdot 10^2$    | $1.30072 \cdot 10^3$    | $6.07673 \cdot 10^3$    | $3.03770 \cdot 10^4$    | $1.62017 \cdot 10^5$    |
| 3.5      | 1.18372                 | 6.07951·1               | 9.64548·1               | $4.25318 \cdot 10$      | $2.01275 \cdot 10$      | 8.40957·10              | $3.01710 \cdot 10^2$    | $1.22049 \cdot 10^3$    |
| 4.0      | 3.63232                 | 4.56873                 | 1.08554                 | 1.03929                 | 2.01275·10              | 8.40957·10              | $3.01710 \cdot 10^2$    | $1.22049 \cdot 10^3$    |
| 4.25     | 4.83281                 | 5.12407                 | 3.23308                 | 7.36669·1               | 4.69204·1               | 1.85441·10              | $1.42159 \cdot 1$       | 3.42317·10              |
| 4.5      | 6.23333                 | 6.15196                 | 4.96569                 | 6.76198                 | 6.89806                 | 1.03681                 | $1.85441 \cdot 10$      | 3.42317·10              |
| 5.0      | 1.00763·10              | 9.53011                 | 8.71639                 | 8.76330                 | 2.03926·10              | 1.96554                 | $1.80996 \cdot 10$      | 1.89725                 |
| 6.0      | 2.58023                 | 2.42343·10              | 2.28086·10              | 2.16210·10              | 5.03990                 | 5.05838                 | 4.82680                 | 4.54473·10              |
| 7.0      | 6.60872                 | 6.22516                 | 5.88379                 | 5.57969                 | 1.37742·10 <sup>2</sup> | 1.31571·10 <sup>2</sup> | 1.25925·10 <sup>2</sup> | 1.20770·10 <sup>2</sup> |
| 8.0      | 1.69766·10 <sup>2</sup> | 1.60412·10 <sup>2</sup> | 1.52053·10 <sup>2</sup> | 1.44540·10 <sup>2</sup> | 2.22118                 | 2.12367                 | 2.03443                 | 1.95257                 |
| 8.5      | 2.72386                 | 2.57754                 | 2.44644                 | 2.32828                 | 3.58339                 | 3.42926                 | 3.28800                 | 3.15810                 |
| 9.0      | 4.37333                 | 4.14418                 | 3.93832                 | 3.75233                 | 9.33852                 | 8.95254                 | 8.60432                 | 8.25956                 |
| 10.      | 1.12952·10 <sup>3</sup> | 1.07313·10 <sup>3</sup> | 1.02221·10 <sup>3</sup> | 9.75996                 | 6.63731·10 <sup>3</sup> | 6.12833·10 <sup>3</sup> | 5.90248                 | 5.69139·10 <sup>3</sup> |
| 12.      | 7.58664                 | 7.24070                 | 6.92559                 | 6.63731·10 <sup>3</sup> | 4.37305·10 <sup>4</sup> | 4.21698·10 <sup>4</sup> | 4.07184                 | 3.93650·10 <sup>4</sup> |
| 14.      | 5.13649·10 <sup>4</sup> | 4.92111·10 <sup>4</sup> | 4.72345·10 <sup>4</sup> | 4.54136·10 <sup>4</sup> | 4.37305·10 <sup>4</sup> | 4.21698·10 <sup>4</sup> | 4.07184                 | 3.93650·10 <sup>4</sup> |





