ON THE INTERATOMIC POTENTIAL OF NEON

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On The Interatomic Potential Of Neon

being

a thesis presented by

Wilson Menzies Nicol B.Sc.

to the

University of St Andrews

in application for the degree of

Doctor of Philosophy.

Declaration.

I hereby declare that the following thesis is based on the results of research carried out by me, that the thesis is my own composition, and that it has not previously been presented for a higher degree.

[redacted]

July, 1956.

Certificate.

We certify that Wilson M. Nicol B.Sc. has spent nine terms in Research under our direction, that he has fulfilled the conditions of Ordinance No 16 (St Andrews) and is qualified to submit the accompanying thesis in application for the Degree of Doctor of Philosophy.

[redacted]

July, 1956.

Background.

I matriculated in the University of St Andrews in October 1949 and read Pure Science leading to my graduating B.Sc. (First Class Honours in Natural Philosophy) in June 1953. I am deeply indebted to the Sir James Caird Trust for the award of a Travelling Scholarship enabling me in August 1953 to commence research, the result of which is now presented in this thesis. I should like to express my sincere gratitude to my many friends and particularly Dr D. ter Haar who have ably discussed the project and who have made helpful suggestions during its progress.

On The Interatomic Potential Of Neon.

Chapter 1.

Chapter 2.

Chapter 3.

Chapter 4.

Chapter 5.

Chapter 1.

1·1 Introduction.

It is not an exaggeration to say that the knowledge of the interatomic potential energy is the stepping stone to the physical properties of matter. In the case of gases the most important commutation on the path of development is between the interatomic potential energy on the one hand and the equation of state and the transport properties - viz. conductivity, viscosity and diffusion - on the other hand. However, for the solid state, the role of interatomic forces in crystal structures should not be overlooked. It is clear that the development is reversible in that the potential energy could be determined from one or more of the physical properties mentioned above, and vice versa. A great many of the existing interatomic potential energies in the literature (E.A. Mason and W.E. Rice,1954; B.N. Srivastava and M.P. Madan,1953; T.Kihara, Y.Midzuno and T.Shizume,1955)* are of this phenomenological kind obtained by fitting the experimental results to an analytic function. Theoretically it should be possible to determine this energy from first principles and thereby arrive at values for the physical properties for comparison with the experimental results. The latter is the objective of this investigatio

1·2 The form of the potential.

The force $F_i = \partial \phi / \partial x_i$ and therefore the potential ϕ

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* The references have been collected and arranged alphabetically at the end of the work.

between non-polar atoms is a function of the interatomic separation r,

$$\phi = \phi(r)$$

The cohesion of matter (J.E. Lennard-Jones, 1931.) dictates that there must be an attractive force between molecules while at the same time to prevent a total collapse of matter there must be also very strong repulsive forces. This is reconciled by the a priori assumption that the potential energy is due to a long range attractive force and a short range repulsive force: the justification being that it accounts for the nature of cohesion.

The long range, or so called van der Waals forces have been studied in detail and the main contributions to these arise from the electrostatic, induction and dispersion effects which lead to an attractive term in the potential energy proportional to the inverse sixth power of the interatomic separation. Higher multipoles such as quadrupoles, octopoles, etc., give rise to inverse 8th, 10th, etc. power terms, but in the main it is unnecessary and indeed even too complex to account for these.

Theory has not been so successful in dealing with the short range forces. Experimentalists for the want of a lead have tried various functional representations to fit their results. This has led to two main forms - the inverse 12th power of interatomic separation and the negative exponential of the separation.

The most widely used form is the Lennard-Jones 6 - 12 potential

$$\phi(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right]$$

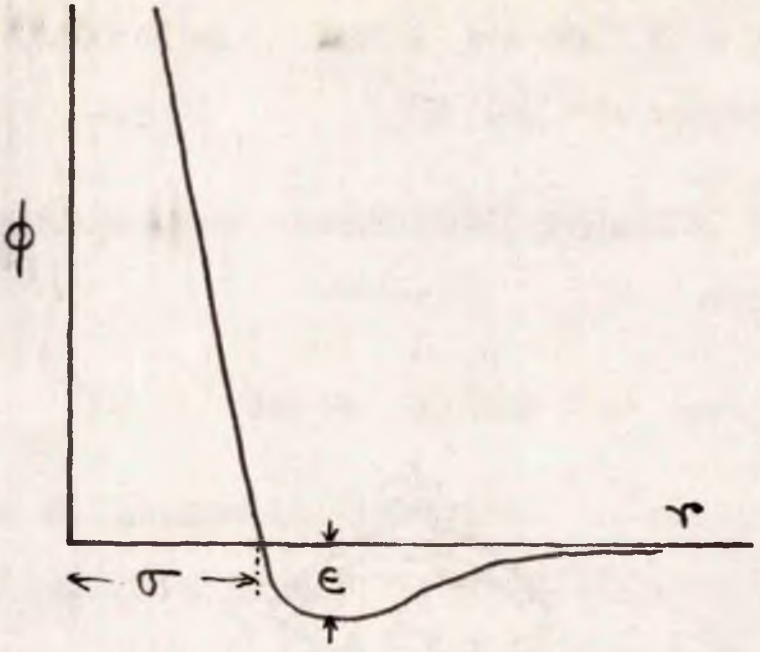

Figure 1·1

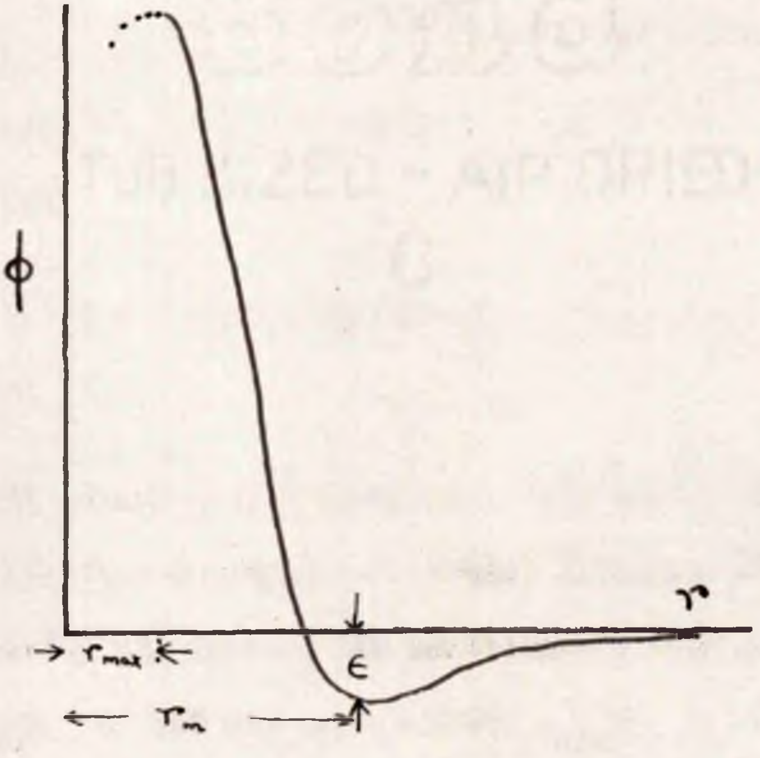

Figure 1·2

where $\phi(r) = 0$ at $r = \sigma$, and ϵ is the depth of the potential well which occurs at $r = 2^{1/6}\sigma$ (Figure 1·1).

R.A. Buckingham (1938) however used the exponential form for the repulsion term

$$\phi(r) = b\exp(-ar) - c/r^6 - d/r^8$$

where a,b,c, and d are variable parameters. He included the contribution due to the quadrupole moment as being of sufficient importance. This latter empirical function was criticised on the grounds that it went to minus infinity at $r = 0$ whereas it is more natural to expect that it should go to plus infinity. Buckingham and Corner (1947) and Corner (1948) took this anomaly into account and proposed the functions

$$\phi(r) = \frac{\epsilon}{\alpha(1+\beta) - 6 - 8\beta}\Big[(6+8\beta)\exp\{-\alpha(r/r_m - 1)\} - \alpha(r_m^6/r^6 + \beta r_m^8/r^8)\exp\{-4(r_m/r - 1)^3\}\Big] \qquad \text{for } r \leqslant r_{max}$$

and

$$\phi(r) = \frac{\epsilon}{\alpha(1+\beta) - 6 - 8\beta}\Big[(6+8\beta)\exp\{-\alpha(r/r_m - 1)\} - \alpha(r_m^6/r^6 + \beta r_m^8/r^8)\Big] \qquad \text{for } r > r_{max}$$

Finally the Wisconsin group (E.A. Mason, 1954) under Hirschfelder presented the modified (exp-6) Buckingham potential (Figure 1·2) which is receiving much attention in the present day literature. The stipulation is that for $r \leqslant r_{max}$, $\phi(r) = \infty$, and for $r > r_{max}$,

$$\phi(r) = \frac{\epsilon}{1 - 6/\alpha}\Big[(6/\alpha)\exp\{\alpha(1 - r/r_m)\} - (r_m/r)^6\Big]$$

where r_m = position of energy minimum $\phi(r_m) = -\epsilon$

ϵ = greatest attractive energy, while α is a measure of the steepness of the repulsive curve.

1·3 The equation of state and the second virial coefficient.

The equation of state for a perfect gas is

$$p V = R T$$

where p is the pressure of the gas, V its molar volume, R = Nk the gas constant and T the absolute temperature. It is experimentally and theoretically obvious that real gases are not perfect due to the interaction and finite size of the molecules for example, and it is then usual to define the equation of state by a series - the virial series

$$p V = NkT \left(1 + B(T)/V + C(T)/V^2 + \ldots\ldots\ldots \right).$$

The coefficients B(T), C(T), ... are respectively the 2nd, 3rd, ... virial coefficients which can be expressed in terms of the intermolecular potential by straight forward statistical mechanical reasoning which becomes somewhat tedious for the higher coefficients. The first two are:

$$B(T) = 2\pi N \int_0^\infty \left[1 - \exp\left\{ -\phi(r)/kT \right\} \right] r^2 \, dr$$

$$C(T) = N^3/3 \int_0^\infty \left[1 - \exp\left\{ -\phi(r_{12})/kT \right\} \right] \left[1 - \exp\left\{ -\phi(r_{23})/kT \right\} \right] \left[1 - \exp\left\{ -\phi(r_{13})/kT \right\} \right] d\vec{x}_{12} \, d\vec{x}_{13}$$

The second coefficient is the result of binary collisions and the third of tertiary collisions, etc., so that it is seen that at low gas densities where only binary collisions are of importance very few coefficients are required. The series is divergent for the liquid state and is no longer of practical use. The theory is based on the assumption that the potential energies of and between the particles are additive. This matter has been recently discussed by Jansen and Slawsky, (1954), and McGinnies and Jansen, (1956).