TABLE VII.  $D_p^{mn}$

| $m$ | $n$ | $p$ |    |    |     |    |    |     |    |    |    |    |
|-----|-----|-----|----|----|-----|----|----|-----|----|----|----|----|
|     |     | 0   | 1  | 2  | 3   | 4  | 5  | 6   | 7  | 8  | 9  | 10 |
| 0   | 0   | 1   |    |    |     |    |    |     |    |    |    |    |
|     | 1   | 1   | -1 |    |     |    |    |     |    |    |    |    |
|     | 2   | 1   | -2 | 1  |     |    |    |     |    |    |    |    |
|     | 3   | 1   | -3 | 3  | -1  |    |    |     |    |    |    |    |
|     | 4   | 1   | -4 | 6  | -4  | 1  |    |     |    |    |    |    |
|     | 5   | 1   | -5 | 10 | -10 | 5  | -1 |     |    |    |    |    |
| 1   | 0   | 1   | 1  |    |     |    |    |     |    |    |    |    |
|     | 1   | 1   | 0  | -1 |     |    |    |     |    |    |    |    |
|     | 2   | 1   | -1 | -1 | 1   |    |    |     |    |    |    |    |
|     | 3   | 1   | -2 | 0  | 2   | -1 |    |     |    |    |    |    |
|     | 4   | 1   | -3 | 2  | 2   | -3 | 1  |     |    |    |    |    |
|     | 5   | 1   | -4 | 5  | 0   | -5 | 4  | -1  |    |    |    |    |
| 2   | 0   | 1   | 2  | 1  |     |    |    |     |    |    |    |    |
|     | 1   | 1   | 1  | -1 | -1  |    |    |     |    |    |    |    |
|     | 2   | 1   | 0  | -2 | 0   | 1  |    |     |    |    |    |    |
|     | 3   | 1   | -1 | -2 | 2   | 1  | -1 |     |    |    |    |    |
|     | 4   | 1   | -2 | -1 | 4   | -1 | -2 | 1   |    |    |    |    |
|     | 5   | 1   | -3 | 1  | 5   | -5 | -1 | 3   | -1 |    |    |    |
| 3   | 0   | 1   | 3  | 3  | 1   |    |    |     |    |    |    |    |
|     | 1   | 1   | 2  | 0  | -2  | -1 |    |     |    |    |    |    |
|     | 2   | 1   | 1  | -2 | -2  | 1  | 1  |     |    |    |    |    |
|     | 3   | 1   | 0  | -3 | 0   | 3  | 0  | -1  |    |    |    |    |
|     | 4   | 1   | -1 | -3 | 3   | 3  | -3 | -1  | 1  |    |    |    |
|     | 5   | 1   | -2 | -2 | 6   | 0  | -6 | 2   | 2  | -1 |    |    |
| 4   | 0   | 1   | 4  | 6  | 4   | 1  |    |     |    |    |    |    |
|     | 1   | 1   | 3  | 2  | -2  | -3 | -1 |     |    |    |    |    |
|     | 2   | 1   | 2  | -1 | -4  | -1 | 2  | 1   |    |    |    |    |
|     | 3   | 1   | 1  | -3 | -3  | 3  | 3  | -1  | -1 |    |    |    |
|     | 4   | 1   | 0  | -4 | 0   | 6  | 0  | -4  | 0  | 1  |    |    |
|     | 5   | 1   | -1 | -4 | 4   | 6  | -6 | -4  | 4  | 1  | -1 |    |
| 5   | 0   | 1   | 5  | 10 | 10  | 5  | 1  |     |    |    |    |    |
|     | 1   | 1   | 4  | 5  | 0   | -5 | -4 | -1  |    |    |    |    |
|     | 2   | 1   | 3  | 1  | -5  | -5 | 1  | 3   | 1  |    |    |    |
|     | 3   | 1   | 2  | -2 | -6  | 0  | 6  | 2   | -2 | -1 |    |    |
|     | 4   | 1   | 1  | -4 | -4  | 6  | 6  | -4  | -4 | 1  | 1  |    |
|     | 5   | 1   | 0  | -5 | 0   | 10 | 0  | -10 | 0  | 5  | 0  | -1 |

other functions available, it did not appear advisable to go to the labor of preparing them in view of the fact that the present theory is probably of a temporary nature. From the tables given here, the other functions for specific values of the arguments can be computed in a reasonably short time.

Using the functions and quantities mentioned, the integrals can be evaluated and are listed below. Those which can be obtained by interchanging  $a$  and  $b$ ,  $\alpha$  and  $\beta$ , and  $m$  and  $n$  in integrals already listed are omitted. The integrals given are for normalized wave functions. Corresponding integrals for unnormalized functions can be obtained from those below by multiplying  $I$  and  $J_1(b)$  by  $C_a C_b / N_a N_b$ ,  $K_1(b)$  by  $C_a^2 / N_a^2$ ,  $J_2$  and  $K_2$  by  $C_a^2 C_b^2 / N_a^2 N_b^2$  and  $J_3(a)$  by  $C_a^3 C_b / N_a^3 N_b$ .