Two approaches can now be made to the problem. The empirical potential energy function can be fitted to the experimental data, or , using a trial potential function the second virial coefficient integral can be integrated analytically to obtain the second virial coefficient.

Writing the potential energy function in the Lennard-Jones form

$$\phi(r) = c\epsilon(1/r^{*n} - 1/r^{*m})$$

where $r^* = r/\sigma$ the reduced distance and ϵ is the depth of the well, B becomes a function of σ and ϵ for any set of n and m. As we have seen, the attractive van der Waals part of the potential implies that $m = 6$. The experimental values of B and T are used in a plot of $\ln B$ against $\ln T$; and by trial and error for various values of n, the empirical curve of $\ln B^* = \ln B - 3 \ln\sigma$ against $\ln T^* = \ln T + \ln k - \ln\epsilon$ is compared with it. Lennard-Jones found that the curve was rather insensitive to the value of n and that indeed any value of n between 8 and 14 would give a reasonable correspondence: $n = 12$ was chosen as a matter of convenience. The relative linear displacements of the graphs with respect to each other determines σ and ϵ . (Lennard-Jones, 1924; and de Boer, 1940.)

Theoretically then the constants in the potential energy function are determined and the other virial coeffisients could be computed. In the main this has not been applied except to the third virial coefficient simply because the expressions for the higher coefficients are so complex.

Rice and Hirschfelder (1954) using the modified Buckingham potential have prepared tables of the second virial coefficient for $a = 12{\cdot}0\ (0{\cdot}5)\ 15{\cdot}0$ and T^* from $0{\cdot}4$ to 20 by numerical integration of the reduced equation

$$B^*(a,T^*) = -1/T^* \int_0^\infty r^{*3}\, d\,\phi^*(r^*)/dr^* \;\; \exp\left[-\phi^*(r^*)/T^*\right] dr^*$$

1·4 The Transport Phenomena.

The transport phenomena is the collective name for the group of physical properties arising from the presence of gradients in matter. It comprises conductivity - in gases usually confined to thermal conductivity - being the transfer of heat along a temperature gradient; viscosity which is the transfer of momentum across a velocity gradient; and diffusion, the transfer of mass and perhaps energy due to a non-uniform particle distribution.

The foundation of the theoty of transport phenomena is rigorously expounded in the classical treatise of Chapman and Cowling (1939). The theory will not be re-recorded here because of its length and of its incomparable presentation in the above.

The outcome of the theory is that the transport coefficients D, η and λ ; of diffusion, viscosity and conductivity respectively can all be expressed relative to one set of integrals, the collision integrals, $\Omega^{(\ell,s)}$. Despite its prolixity, the Chapman - Enskog treatment is subject to severe limitations which in brief are:

1. Binary collisions only are included, thus restricting the application to low density gases.
2. Being a classical theory, temperature regions where quantum effects become important must be treated with caution.
3. The zeroth approximation theory can only be used when the physical gradients are small. Higher approximations lead to the Navier - Stokes and the Burnett equations.

For a constructive discussion on the Chapman - Enskog theory we refer to Uhlenbeck, (1955a).

Following common usage, reduced values will be incorporated. The reduced collision integrals $\Omega^{(\ell,n)*}(T^*)$ are functions of the reduced cross sections $S^{(1)}(K)$ which in turn are dependent on the angle of deflection χ of the binary collision.

We shall merely present the functions here and refer to Mason, (1954), for details. It is clear that the transport properties depend fundamentally on the intermolecular potential energy $\phi(r)$.

$$\Omega^{(l,\nu)*}(T^*) = 2\left\{(n+1)!\,(T^*)^{n+2}\right\}^{-1} \int_0^\infty (1 - \cos^l\chi)\, \beta\, d\beta$$

$$S^{(l)}(K) = 2\left\{1 - \tfrac{1}{2}\,\frac{1+(-1)^l}{1+l}\right\}^{-1} \int_0^\infty (1 - \cos^l\chi)\, \beta\, d\beta$$

$$\chi(v,b) = \pi - 2b \int_{r_c}^{\infty} \left[1 - b^2/r^2 - 2\,\phi(r)/\mu v^2\right]^{-\frac{1}{2}} dr/r^2$$

$$\eta = \frac{5}{16}\left(\frac{M\,R\,T}{\pi}\right)^{\frac{1}{2}} \frac{f_\eta}{N_0\, r_m^2\, \Omega^{(2,2)*}(T^*)}$$

$$\lambda = \frac{25}{32}\left(\frac{R\,T}{\pi\,M}\right)^{\frac{1}{2}} \frac{C_v}{N_0\, r_m^2}\ \frac{f_\lambda}{\Omega^{(2,2)*}(T^*)}$$

$$D_{12} = \frac{3}{16}\left(\frac{M_1 + M_2}{M_1 M_2}\cdot\frac{2\,R\,T}{\pi}\right)^{\frac{1}{2}} \frac{f_D}{n(r_m)_{12}^2\, \Omega_{12}^{(1,1)*}(T^*)}$$

where $K = \mu v^2/2\epsilon$, $T^* = kT/\epsilon$, $\beta = b/r_m$

v = absolute value of the relative initial velocity,

b the collision parameter, μ the reduced mass of the colliding molecules, r_c is the closest approach during collision and f_η, f_λ and f_D are rapidly converging polynomials of the collision integrals.

1·5 The Crystal Properties.

Because of the regular though dense arrangement of atoms and molecules in a crystal yet another method is available in the determination of the interatomic potential energy. For example, Neon forms a face centred cubic crystal. If we denote the atomic separation by r and the equilibrium separation by r_0, then the general expression for the potential energy (Lennard-Jones and Ingham, 1925) is

$$\phi(r) = 24\lambda/r^s - 24\mu/r^6 - 4{\cdot}908\ c/r^6 - 1{\cdot}604\ d/r^8$$

or as Buckingham (1938) suggests

$$\phi(r) = 24\ b\ \exp(-r/\rho) - 24\mu/r^6 - 4{\cdot}908\ c/r^6 - 2{\cdot}136\ d/r^8$$

Besides, the energy of the crystal containing N atoms is

$$U_o = 0{\cdot}25\ N\ \phi(r_o)$$

and therefore from the experimental values of r_o and U_o we can attempt to fit values to the constants s or ρ, λ or b, μ, c and d. With the development of Buckingham's idea of the exponential repulsion term, Corner (1948) recalculated the interatomic potential using crystal data, while still later Mason and Rice (1954) used the modified Buckingham potential mentioned in section 1·2. We refer to these papers for further details.

1·6 <u>Theoretical Considerations.</u>

The assumption in the definition of a perfect gas is that there is no interaction between the particles making up the gas. That is, of course, unrealistic, and long ago it was realised that the perfect gas equation

$$p\,V = R\,T$$

as defined previously could not possibly explain the real gas state. Many attempts therefore were made to formulate an equation of state which would do just this.

The equation derived by J.D. van der Waals was both simple and plausible

$$(p + a/V^2) (V - b) = R T.$$

The constants a and b account for the mutual attraction of the molecules and their finite size respectively. The latter determines the degree of interpenetrability or the short range repulsion of the atoms or molecules. Although the van der Waals equation took the intermolecular forces into account, his theory in no way explained the physical basis of these forces. It is in fact a phenomenological equation. Following van der Waals, many famous physicists - Laplace, Maxwell, Boltzmann and Sutherland - contributed to the solution of the fundamental problem, but the first conclusive results were those of Keesom (1921) and Debye (1920). Keesom followed up a suggestion of Reinganum who pointed out that the forces due to molecules having a dipole moment are undoubtedly dependent on the orientation of the dipole.

The result of averaging over all orientations leads to a mean interatomic energy contribution proportional to the inverse sixth power of the atomic separation. This, the Keesom Richteffekt, is however negligible at high temperatures where the actual interatomic attraction is observed to persist.

Including molecules having no dipole moments and countering also the temperature dependence of the Richteffekt, Debye's theory introduced the polarisability and treated the molecule as a deformable structure. This became known as the Induction effect. A dipole contribution gave a term proportional to $1/r^6$, while the quadrupole contribution was proportional to $1/r^8$.

$$V = -2\alpha\, p^2/r^6 \qquad \text{for dipole-dipole}$$

$$= -1{\cdot}5\, \alpha\, q^2/r^8 \qquad \text{for quadrupole-dipole.}$$

The above two effects do not in themselves explain the deviation of the rare gas atoms from the perfect gas laws. In the later 1920's with the advancement of the quantum theory the problem was viewed from a different angle. Heitler and London (1927) gave a first order perturbation quantum mechanical treatment of Hydrogen and Helium in amplification of the earlier paper by Wang in the same year. By 1930, London and Eisenschitz (1930) had considered the second order perturbation from which arose the formulation of the so called dispersion effect because of its correlation with optical dispersion.

To study the repulsion between atoms the paper by Heitler and London (1927) is the best starting point: most of the above references are concerned mainly with the longer range attractive forces. Pursuing a quantum mechanical argument, they attempted a solution of the Schrödinger wave equation first using a zero order wave function and then allowing for the wave function distortions due to the interactions of the functions from the two centres. The first order perturbation energy calculation was carried out for two hydrogen atoms, the two solutions being shown qualitatively in figure 1·3. They are a direct consequence of the Pauli

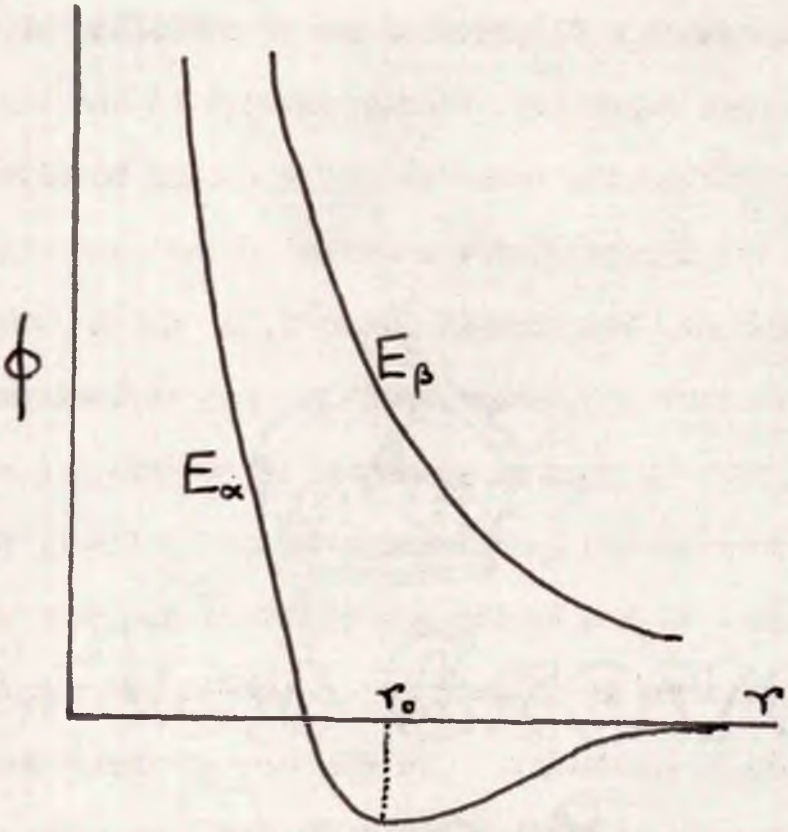

Figure 1·3

principle. E_α corresponds to a binding solution there being at r_0 an attractive stationary state corresponding to the equilibrium separation of the atoms: while E_β gives at all distances repulsion, the two electrons having the same spin in this case.

An analogy illustrates the plausibility of this: as the atoms approach each other the 'charge clouds' of the 1s electron in each atom overlap. Should the spins of the electrons be different, it is possible that the two charge clouds coalesce to form one distorted s shell charge cloud enclosing both nuclei (case E_α). On the other hand, if the electrons are of the same spin they cannot be accommodated in the same s shell and so there is exclusion or repulsion of the atoms (case E_β).

Heitler and London ran into difficulties, though, on applying their theory to two Helium atoms, for of the four solutions to the eigenproblem only one is allowed (corresponding to complete antisymmetry) and that leads to repulsion. In the view of their theory, a bound state would necessitate fitting the four electrons into one combined s shell encompassing both nuclei, which is clearly impossible from the quantum conditions. Of course, the valence bond theory will always give repulsion when applied to closed shell atoms such as Helium, Neon, Argon etc.

The first order perturbation gives always repulsion with these elements and so we must examine the second order perturbation. This was done by Eisenschitz and London (1930). Two types of terms arise from this work, the coulomb and the exchange forces, of which the former leads to a long range attraction - the so called dispersion forces - and the latter, discussed later, to repulsion.

There are two principal methods of solution of the quantum mechanical problem: the perturbation method as used above, or the variational method which has certain advantages over the former. It always gives a result which is greater than the actual, but includes both the long and short range effects. By suitable or iterative adjustment of the wave function parameters it is possible to make the method more and more accurate. Hartree by a further extension developed his method of the self consistent field but this will be discussed in chapter 2.

The general trend in present day quantum mechanical treatments of the multi-electron problem is to use the variational method to obtain a good approximation to the wave function and then use the perturbation methods for the interatomic potential determination.

The interaction of two rare gas atoms can be written as the sum of three terms, assuming the additivity of the component potentials, of course

$$V = V_s + V_e + V_d$$

where V_s is the short range or valence energy of repulsion resulting from the first order perturbation. This is in fact the only term which will be considered in the later stages of this work. V_e is the second order exchange energy resulting from the second order perturbation. Margenau (1939) has shown this to be negligibly small for Neon atoms. V_d is the dispersion energy resulting from the coulombic terms of the second order perturbation. It can consist of a series of terms varying as $1/r^6$, $1/r^8$, etc., corresponding to the energy of the induced dipole-dipole, quadrupole-quadrupole, etc.

The energy of repulsion of two Neon atoms has been calculated previously by Bleick and Mayer (1934) using the Heitler - London first order perturbation. The wave function employed were those of Brown (1933) obtained from a self consistent field calculation. However this paper is vague in its presentation and makes assumptions which may be misleading, as commented by Margenau and Rosen (1953). In view of this it was considered that a more thorough investigation of the repulsive potential between two Neon atoms should be made.

1·7 The Theory of Kirkwood.

Of interest is the theory of Kirkwood et al. (1941 et seq.). He chooses a Gaussian potential form corresponding to repulsive forces only

$$\exp -\phi(r) = 1 - \exp -ar^2$$

and finds that a gas of elastic spheres (only repulsive forces between the molecules) shows a phase transition. At high pressures we get a solid phase surrounded by a liquid phase whose densities and entropies are different. It has been suggested (Uhlenbeck, 1955b) that this transition may help to explain the solidification of Helium at high pressures when the temperature is above the critical temperature. The weak attractive forces in Helium are of the order of kT_{crit} (T_{crit}

is about $5^{\circ}K$) and can hardly account for the solidification at these higher temperatures.

It appears that the solid state could be reached at any temperature if the pressure applied were great enough. Such a state of affairs would suggest a sharp repulsive core.

If the Gaussian model for purely attractive forces is chosen, we find there is a divergence from fact since this theory results in the free energy being proportional to N^2 instead of to N. Van Hove (1949) has shown that the sharp repulsive core is necessary for the proportionality of all thermodynamical quantities with N and therefore for the existence of the equation of state.

* * *

Chapter 2.

2·1 The General Quantum Mechanical Problem.

Atomic units will be used throughout the text unless specifically stated to the contrary. (see Appendix I).

The fundamental Schrödinger equation can be written in the form

$$H_{op} \Psi = E \Psi$$

where H_{op} is the hamiltonian operator incorporating the kinetic energy and potential energy operators, and E is the set of eigenvalues of the energy. We shall restrict ourselves to the ground state energy and so to E_o. The first requirement is the construction of a suitable molecular wave function Ψ.

For a single electron it is possible to find a wave function which will give an exact solution to the equation, but when more electrons are added with their consequent interactions, such exactness is well nigh impossible. Any method of solution, then, must necessarily be one of approximation of which there are several well known types:

(a) The perturbation method as used in the Heitler - London atomic case and by Slater to include the molecular case.

(b) The variation method extended and improved by D.R. Hartree (1927) in his method of self consistent field, the solution of which is numerical. It was further developed by Fock (1930) resulting in the well known Hartree - Fock variational equations.

(c) The simple analytic method as used by Hylleraas (1930) and by Zener and Guillemin (1930). This method was improved upon by Morse, Young and Haurwitz (1935) and later by Duncanson and Coulson (1944).

(d) The W.K.B. method which is only a good approximation for high quantum numbers and is therefore not very suitable for the ground state problem which interests us.

2·2 The Wave Function.

In the case of Helium where there are only two electrons in the atom several stages of approximation have been attempted. However when the number of electrons reaches the order of ten as in the Neon atom such an optimistic procedure would involve so much labour that the task would indeed be monumental. In fact, as we shall see, the zeroth order approximation already entails enough complexity.

The zeroth order approximation to the wave function is obtained by permuting the product of the single electron wave functions.

$$\phi_1\phi_2\phi_3\phi_4\phi_5 \;\ldots\ldots\; \phi_n$$

The wave function of the j-th electron in the i-th orbital state will be written $\phi_i(j)$ and will include spin. The permutation set is identically represented by a determinant

$$\Phi = \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots\cdots\cdots\cdots\cdots & \phi_1(n) \\ \phi_2(1) & \cdots\cdots\cdots & & \\ \cdots\cdots\cdots & & & \\ \cdots\cdots\cdots & & & \\ \cdots\cdots\cdots & & & \\ \phi_n(1) & \phi_n(2) & \cdots\cdots\cdots\cdots\cdots & \phi_n(n) \end{vmatrix}$$

If the atom M contains n electrons then the symmetric molecule M_2 will contain 2n electrons and the zero order wave function will be as above but where now the determinant will be of order 2n instead of n. It is pointed out, too, that any one ϕ_1 and (j) can appear but once in any one permutation of the single wave functions.

Discussion of the wave function.

To obtain a solution to the Schrödinger wave equation for the case of poly-electron atoms and molecules it is necessary to find an approximate wave function which will allow a solution. Probably the most accurate approximation is that of the self consistent field method of Hartree (section (b) Of 2·1). Unfortunately this method yields only numerical solutions which have to be fitted to analytic functions to be of practical use in our problem. Slater (1932) has shown this to be possible. These orthogonalised functions contain nodes but they can be expressed as a linear combination of the nodeless functions of Slater (1931) which are of the form

$$\text{1s type} \qquad (k^3/\pi)^{\frac{1}{2}}\, e^{-kr}$$

$$\text{2s type} \qquad (k^5/3\pi)^{\frac{1}{2}}\, r\, e^{-kr}$$

$$\left.\begin{matrix} 2p_x \\ 2p_y \\ 2p_z \end{matrix}\right\}\text{type} \qquad (k^5/\pi)^{\frac{1}{2}} \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} e^{-kr}$$

where $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, and $z = r \cos\theta$

Looking ahead to the calculation of the interaction energy we find that all the recent surveys of the evaluation of the inherent integrals employ the wave functions in the nodeless Slater form (Barnett and Coulson, 1951; Roothaan and Rüdenberg, 1951). It is desirable therefore that we choose our wave functions to be of this type also.