1.  $\alpha = \beta$

$$I = \frac{(\alpha R)^{m+n+1}}{((2m)!(2n)!)^{1/2}} \sum_{k=0}^{\leq (m+n)/2} \frac{D_{2k}^{mn}}{2k+1} A_{m+n-2k}(\alpha R), \tag{46}$$

$$K_1(b) = \frac{1}{R} + \frac{(2\alpha R)^{2m}}{(2m)!R} [(2\alpha R - 2m)A_{2m-1}(2\alpha R) - e^{-2\alpha R}], \quad (47)$$

$$K_2 = K_1(b) - \frac{\alpha(\alpha R)^{2m}}{n(2m)!} \sum_{\nu=0}^{2n-1} \frac{2n-\nu}{\nu!} (\alpha R)^\nu \sum_{p=0}^{\leq m+(\nu-1)/2} \frac{D_{2p}^{2m-1,\nu}}{2p+1} A_{2m+\nu-1-2p}(2\alpha R), \quad (48)$$

(or the same with atomic quantities interchanged),

$$J_1(b) = \frac{2\alpha(\alpha R)^{m+n}}{((2m)!(2n)!)^{1/2}} \sum_{k=0}^{\leq (m+n-1)/2} \frac{D_{2k}^{m,n-1}}{2k+1} A_{m+n-1-2k}(\alpha R), \quad (49)$$

$$J_2 = \frac{\alpha(\alpha R)^{2m+2n+1}}{(2m)!(2n)!} \sum_{r=0}^{m+n} \sum_{s=0}^{m+n} D_r^{mn} D_s^{mn} \sum_{\tau=0}^{\leq r,s} (2\tau+1) R_\tau^r R_\tau^s$$

$$\left\{ \sum_{j=0}^{\tau} \sum_{i=0}^{\tau} p_\tau^i A_{m+n-s+j}(\alpha R) [p_\tau^i F_{m+n-r+i}(\alpha R) + q_\tau^i A_{m+n-r+i}(\alpha R)] \right.$$

$$- \sum_{j=0}^{\tau} \sum_{i=0}^{\tau} p_\tau^i (m+n-s+j)! (\alpha R)^{-(m+n-s+i+1)}$$

$$\left. [p_\tau^i F_{m+n-r+i}(2\alpha R) + q_\tau^i A_{m+n-r+i}(2\alpha R)] \right\}, \quad (50)$$

$$J_3(b) = J_1(b) - \frac{\alpha(\alpha R)^{2m}}{n((2m)!(2n)!)^{1/2}} \sum_{\nu=0}^{2n} \frac{2n-\nu}{\nu!} (\alpha R)^\nu$$

$$\sum_{k=0}^{\leq (m+n+\nu-1)/2} \frac{D_{2k}^{m,n+\nu-1}}{2k+1} A_{m+n+\nu-1-2p}(2\alpha R). \quad (51)$$

2.  $\alpha \neq \beta$

$$I = \frac{1}{2} \left( \frac{(\alpha R)^{2m+1} (\beta R)^{2n+1}}{(2m)!(2n)!} \right)^{1/2} \sum_{p=0}^{m+n} D_p^{mn} B_p \left( \frac{R}{2} (\alpha - \beta) \right) A_{m+n-p} \left( \frac{R}{2} (\alpha + \beta) \right), \quad (52)$$

$$K_1(b) = \frac{1}{R} + \frac{(2\alpha R)^{2m}}{(2m)!R} [(2\alpha R - 2m)A_{2m-1}(2\alpha R) - e^{-2\alpha R}], \quad (53)$$

$$K_2 = K_1(b) - \frac{\alpha(\alpha R)^{2m}}{2(2m)!n} \sum_{\nu=0}^{2n} \frac{2n-\nu}{\nu!} (\beta R)^\nu$$

$$\sum_{p=0}^{2m-1+\nu} D_p^{2m-1,\nu} B_p(R(\alpha - \beta)) A_{2m-1+\nu-p}(R(\alpha + \beta)), \quad (54)$$

$$J_1(b) = \frac{1}{R} \left( \frac{(\alpha R)^{2m+1} (\beta R)^{2n+1}}{(2m)!(2n)!} \right)^{1/2}$$

$$\sum_{p=0}^{m+n-1} D_p^{m,n-1} B_p \left( \frac{R}{2} (\alpha - \beta) \right) A_{m+n-1-p} \left( \frac{R}{2} (\alpha + \beta) \right), \quad (55)$$