Let us examine now the wave functions for Neon in the literature.

1. Morse, Young and Haurwitz (1935) using a variational and simple analytic method found an approximate set of wave functions for Neon containing four variable parameters. Their calculations were repeated by Duncanson and Coulson (1944) who corrected several major errors. The numerical results quoted will be those of the latter group.

In the ground state of the atom an absolute minimum exists, it is therefore possible to determine the parameters by minimising the energy with respect to variations in the parameters: μ defined below is in effect a scale factor and can be determined analytically, while a, b and c are found numerically. Although the wave functions obtained by this method are not so accurate as those resulting from the Hartree self consistent field method, they have the advantage of being much simpler. Furthermore they are accurately orthonormal on the atom and include exchange. The wave functions are:

$$(1s) = (k_1^3 / \pi)^{\frac{1}{2}} \; e^{-k_1 r}$$

$$(2s) = (k_2^5 / 3\pi N)^{\frac{1}{2}} \, (r \, e^{-k_2 r} - 3\lambda / k_2 \, . \, e^{-k_3 r})$$

$$(2p_z) = (k_4^5 / \pi)^{\frac{1}{2}} \; r \cos \theta \; e^{-k_4 r}$$

$$(2p_x) = (k_4^5 / \pi)^{\frac{1}{2}} \; r \sin \theta \cos \phi \;\; e^{-k_4 r}$$

$$(2p_y) = (k_4^5 / \pi)^{\frac{1}{2}} \; r \sin \theta \sin \phi \;\; e^{-k_4 r}$$

where the parameters k_i are

$k_1 = \mu a = 9{\cdot}66$ $\qquad a = 3{\cdot}29$

$k_2 = \mu = 2{\cdot}934$

$k_3 = \mu b = 8{\cdot}97$ $\qquad b = 3{\cdot}06$

$k_4 = \mu c = 2{\cdot}88$ $\qquad c = 0{\cdot}98$

μ has an accuracy of 2% while the absolute accuracy of a, b and c is 0·01, and of these c is the least accurate since the variation of energy with it is slow. N is the normalisation factor and λ is a constant determined by the orthogonality of the 1s and 2s functions. It is found on solving the normalising and orthogonalising equations simultaneously that

$$\lambda = (a + b)^3 / (1 + a)^4 = 0{\cdot}754$$

and $$N = 1 - 48 \lambda / (1 + b)^4 + 3 \lambda^2 / b^3 = 0{\cdot}926$$

It is clear that the 2s function can be put into the form

H 2s' - H' 1s'

for, on expanding,

$$2s = N^{-\frac{1}{2}} (\mu^5/3\pi)^{\frac{1}{2}} e^{-k_2 r} - 3\lambda(3Nb^3)^{-\frac{1}{2}} (k_3^3/\pi)^{\frac{1}{2}} e^{-k_3 r}$$

$$= H (\mu^5/3\pi)^{\frac{1}{2}} e^{-k_2 r} - H' (k_3^3/\pi)^{\frac{1}{2}} e^{-k_3 r}$$

where $H = 1{\cdot}039$ and $H' = 0{\cdot}254$

$H^2 = 1{\cdot}080$ $\quad H'^2 = 0{\cdot}0645$ $\quad 2HH' = 0{\cdot}528$

Tabulating the numerical values of the k_1 of the Slater-like wave functions, we have

$k(1s) = k_1 = 9{\cdot}66$

$k(2s') = k_2 = 2{\cdot}934$

$k(1s') = k_3 = 8{\cdot}97$

$k(2p) = k_4 = 2{\cdot}88$

2. Brown (1933) has calculated the Hartree field for neutral Neon taking into account 2p electron exchange. In this method it is assumed that the electron wave functions can be written as a product of the radial and angular functions:

$$\psi(x,y,z) = R(r) . Y(\theta,\phi)$$

Both partial functions are normalised separately as will be shown in the following discussion. The energy is calculated by Slater's method (1929) and minimised with respect to the radial functions. As was mentioned previously, the Hartree method gives a numerical solution for each function which must be fitted analytically to a sum of nodeless functions of the Slater type. To take full advantage of the accuracy of the numerical

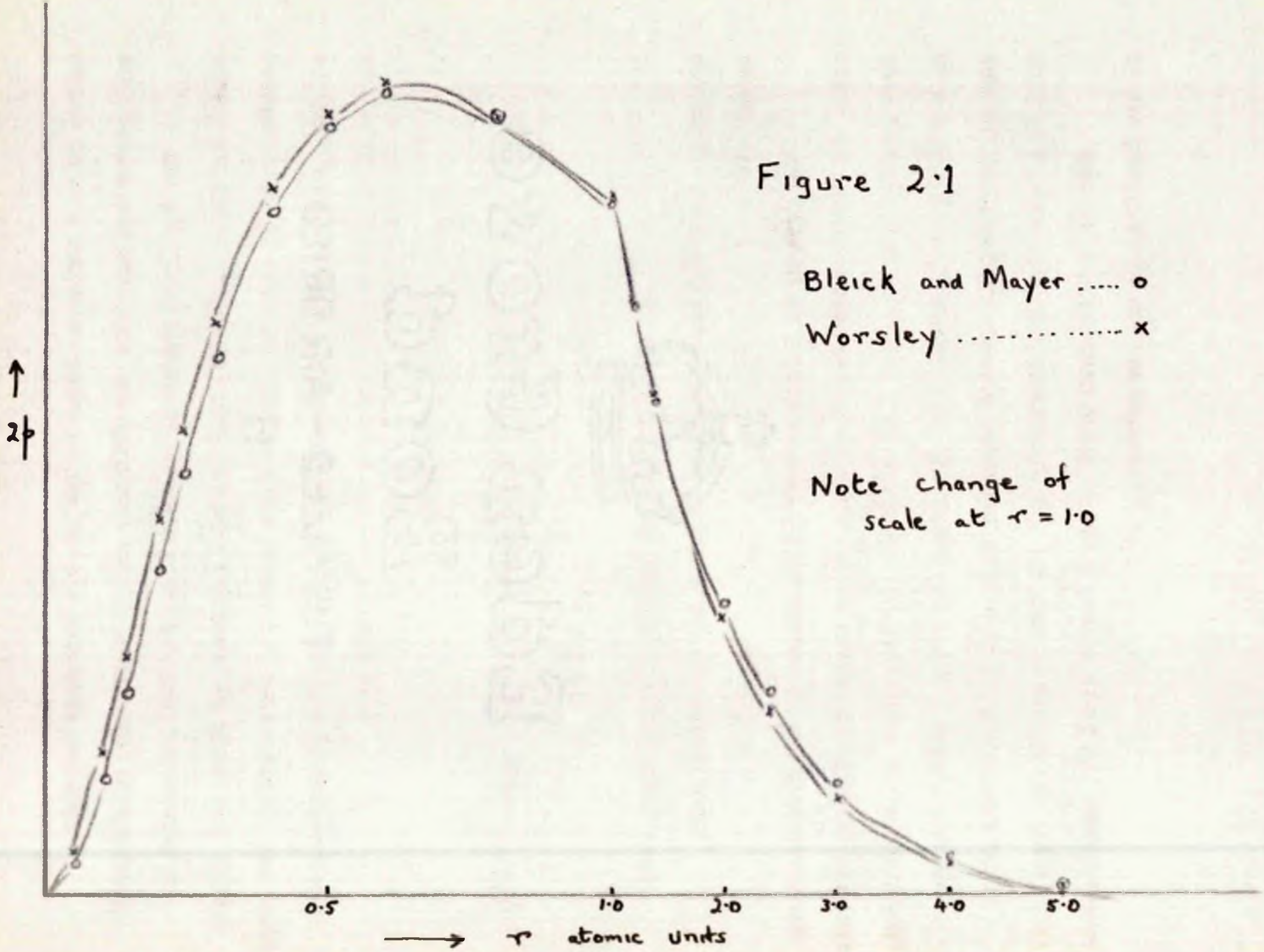

Figure 2·1

Bleick and Mayer ..... o
Worsley x
Note change of scale at r = 1·0
2p
0·5
1·0
2·0
3·0
4·0
5·0
r atomic units

method quite a number of terms in the sum are necessary and this complicates and lengthens the molecular energy calculation considerably.

The repulsion energy of two Neon atoms has been calculated by Bleick and Mayer (1934) who used the wave functions of Brown with slight modifications to make the approximation better for large radii. The paper suffers, however, from a vagueness in not detailing the assumptions made in the work. The radial functions quoted and used are:

$$R_{1s}(r) = 60\cdot70\ r\ e^{-9\cdot73r}$$

$$R_{2s}(r) = 13\cdot6\ e^{-8\cdot22r} - r(14\cdot7\ e^{-3\cdot69r} + 4\cdot76\ e^{-2\cdot15r})$$

$$R_{2p}(r) = r(\ 17\cdot9\ e^{-3\cdot80r} + 2\cdot30\ e^{-1\cdot69r}\ )$$

The energy was calculated to the Heitler - London first order approximation although an allowance was made for the second order contribution.

The most up to date numerical determination of the Neon functions using the Hartree self consistent field method including exchange has been done by Miss B.H. Worsley. I received the results, which are unpublished, in a private communication from the author for which I should like to express my gratitude, and on comparing them with the Bleick and Mayer data it is seen that the difference between them is small, see figure 2·1.

This is a convenient point to say a little about the normalisation of the functions in the two methods.

Duncanson and Coulson have chosen their normalisation constants such that

$$\int \psi^*(x,y,z)\psi(x,y,z)\, dx\, dy\, dz = 1.$$

In the Hartree treatment the wave function is split up into radial and angular parts, both being normalised separately,

since $\psi(x,y,z) = R(r)\, Y(\theta,\phi)$ and $dx\, dy\, dz = r^2 \sin\theta\, d\theta\, d\phi\, dr$

$$\int r^2 R^*(r) R(r)\, dr = 1$$

$$\int Y^*(\theta,\phi)\, Y(\theta,\phi) \sin\theta\, d\theta\, d\phi = 1$$

To come into line with the literature we shall introduce

$$f(r) = r\, R(r)$$

for it is the f values which are tabulated in the Hartree numerical solution. The radial normalisation is therefore

$$\int_0^\infty f^*(r)\, f(r)\, dr = 1$$

Let us now split up the Duncanson and Coulson type functions into radial and angular parts. Starting with the 1s function $(k_1^3/\pi)^{\frac{1}{2}} e^{-k_1 r}$

$$f_{1s}(r) = r(k_1^3/\pi)^{\frac{1}{2}} e^{-k_1 r}$$

which when normalised leads to

$$\int_0^\infty f^*(r)\, f(r)\, dr = k_1^3/\pi \int_0^\infty r^2 e^{-2k_1 r}\, dr$$

$$= 2k_1^3 / (2k_1)^3 \pi = 1 / 4\pi$$

The normalisation of the angular function is

$$\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = 4\pi$$

and so $\int f^*(r)\, f(r) \sin\theta\, d\theta\, dr = 1$ as stated.

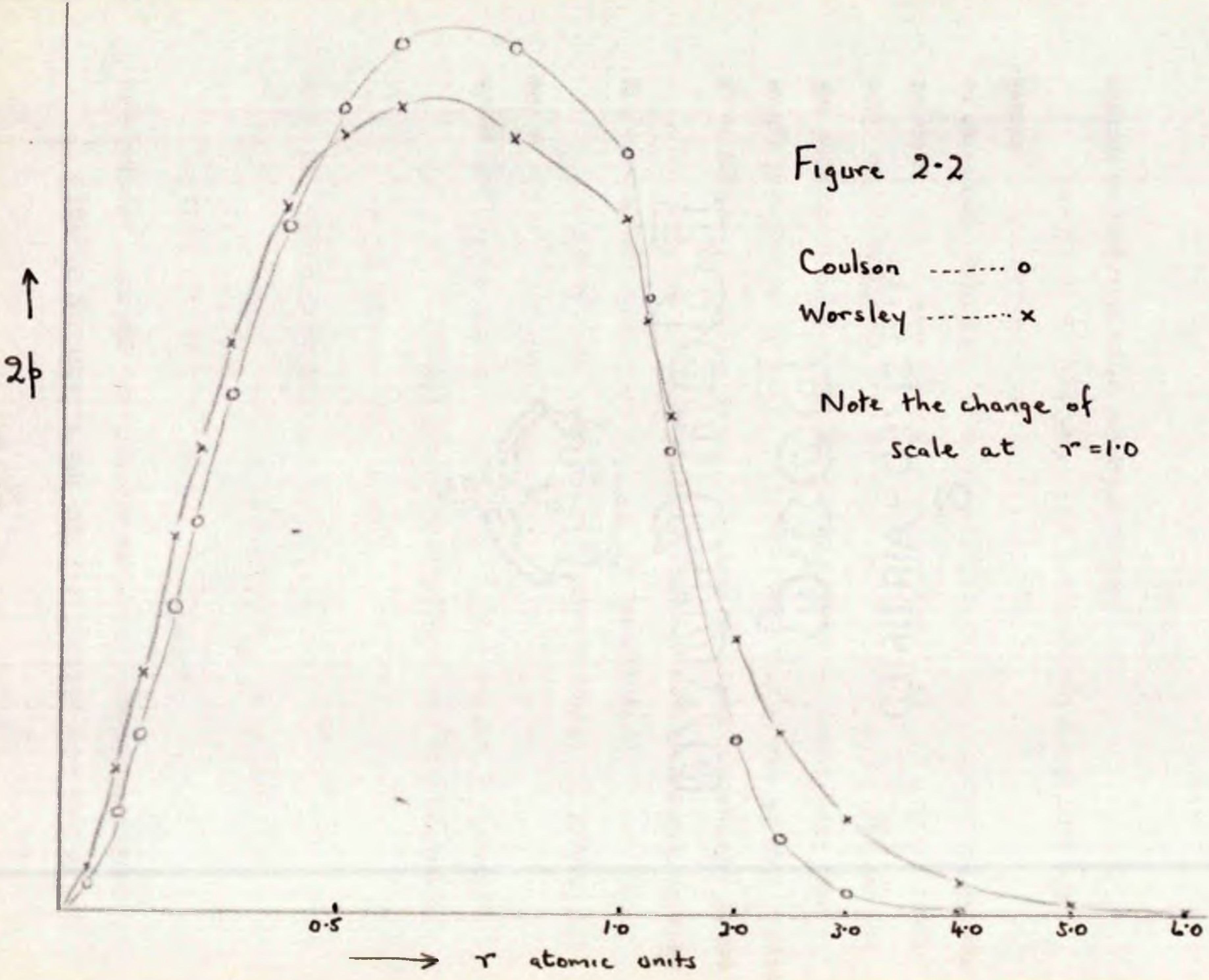

Figure 2·2

Coulson .... o
Worsley x
Note the change of scale at r = 1·0
2p
r atomic units
0·5
1·0
2·0
3·0
4·0
5·0
6·0

A similar splitting of the 2s type function will lead to the same factors. For the 2p function the radial normalisation gives

$$\int_0^\infty f^*(r)\ f(r)\ dr \quad = \quad k_4^5/\pi \int_0^\infty r^4\ e^{-2k_4r}\ dr$$

$$= \quad k_4^5/\pi\ .\ 24/(2k_4)^5 \quad = \quad 3/4\pi$$

while the angular function is

$$\int_0^\pi \cos^2\theta\ \sin\theta\ d\theta \int_0^{2\pi} d\phi \quad = \quad 4\pi/3$$

In order to compare the two functions, it will be necessary to divide the Hartree method f values by $1/(4\pi)^{\frac{1}{2}}$ for the s functions and by $(3/4\pi)^{\frac{1}{2}}$ for the p functions.

The 1s and 2s functions are almost identical and figure 2·2 shows the degree of comparison of the 2p functions.

A little foresight is invaluable here because of the work involved in evaluating the integrals, and especially the exchange integrals, in the energy calculation. Although the Hartree type results are the more accurate the tremendous computational problem to which their choice would lead could not be undertaken with the means and time available. Only the 2p function seems to show the loss of an extra term, the 2s function being in quite good agreement. We shall therefore use the Duncanson and Coulson results in our calculations.

Finally we see that these wave functions are wholly real and contain no imaginary part; therefore in fact

$$\psi^* = \psi$$

2·3 The Energy Determination.

Writing the Schrödinger equation once again for a symmetric molecule in the ground state, it is

$$H_{op}\,\Phi = E\,\Phi$$

Multiply now by the complex conjugate Φ^* and integrate over the coordinate space of all 2Z electrons, dt being the volume element of the coordinate space; Z is the atomic number which is 10 for Neon.

$$\therefore \int \Phi^* H_{op}\,\Phi\,dt = \int \Phi^* E\,\Phi\,dt$$

$$= E\int \Phi^*\,\Phi\,dt$$

$$\therefore \qquad E = \int \Phi^* H_{op}\,\Phi\,dt \Big/ \int \Phi^*\,\Phi\,dt$$

$dt = \prod_{m=1}^{2Z} dt_m$ where dt_m is the volume element of the m-th electron space.

We have chosen our atomic wave functions such that they are orthonormal: that is

$$\int_0^\infty \phi_k(i)\,\phi_k(j)\,dt = \delta_{ij}$$ separately on each centre a and b.

δ is the Kronecker symbol which $= 0$ when $i \neq j$

$= 1$ when $i = j$

From now on the complex conjugate sign * will be omitted, the justification having been given at the close of section 2·2.

It should be noted that this orthonormality is not true when i and j are on different atoms in the molecule, hence the restriction to the separate centres. The wave functions of the electrons in the first atom or the second atom have coordinates relative to their own nucleus and therefore can be made orthonormal without question. When the electron wave functions i and j belong to different nuclei the coordinates of each are with respect to different origins and we are not likely in the general case to get orthonormality. This is discussed independently of this work by Margenau and Rosen (1953). A similar difficulty arises when we take the zeroth order approximation of the molecular wave function.

We know from the Pauli Principle that each state is doubly occupied viz. that two electrons of opposite spin can have the same spatial coordinates. Consequently we can split the total electron wave function up into the spatial and spin components:

$$\phi_k(i) = \psi_k(i)\,\sigma_k(\gamma)$$

where σ is the spin component of the wave function and the spin denomination γ is either α or β according as the spin is in one direction or the opposite; $\psi_k(i)$ is the spatial function. As is customary the spin wave function will be taken to be orthonormal both between the centres of integration and on each of them

$$\int \sigma_k(\gamma)\,\sigma_k(\gamma')\,d = \delta_{\gamma\gamma'}$$

The result of the orthonormality condition is to reduce the number of different permutations from (2Z)! to Z! the total number of permutations being the sum of the identical permutation and twice the remaining permutations of the spatial wave functions. Care must be taken not to duplicate the identity permutation as it is unique and must therefore be treated separately.

The ground state when written out in full is:

$$E = \frac{\int \sum\limits_{k=1}^{(2Z)!} (-1)^{k-1} P_k \phi_1(1)\ldots\phi_{2Z}(2Z)\ H_{op} \sum\limits_{m=1}^{(2Z)!} (-1)^{m-1} P_m \phi_1(1)..\phi_{2Z}(2Z)\ dt}{\int \sum\limits_{k=1}^{(2Z)!} (-1)^{k-1} P_k \phi_1(1)\ldots\phi_{2Z}(2Z) \quad \sum\limits_{m=1}^{(2Z)!} (-1)^{m-1} P_m \phi_1(1)..\phi_{2Z}(2Z)\ dt}$$

$$= \frac{\int \sum\limits_{k=1}^{(2Z)!} P_k \ H_{op} \sum\limits_{m=1}^{(2Z)!} P_m \ dt}{\int \sum\limits_{k=1}^{(2Z)!} P_k \ \sum\limits_{m=1}^{(2Z)!} P_m \ dt}$$

where we have introduced the notation

$$P_k = (-1)^{k-1} P_k \phi_1(1)\ldots\ldots\phi_{2Z}(2Z)$$

Note that the identical permutation is

$$P_1 = \prod_{i=1}^{2Z} \phi_i(i)$$

P_k is the result of the k-th permutation operating on P_1. It is well known that the (2Z)! permutations form a group as defined in group theory. Each element in the group has a reciprocal and it is also a member of the group. The reciprocal permutation P_{-k} must therefore be one of the (2Z)! permutations, say P_i Therefore

$$P_{-k} P_k = P_i P_k = P_1$$

by definition of the reciprocal.