$$\begin{aligned}
J_2 = & \frac{(\alpha R)^{2m+1}(\beta R)^{2n+1}}{(2m)!(2n)!R} \sum_{r=0}^{m+n} \sum_{s=0}^{m+n} D_r^{m,n} D_s^{m,n} \\
& \sum_{\tau=0}^{\infty} (2\tau+1) G_{\tau}^r \left( \frac{R}{2}(\alpha-\beta) \right) G_{\tau}^s \left( \frac{R}{2}(\alpha-\beta) \right) \\
& \left\{ \sum_{j=0}^{\tau} \sum_{i=0}^{\tau} p_{\tau}^i A_{m+n-s+j} \left( \frac{R}{2}(\alpha+\beta) \right) \left[ p_{\tau}^i F_{m+n-r+i} \left( \frac{R}{2}(\alpha+\beta) \right) \right. \right. \\
& \left. \left. + q_{\tau}^i A_{m+n-r+i} \left( \frac{R}{2}(\alpha+\beta) \right) \right] \right. \\
& \left. - \sum_{j=0}^{\tau} \sum_{i=0}^{\tau} p_{\tau}^i (m+n-s+j)! \left[ \frac{R}{2}(\alpha+\beta) \right]^{-(m+n-s+j+1)} \right. \\
& \left. \left[ p_{\tau}^i F_{m+n-r+i}^{m+n-s+j}(R(\alpha+\beta)) + q_{\tau}^i A_{m+n-r+i}^{m+n-s+j}(R(\alpha+\beta)) \right] \right\}, \quad (56)
\end{aligned}$$

$$\begin{aligned}
J_3(b) = & J_1(b) - \frac{1}{2nR} \left( \frac{(\alpha R)^{2m+1}(\beta R)^{2m+1}}{(2m)!(2n)!} \right)^{1/2} \sum_{\nu=0}^{2n} \frac{2n-\nu}{\nu!} (\beta R)^{\nu} \\
& \sum_{p=0}^{m+n-1+\nu} D_p^{m,n-1+\nu} B_p(R(\alpha-\beta)) A_{m+n-1+\nu-p}(R(\alpha+\beta)). \quad (57)
\end{aligned}$$

It is to be noted that the expression for  $J_2$  for  $\alpha \neq \beta$  involves an infinite (convergent) summation. The term at which this is to be cut off depends of course on the accuracy desired. The error involved in cutting off the expansion at the term  $\tau = k$  is measured by the error in cutting off the expansion of  $\mu^s e^{-(R/2)(\alpha-\beta)\mu}$  in a series of Legendre polynomials  $P_{\tau}(\mu)$  at the  $k$ th term. From the theory of expansions in terms of orthogonal functions it follows that the root mean square error over the interval  $(-1, +1)$ , which results in cutting off this series at the  $k$ th term is less than that for the corresponding situation in an expansion in terms of any other polynomials, in particular in a power series. Now in the expansion

$$\mu^s e^{-(R/2)(\alpha-\beta)\mu} = \sum_{\tau=0}^{\infty} \frac{\left[ \frac{R}{2}(\beta-\alpha) \right]^{\tau}}{\tau!} \mu^{s+\tau}$$

it is known from elementary theory that the error in the function in the range  $(-1, +1)$  on cutting off at the  $k$ th term is less than

$$\frac{\left| \frac{R}{2}(\beta-\alpha) \right|^{k+1}}{(k+1)!}.$$

Consequently the magnitude of this can be taken as a rough measure of the error in the approximate expansion above, and may be helpful in determining the number of terms to keep in the series.

From Eqs. (46), (48) and (51) and the analogous equations in the second group, bearing in mind the definitions of the various functions, one can see that in most cases the following approximations may be made

$$I^2 K_2 \sim I^2 / R, \quad (58)$$

$$IJ_3(b) \sim IJ_1(b). \quad (59)$$

#### IV. APPLICATIONS

It may be well to say a few words on the technique of these calculations. The most essential point is to be systematic. All the functions required should be calculated for the values of the arguments needed before beginning the lengthy summations that occur in some of the integrals. The summations should be carried out in tabular form; and it is wise to carry along the calculations for the various values of the argument simultaneously. This helps to avoid mistakes. Finally one should carry perhaps two or three more significant figures through the work than are required in the final result, because of the large number of subtractions of nearly equal quantities that occurs.