Multiplying the energy equation above by P_{-k}, the energy remains unchanged on the permutation of the electron coordinates, and so we have,

$$E = \frac{\int \sum_{k=1}^{(2Z)!} P_{-k} P_k \; H_{op} \sum_{m=1}^{(2Z)!} P_i \, P_m \, dt}{\int \sum_{k=1}^{(2Z)!} P_{-k} P_k \sum_{m=1}^{(2Z)!} P_i \, P_m \, dt}$$

Put $P_i \, P_m = P_j$. It is clear that P_k, P_m, P_i and P_j are all members of the same $(2Z)!$ order group.

Now $\sum P_{-k} P_k = (2Z)! \; P_1$

$$\therefore E = \frac{\int P_1 \, H_{op} \sum_{j=1}^{(2Z)!} P_j \, dt}{\int P_1 \sum_{j=1}^{(2Z)!} P_j \, dt}$$

where

$$(-1)^{j-1} = (-1)^{|m-k-2|}$$

The Hamiltonian Operator.

On the assumption that the molecule as a whole is at rest, the hamiltonian operator is the sum of the kinetic and potential energy operators, respectively

$$H_{op} = T_{op} + V_{op}$$

where $T_{op} = \sum_{w=1}^{2Z} \frac{1}{2} \nabla_w^2$, ∇ being the gradient operator; and where

$$V = \left[\sum_{i,j=1}^{Z} 1/r_{ij} - \sum_{i=1}^{Z} \left(Z/r_{ai} + Z/r_{bi} \right) + Z^2/R \right]$$

R is the internuclear distance ab, r_{ai} and r_{bi} are the electron-nuclear distances and r_{ij} is an electron-electron distance.

The hamiltonian now reads:

$$H_{op} = \sum_{w=1}^{2Z} \tfrac{1}{2}\nabla_w^2 + \sum_{i,j=1}^{Z} 1/r_{ij} - \sum_{i=1}^{Z}(Z/r_{ai} + Z/r_{bi}) + Z^2/R$$

In view of this, the ground state energy equation becomes a sum of four terms

$$E = T + V_1 + V_2 + V_3$$

each of which will be treated in turn. Now the ground state energy of the molecule is the sum of the ground state energies E_a and E_b of the individual atoms which to a fair approximation are independent of R and the intermolecular potential E', the last of which is of immediate interest to us.

$$E = E_a + E_b + E'$$

From now on we shall only be concerned with those terms which contribute to the intermolecular potential E' : all other terms will be omitted.

2·4 The Integrals.

The $(2Z)!$ permutations $\sum_{j=1}^{(2Z)!} P_j = P$ are made up from the permutations P_a amongst the functions solely on centre a; from the permutations P_b amongst the functions solely on centre b; and from the permutations P_{ab} between the functions of the two centres.

Consider first the integrals of the type

$$P_1 \sum_{j=1}^{(2Z)!} P_j \, dt = L_j$$

the so called overlap integrals.

Because of the orthonormality of the chosen atomic wave functions, all of the P_a and P_b will lead to zero except the identical permutation. For the interatomic contribution P_{ab} to the permutations, it is recalled that between the centres it is assumed that the spin wave functions are orthonormal and that the spatial wave functions are neither orhtogonal nor normalised. If we define the product wave function

$$\phi_1(1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \phi_{2Z}(2Z)$$

in such a way that the alternate ϕ's are all of the same spin, we see immediately that all the non-zero permutations are effected by interchange of electrons of the <u>same</u> spin.

We must consider each of the 2Z cases where we permute K electrons at a time ($K = 0 \ldots\ldots\ldots 2Z$). Since Neon is a closed shell element, electrons can only be permuted in pairs for our interatomic case. It is clear that if K is odd we find that one of the factors will be $a_i a_j$ or $b_i b_j$ which either reduces the permutation to the K-1 order when $i = j$ or makes it zero for $i \neq j$ (orthonormality of atomic wave functions). Therefore we may only permute pairs of electrons, one of the pair from each atom.

It is convenient to relabel the spatial wave functions

$$\psi_1(1) \ldots\ldots\ldots\ldots \psi_{10}(10) \quad \text{by} \quad a_1(1) \ldots\ldots\ldots\ldots a_{10}(10)$$

and

$$\psi_{11}(11) \ldots\ldots\ldots\ldots \psi_{20}(20) \quad \text{by} \quad b_1(11) \ldots\ldots\ldots\ldots b_{10}(20)$$

signifying the centres to which they belong. In further simplification the number in the brackets will be omitted if it is the same as the suffix or if it is clear from the context what it should be. It follows from the two fold degeneracy of the spatial wave functions ψ and from the symmetry of the two atoms that

$$\begin{aligned}
\int a_1b_1\,dt &= \int b_1a_1\,dt = (I) = (IX) = \int a_2b_2\,dt = \int b_2a_2\,dt \\
\int a_3b_3\,dt &= \int b_3a_3\,dt = (II) = (X) = \int a_4b_4\,dt = \int b_4a_4\,dt \\
\int a_5b_5\,dt &= \int b_5a_5\,dt = (III) = (XI) = \int a_6b_6\,dt = \int b_6a_6\,dt \\
\int a_7b_7\,dt &= \int b_7a_7\,dt = (IV) = (XII) = \int a_8b_8\,dt = \int b_8a_8\,dt \\
\int a_9b_9\,dt &= \int b_9a_9\,dt = (V) = (XIII) = \int a_{10}b_{10}\,dt = \int b_{10}a_{10}\,dt \\
\int a_1b_3\,dt &= \int b_1a_3\,dt = (VI) = (XIV) = \int a_2b_4\,dt = \int b_2a_4\,dt \\
\int a_1b_5\,dt &= \int b_1a_5\,dt = (VII) = (XV) = \int a_2b_6\,dt = \int b_2a_6\,dt \\
\int a_3b_5\,dt &= \int b_3a_5\,dt = (VIII) = (XVI) = \int a_4b_6\,dt = \int b_4a_6\,dt
\end{aligned}$$

To complete the representation the identical permutation will be denoted by (0). The roman numerals in brackets are a more symbolic representation of which a general member will be denoted by (i), (j), etc. The remaining overlap integrals i.e. those of a_1b_7, a_2b_8, a_1b_9, a_2b_{10}, a_3b_7, a_4b_8, a_3b_9, a_4b_{10}, a_5b_7, a_6b_8, a_5b_9, a_6b_{10}, a_7b_9, a_8b_{10} are zero because the integral of their angular component is zero.

The totality of overlap integrals can then be written

$$L = (0) - \sum_{i=1}^{16}(i)^2 + \sum_{j\neq i=1}^{16}(i)^2(j)^2 - \sum_{k\neq j\neq i=1}^{16}(i)^2(j)^2(k)^2 + \ldots\ldots$$

$$\ldots\ldots + \sum_{p\neq o\neq n\neq m\neq l\neq k\neq j\neq i=1}^{16}(i)^2(j)^2(k)^2(l)^2(m)^2(n)^2(o)^2(p)^2$$

The last term is the one in which we take 16 electrons at a time. When more than 16 electrons are all permuted, at least one of the zero integrals detailed above is bound to be included, and so we have in fact accounted for all the non-zero overlap integrals.

We recall that the energy integral is

$$E' L = \int a_1 \ldots\ldots\ldots b_{10} \; H_{op} \; P \; a_1 \ldots\ldots\ldots b_{10} \, dt$$

where P of course is the set of permutations P_{ab}. As we have seen in section 2·2 the splitting of the hamiltonian operator leads to a sum of four terms:

$$E' L = (T + V_1 + V_2 + V_3) L$$

$$= \int a_1 \ldots b_{10} \left[\sum_{w=1}^{20} \tfrac{1}{2} \nabla_w^2 + \sum_{i,j=1}^{10} 1/r_{ij} - \sum_{i=1}^{10} (Z/r_{ai} + Z/r_{bi}) + Z^2/R \right] P \; a_1 \ldots b_{10} \, dt$$

<u>The Kinetic Energy Integral, T.</u>

$$T L = \int a_1 \ldots\ldots b_{10} \sum_{w=1}^{20} \tfrac{1}{2} \nabla_w^2 \; P \; a_1 \ldots\ldots b_{10} \, dt$$

for electron w we have

$$\sum_{v,w=1}^{10} \int \left[a_w \tfrac{1}{2} \nabla_w^2 b_v + b_w \tfrac{1}{2} \nabla_w^2 a_v \right] dt_w$$

$$= \sum_{w=1}^{10} \int \left[a_w \nabla_w^2 b_v \right] dt_w$$

since both atoms are identical.

$$\therefore \; T L = \sum_{v,w=1}^{10} \int \left[a_w \nabla_w^2 b_v \right] dt_w \int \pi a'_w \; \pi b \; P \; \pi a \; \pi b'_v \; dt'_w$$

where πb expresses the product $b_1 \ldots\ldots b_{10}$

and where $\pi b'_v$ expresses πb without the factor b_v
similarly dt'_w is dt without the factor dt_w

$$dt = \prod_{w=1}^{20} dt_w$$

The spin orthonormality conditions restrict the v, w summations in such a way that it is reduced to

$$2 \sum_{v,w=1}^{5}$$

$$\therefore \quad T\,L = 2 \sum_{v,w=1}^{5} (a_w\, T\, b_v)\; L_{w,v}$$

where $L_{w,v} = \int \pi a'_w\, \pi b \quad P \quad \pi a\, \pi b'_v \;\; dt'_w$

and $(a_w\, T\, b_v) = \int a_w \;{}_w^{2}\, b_v\, dt_w$

The Potential Energy, V_1.