In the actual calculation again there are two different procedures depending on whether the problem is one of attraction or repulsion. In the first case what one generally desires is the equilibrium distance between the atomic nuclei, the energy at this position, and often the fundamental vibration frequency. Consequently one calculates the interaction energy for a number of values of the distance until one finds three consecutive values (fairly close together) such that the energy for the middle one is less than that for the other two. One can then assume that the energy as a function of the distance can be represented by a parabola in this region and thus determine the minimum energy and the corresponding distance  $R_0$ . If now the parabola is represented in the form

$$E = \frac{1}{2}k(R - R_0)^2 + E_0,$$

one can determine  $k$  and then get the fundamental frequency (in wave numbers) by the relation

$$\omega_0 = \frac{1}{2\pi c} \left( \frac{k}{M} \right)^{1/2},$$

where  $M$  is the reduced mass

$$M = \frac{M_a M_b}{M_a + M_b},$$

and  $c$  the velocity of light.

In the case of a repulsion problem, what is generally desired is a knowledge of the energy as a function of the distance. One can therefore calculate it for a number of values of the distance (choosing them so as to have the arguments of the functions among the values found in the tables in order to avoid interpolation) and make a plot. It is advisable to plot  $\log E$  against the distance because of its rapid rate of change; it is generally found that this will give a curve not differing greatly from a straight line.

As illustration of the method we may consider two typical calculations:

### 1. Sodium molecule ( ${}^1\Sigma$ state)

Using Slater's rule it is found that for a sodium atom the outer electron has a shielding constant of 8.8, and quantum number  $n=3$ , so that

$$\alpha = \frac{Z}{na_0} = 1.385 \times 10 A^{-1}.$$

Carrying out the calculation one finds the following values for the energy ( $\Delta E = W - E_0$ ):

| $\frac{\alpha R}{}$ | $\frac{R(\text{in } A)}{}$ | $\frac{\Delta E(\text{in volts})}{}$ |
|---------------------|----------------------------|--------------------------------------|
| 4.00                | 2.888                      | -0.831                               |
| 4.25                | 3.069                      | .837                                 |
| 4.50                | 3.249                      | .801                                 |

From these values one gets for the minimum energy  $\Delta E_m = -0.84$  electron-volts, at a distance of separation  $R_0 = 3.01A$ . and a fundamental vibration frequency of  $1.7 \times 10^2 \text{ cm}^{-1}$ . These compare favorably with the experimental values  $-1.0 \pm 0.1$  volts,  $3.07A$ ., and  $158 \text{ cm}^{-1}$ , as given by Loomis.<sup>8</sup> Incidentally, the present tendency is to consider Loomis' value for the energy as too high, about 0.8 volts being thought correct.<sup>9</sup> In particular Kinsey<sup>10</sup> finds it to be  $0.85 \pm .02$  volts. For comparison, it might be mentioned that the calculated energy of the triplet has values for the distances given above of  $+1.11$ ,  $0.78$ , and  $0.68$  volts.

At this point the question naturally arises as to what is the effect of the inner shells, the interactions of which had been neglected, on the energy. To give an accurate answer to this question would involve considerable calculation but we can set up a rough argument to indicate the order of magnitude of the energy due to the inner shells. By the latter is meant the interaction between the outer electron of each atom with the inner shell of the second, for the interaction between the two inner shells must be exceedingly small. The argument is based on the fact that the interaction between two atoms having electrons with wave functions of the form  $r^{m-1}e^{-\alpha r}$  and  $r^{n-1}e^{-\beta r}$  gives rise to an energy of the form  $Pe^{-(\alpha+\beta)R}$  where  $P$  is a polynomial in  $R$  which changes relatively little compared to the change in the exponential for changes in  $R$  or even in the kinds of atoms. Consequently, in calculating orders of magnitude one may assume  $P$  constant. Now consider the interaction between a neon atom and an argon atom. Although such atoms have not been treated in the theory of this paper, for such a rough calculation one may assume that the repulsion will be of the same form as in the cases that have been considered. Slater's rule (which can be used here for the accuracy desired, even if this is a repulsion problem) gives for neon  $Z-s=5.85$ ,  $n=2$  (so that  $\alpha=5.52A^{-1}$ ) and for argon  $Z-s=11.25$ ,  $n=3$  ( $\beta=4.25A^{-1}$ ), whence

<sup>8</sup> Loomis, Phys. Rev. **29**, 607 (1927) and **31**, 323 (1928). See Birge, Int. Crit. Tab. V, pp. 415, 418, New York (1929).

<sup>9</sup> Ladenburg and Thiele, Zeits. f. Physik. Chem. **7**, 161 (1930).

<sup>10</sup> Kinsey, Proc. Nat. Acad. Sci. **15**, 37 (1929).

$$\Delta E \sim P e^{-9.77R}$$

Now the kinetic theory radii for neon and argon are 1.1 and 1.3A respectively.<sup>11</sup> Hence a neon and an argon atom approach to about 2.4A at ordinary temperature; so that this distance corresponds to an energy of about  $10^{-2}$  volts. For  $R=3A$  this gives, considering  $P$  unchanged (it certainly cannot change by more than a small factor),

$$\Delta E \sim 10^{-5} \text{ volts.}$$

Now for the interaction between the outer shell of each of two sodium atoms with the inner shell of the other for the same value of  $R$ , the energy will be different because of the different values for  $\alpha$  and  $\beta$ , because the number of electrons is less (we can make a rough allowance for this by dividing the results obtained by 4) and because  $P$  is different. Neglecting the change in  $P$  which cannot be very large since the atoms are not very different in kind from the preceding, we need only to consider the change in the exponential factor. For the inner shell, Slater's rule gives  $\alpha=6.47A^{-1}$ , for the outer,  $\beta=1.39A^{-1}$ . Hence the exponential in this case is  $e^{-7.86R}$  instead of  $e^{-9.77R}$  as above. Taking this into account and also the decreased number of electrons

$$\Delta E \sim 10^{-3} \text{ volts}$$

which is negligible.

Admittedly this is a very rough calculation but it should serve to give the right order of magnitude. If for some reason the energy is somewhat larger than this estimate, no harm is done for it tends to balance the effect of polarization of the outer shells which has not been considered.

## 2. Helium atoms.

If each electron of a helium atom  $A$  has a wave function  $u(a)$ , then the charge at any point is given by  $2u^2(a)$ . If now one uses Hartree's charge distribution for helium in the range 0.5A to 2A and one assumes a simple exponential form for the wave function one finds as a good approximation

$$u = 3.20e^{-1.48r/a_0}$$

where  $r$  is measured in A. However, this wave function is not normalized; it is too low in the inner part of the atom. This can be compensated by imagining additional electron charge concentrated at the center of the atom. The exact position of the charge is not important for its effect on the result is small. The simplest way of proceeding at this point is to use the expressions for the integrals given in III modified by a appropriate factors  $C_a/N_a$  etc., as indicated there, with the exception that the terms  $1/R$  are not to be changed. It can be verified that this implies neglecting a small part of the interaction between the inner portion of the wave function of one atom and the outer part of the other with respect to the integral  $K_2$ , and also it neglects the contribution of this inner part to the  $J_1$  and  $J_2$  integrals. But these are quite small and tend to balance each other.

<sup>11</sup> Rankine, Phys. Zeits. 11, 745 (1910); Phil. Mag. 29, 554 (1915).

Carrying out the calculation according to the theory of III, 3, one obtains the following values for the interaction energy:

| $\alpha R$ | $R$ (in $A$ ) | $\Delta E$ (in ergs)   | Slater's value         |
|------------|---------------|------------------------|------------------------|
| 4          | 1.430         | $6.38 \times 10^{-13}$ | $1.08 \times 10^{-12}$ |
| 5          | 1.787         | $1.55 \times 10^{-13}$ | $2.09 \times 10^{-13}$ |
| 6          | 2.144         | $3.43 \times 10^{-14}$ | $4.06 \times 10^{-14}$ |
| 8          | 2.859         | $1.37 \times 10^{-15}$ | $1.5 \times 10^{-15}$  |
| 10         | 3.574         | $4.68 \times 10^{-17}$ | $5.8 \times 10^{-17}$  |

In the last column are included for comparison the values calculated by Slater's formula<sup>12</sup>

$$\Delta E = 7.7 \times 10^{-10} e^{-2.43(R/a_0)}.$$

It can be seen that the order of magnitude of the two sets of results is the same and they are nearly equal in the region of 3A. It is difficult deciding which is the more correct.<sup>13</sup>

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<sup>12</sup> Slater, Phys. Rev. **32**, 349 (1928).

<sup>13</sup> Cf. Gentile, Zeits f. Phys., **63**, 795 (1930).