This is the energy of interaction between all pairs of electrons.

$$V_1 L = \int a_1 \,\ldots\ldots\, b_{10} \sum_{i,j=1}^{10} 1/r_{ij} \;\; P \;\; a_1 \,\ldots\ldots\, b_{10}\; dt$$

We see immediately that the integrals of $1/r_{ij}$ are equal to the integrals of $1/r_{ji}$ from the symmetry of the problem. This fact will be used later in the numerical evaluation. Four cases arise:

1. Both electrons centred wholly on the same atom. The integrals resulting in this case are the so called mononuclear integrals M and will not be considered further since they do not depend on R.

2. One electron centred wholly on each atom - the Coulomb integrals denoted by C.

3. One electron centred wholly on one atom, the other electron resonating between the two atoms. The integrals derived from this state are the hybrid integrals I and are an intermediate stage between the coulomb and exchange integrals.

4. Both electrons resonating between the two atoms. These are the exchange integrals A, without doubt the most complex type of molecular integrals to evaluate.

$$V_1 = C + I + A$$

where C, I and A will be defined in full below.

The Coulomb Integrals, C.

$$C\,L = \sum_{i,j,i',j'=1}^{10} \int a_i b_j \frac{1}{r_{12}} a_{i'} b_{j'}\, dt_i\, dt_j \int \pi a'_i\, \pi b'_j\, P\, \pi a'_{i'}, \pi b'_{j'}\, dt'_{ij}$$

Since electrons are indistinguishable it is perhaps better to define the separation of any two as $1/r_{12}$ rather than $1/r_{ij}$. A coulomb integral then is the interaction of two quite unspecified electrons one of which is wholly on one centre and described by wave functions i and i', while the other is wholly on the other centre and described by wave functions j and j'. The iji'j' summation is not unrestricted since the spin conditions make zero any product of the i and i' functions if the spins are in opposition. The i summation is therefore over 10 but the i' only over 5.

Now since the spatial wave functions are doubly degenerate and since the spin functions are orthonormal we need only consider the double summation of the i's of one spin. Therefore the i and i' summations are over 5 instead of 10. Similarly for the j and j' summations making in all

$$\sum_{iji'j'=1}^{10} = 4\sum_{iji'j'=1}^{5}$$

Briefly then we define from the above equation

$$C\,L = 4\sum_{iji'j'=1}^{5} C(a_i b_j :: a_{i'}, b_{j'})\ L_{C\ i,j,i',j'}$$

The Hybrid Integrals. I.

$$I\,L = 4\sum_{iji'j'=1}^{5} \int a_i a_j \frac{1}{r_{12}} a_{i'}, b_{j'}\ dt_i\ dt_j \int \chi a'_i a'_j\ \chi b\ P\ \chi a'_{i'},\ \chi b'_{j'},\ dt'_{ij}$$

A hybrid integral is the interaction of two electrons one of which is described by the wave functions i, i' on one atom, while the other is described by wave functions j, j' on different atoms. We can define

$$I\,L = 4\sum_{iji'j'=1}^{5} I(a_i a_j :: a_{i'}, b_{j'})\ L_{I\ iji',j'}$$

The Exchange Integrals, A.

$$A\,L = 4\sum_{iji'j'=1}^{5} \int a_i a_j \frac{1}{r_{12}} b_{i'}, b_{j'},\ dt_i\ dt_j \int \chi a'_i a'_j\ \chi b\ P\ \chi a\ \chi b'_{i'}, b'_{j'},\ dt'_{ij}$$

Each electron is described by two wave functions one on each atom. As above,

$$A\,L = 4 \sum_{iji'j'=1}^{5} A(a_i a_j :: b_{i'}, b_{j'})\ L_{A\ ij,i'j'}$$

It is important to note the difference between

$$L_{C\ i,j,i',j'} \qquad L_{I\ iji',j'} \qquad \text{and} \qquad L_{A\ ij,i'j'}$$

The Potential Energy, V_2.

Because of the symmetry of the molecule, we need only sum over one centre

$$\therefore\ V_2\,L = -2 \int a_1 \ldots\ldots b_{10} \sum_{i=1}^{10} \frac{Z}{r_{a_i b}}\ P\ a_1 \ldots\ldots b_{10}\, dt$$

Applying the conditions of spin orthogonality, the summation is reduced to 5 instead of 10. Two kinds of terms result from V_2

$$V_2 L = -4 \sum_{ii'=1}^{5} Z \int a_i \frac{1}{r_{a_i b}} a_{i'}\, dt_i \int \chi a_i' \chi b\ P\ \chi a_{i'} \chi b\, dt_i'$$

$$-4 \sum_{ii'=1}^{5} Z \int a_i \frac{1}{r_{a_i b}} b_{i'}\, dt_i \int \chi a_i' \chi b\ P\ \chi a\ \chi b_{i'}'\, dt_i'$$

A convenient notation which is self explanatory is

$$V_2\,L = -4 \sum_{ii'=1}^{5} Z(a_i\ a_{i'})\ L_{Z\ ii'} - 4 \sum_{ii'=1}^{5} Z(a_i\ b_{i'})\ L_{Z\ i,i'}$$

The Potential Energy, V_5.

$$V_5\ L = a_1 \ldots\ldots b_{10}\ (Z^2/R)\ P\ a_1 \ldots\ldots b_{10}\ dt$$

Since Z^2/R is a constant of the particular separation R, it can be taken outside the integration altogether leaving

$$V_5 = Z^2/R$$

* * *

Chapter 3.

3·1 The Problem of the Evaluation of the Integrals.

The computation of the integrals occurring in molecular structure investigations is one of no little difficulty, particularly in the case of the exchange integrals. In atomic integrals where the space of integration is spherically symmetric it is a simple straight forward calculation but the molecular problem has the complication that in general there is no longer spherical symmetry. The integrals have to be evaluated over two or more centres of integration. Many papers (Bartlett, 1931; Rosen, 1931; Furry and Bartlett, 1932; Coulson, 1937) have been published containing such integrations but the various authors were content to restrict their efforts to solving the problems associated only with the particular integrals directly affecting their own requirements, so great was the numerical work involved. As a result there was an agglomeration of different integrals calculated or approximated by various methods using diverse notations.

It was not until a Japanese group led by Professor Kotani (1938, 1940) published their tables of integrals for the calculation of molecular energies that any unified attempt was made to give a comprehensive method of evaluation of all the integrals arising in problems of molecular structure. As was stated in the previous chapter, atomic wave functions can be approximated by a sum of nodeless Slater type wave functions. All the integrals can then be resolved to integrals containing only the Slater type wave functions. With the orbital functions thus chosen, Kotani followed the Heitler - London theory rather than the more elaborate and more highly specialised theory of James and Coolidge (1933). The Neumann expansion for $1/r$ is used in conjunction with elliptic coordinates and the integrals are listed in terms of auxiliary functions which are tabulated at some length in the two papers.

After the war the subject was taken up again and was tackled by various groups in different ways. At the Conference on Quantum Mechanical Methods in Valence Theory, (1951), it was the opinion of those gathered that since none of the methods so far adopted had really been thoroughly proved in their applicability to computing machines, electronic or otherwise, it would be wise to pursue the several methods simultaneously. The necessity and the strength of this bond linking the subject with computing machines is realised when one embarks on the evaluation of the two centred integrals. After my experience in the field I should say that if any degree of accuracy is contemplated the computation can only be done with the aid of electronic computing machines, for the time taken to do the same work on a desk machine is prohibitively long, and even so it is questionable whether the work involved is in many cases not too great for the results obtained (see Discussion). However it is a fallacy to suppose that the bigger the machine the better.

The two main post war methods of evaluation were published just prior to the aforesaid Conference; they are

1. The Barnett and Coulson (1951) method using zeta functions as auxiliaries.

2. The Chicago group under Roothaan (1951) and Rüdenberg (1951) who interpret the integrals as interactions of charge distributions on the atomic centres.

Since the war too Kotani's approach has been expanded and numerical corrections made to the tables. Kotani (1954) himself has made further contributions but more comprehensive is the series of papers by Kopineck (1950, 1951, 1952) and finally Preuss (1954). The latter papers are however restrictive in that they assume all the k_i equal (see chapter 2 for the definition of k_i). Numerical tables have been constructed using the values of the auxiliary functions in the first two papers of Kotahi.

In this chapter we shall consider a selection of all but the exchange integrals which due to their complexity will be the subject of chapter 4.

3·2 The Method of Roothaan.

The reader is referred directly to the original paper (Roothaan, 1951) for the detailed analysis: only a brief outline will be presented here with a slightly altered notation.

Three coordinate systems are introduced:

Cartesian coordinates at centres a and b with the two x and y axes parallel, the z axes being directed towards each other along the line joining the centres a and b, (see figure 4·1).

Spherical coordinates defined by

$$r_a = (x_a^2 + y_a^2 + z_a^2)^{\frac{1}{2}}$$

$$\tan \theta_a = z_a / (x_a^2 + y_a^2)^{\frac{1}{2}} \qquad \tan \phi_a = y_a / x_a$$

and similarly for r_b, θ_b and ϕ_b.

Prolate spheroidal coordinates given by

$$\xi = (r_a + r_b) / R, \qquad \eta = (r_a - r_b) / R,$$

and $$\phi = \phi_a = \phi_b.$$

Slater type wave functions are retained as in previous methods viz.

$$(2k)^{n+\frac{1}{2}} \quad (2n)! \quad r^{n-1} \, e^{-kr} \, S_{lm}(\theta,\phi)$$

where $S_{lm}(\theta,\phi)$ are the normalised real spherical harmonics; and n, l, m are the usual orbital, angular and magnetic quantum number symbols.

The integrals fall into two classes: the one electron type (a:M:b) where M is a totally symmetric operator; and the two electron type $\int (ab: 1/r_{ab}:a'b')\, dt$ abbreviated to (ab::a'b') which is interpreted as the interaction of two charge distributions aa' and bb'. Also coming into this class are the nuclear attraction integrals $\int Z(a \;\; 1/r_{a_1 b} \;\; a')\, dt$ abbreviated to Z(aa') since in effect they are the interactions of the charge Z on atomic centre b with the distribution aa'. These charge distributions are tabulated in the paper as functions of the general charge distribution

$$(N\ L\ M) = \left[\frac{2L+1}{4\pi}\right]^{\frac{1}{2}} \frac{2^{L}(2\underline{K})^{N+2}}{(N+L+1)^{\frac{1}{2}}} \quad r^{N-1}\, e^{-2\underline{k}r}\, S_{\underline{LM}}(\theta,\phi)$$

These basic charge distributions are denoted by (NS), (NPz), (NPx), (NPy), etc., or in general by (Ω).

NOTE the change in notation of the exponent's coefficient from ζ to $\underline{k}$, so that

$$\underline{k} = \tfrac{1}{2}(k + k') \qquad \text{and} \qquad \tau = (k - k')/(k + k').$$

For the coulomb integrals we must define further

$$\underline{k}_a = \tfrac{1}{2}(k_a + k'_a) \qquad\qquad \underline{k}_b = \tfrac{1}{2}(k_b + k'_b)$$

$$\tau_a = (k_a - k'_a)/(k_a + k'_a) \qquad\qquad \tau_b = (k_b - k'_b)/(k_b + k'_b)$$

$$\underline{k} = 0{\cdot}25(k_a + k'_a + k_b + k'_b) \qquad\qquad \tau = \frac{(k_a + k'_a - k_b - k'_b)}{(k_a + k'_a + k_b + k'_b)}$$

Each non-vanishing 'two electron' nuclear attraction and coulomb integral is listed in terms of the basic charge distributions. These distributions which are funct-ions of k and $\rho = kR$ are found in terms of the auxiliary functions

$$A_n(\rho) = \int_1^\infty \zeta^n e^{-\rho\zeta}\, d\zeta = n!\, \rho^{-n-1} e^{-\rho} \sum_{j=0}^{n} \rho^j/j!$$

and

$$B_n(\rho) = \int_{-1}^{1} \eta^n e^{-\rho\eta}\, d\eta = -A_n(\rho) - (-1)^n A_n(-\rho)$$

with the condition that $\rho > 0$ otherwise the former integral diverges.

With the coulomb integrals it is necessary to transform the coordinates of one distribution to those of the other. The integration over the coordinates of one electron amounts to calculating the potential

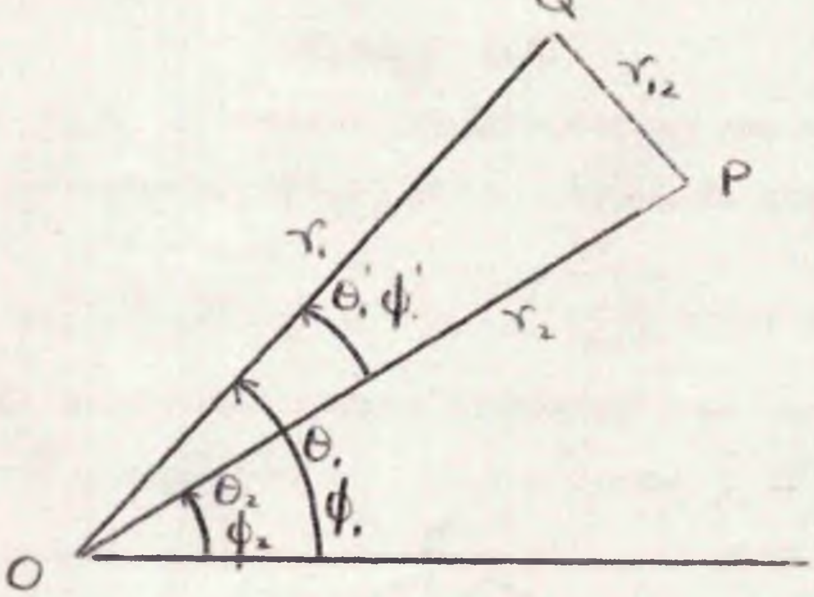

Figure 3·1

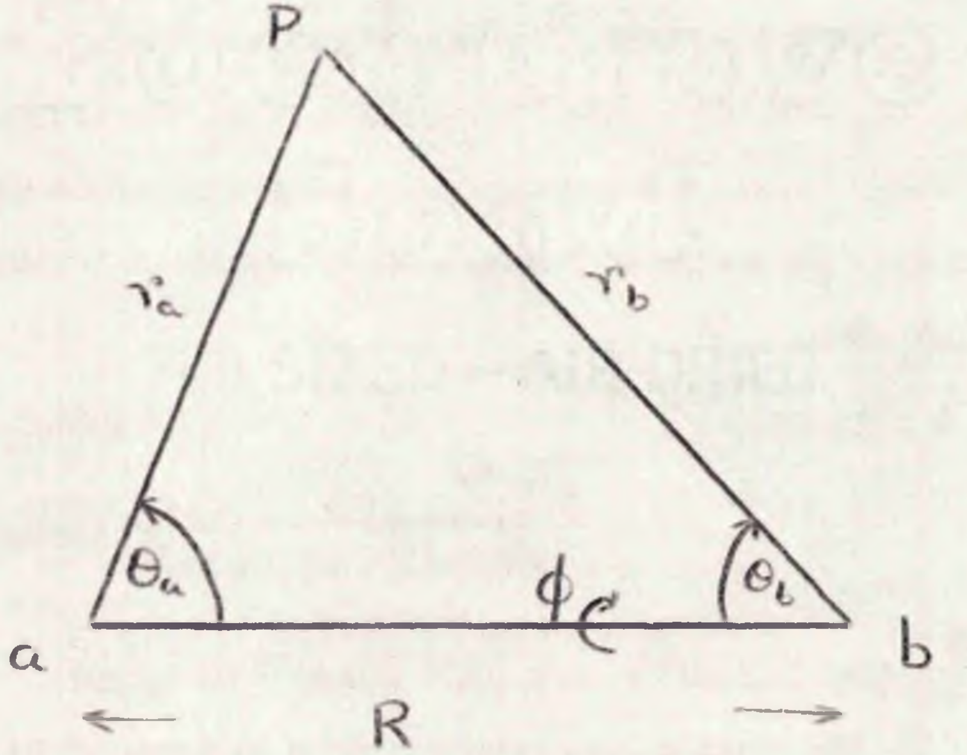

Figure 3·2

of the corresponding charge distribution which we will take to be

$$F(r) \quad S_{LM}(\theta,\phi).$$

That being so, the potential for electron 2 at P due to that charge distribution of electron 1 is (see figure 3·1)

$$U_{NLM}(r_2,\theta_2,\phi_2) = \sum_{M'} c_{M'} \int \left[F(r_1) \; S_{LM'}(\theta_1', \phi_1')/r_{12} \right] r_1^2 \, dr_1 \, d\omega_1'$$

where $c_{M'}$ is a function of spherical harmonics. By identifying a with O, b with P and R with r_2 we have returned to the nuclear attraction integral type.

The non-vanishing coulomb charge distributions are listed in terms of the parameters $k, \tau, \rho, K, \rho_a, \rho_b$, where

$$K = \tfrac{1}{2}\left(\tau + \frac{1}{\tau}\right) \qquad \rho_a = k_a R \qquad \rho_b = k_b R.$$

It is now time to return to the one electron integrals (a:M:b). They comprise the overlap integrals, M = 1; the kinetic energy integrals, $M = -\frac{1}{2}\nabla^2$; and the one electron nuclear attraction integrals, $M = Z/r_b$. The last two are expressed in terms of the first (overlap) type quite simply from

$$\tfrac{1}{2}\nabla^2(n,l,m) = \tfrac{1}{2}\, k^2 \Big\{ (n,\ell,m) - 2\left(2n/(2n-1) \right)^{\frac{1}{2}} (n-1,l,m)$$
$$- \frac{4(n+1)(n-l-1)}{\left[2n(2n-1)(2n-2)(2n-3)\right]^{\frac{1}{2}}} (n-2,l,m)$$

and

$$Z/r \; (n,l,m) = 2Zk\,(2n)^{\frac{1}{2}}\,(2n-1)^{-\frac{1}{2}}\,(n-1,l,m)$$

The overlap integrals are given in terms of the $A_n(\rho)$ and $B_n(\rho)$ defined above. The formulae do not hold in general for $\tau = 0$ nor $\rho = 0$

and in these cases the limits of $\tau \to 0$ and $\rho \to 0$ have to be calculated, and are listed separately. Bingel (1956) presents a method of calculating the nuclear attraction integrals for $0 < \rho < 1{\cdot}0$ using an auxiliary function provided in tabular form.

3·3 The Method of Barnett and Coulson, (1951).

Figure 3·2 defines the notation; a and b are the atomic centres. The wave functions employed are again of the Slater type. The basic plan of this method is to express the wave functions centred on say b in terms of r_a and θ_a by means of an infinite series:

$$r_b^{n-1} \; e^{-kr_b} = \sum_{m=0}^{\infty} \frac{2m+1}{\sqrt{r_a R}} \; P_m(\cos\theta_a) \, \zeta_{n,m}(k, r_a; R) \qquad \ldots\ldots \quad (3{\cdot}1)$$

Watson (1952) page 366.

$$= \; k^{-n+1} \sum_{m=0}^{\infty} \frac{2m+1}{\sqrt{t\rho}} \quad P_m(\cos\theta_a) \, \zeta_{n,m}(1, t; \rho)$$

where t and ρ are the dimensionless variables

$$t = kr_a$$
$$\rho = kR$$

The zeta functions $\zeta_{n,m}$ are the main auxiliary functions and are obtained by partial differentiation with respect to k from the particular function

$$\zeta_{o,m} = I_{m+\frac{1}{2}}(kr_a) \;\; K_{m+\frac{1}{2}}(kR) \qquad\qquad r_a \leqslant R.$$

The I and K are Bessel functions of purely imaginary argument. All the two centre integrals can be reduced to a series of the standard J functions defined as

$$J(i,n_1,n_2) \; = \; e^{-k_1 r_a - k_2 r_b} \cos^i \theta_a \, r_a^{n_1 -1} \, r_b^{n_2 -1} \; dt$$

When the expansion (3·1) is inserted in J the angular integration can be carried out immediately leaving

$$k_2^{(n_1+n_2+1)} J(i,n_1,n_2) \; = \; \frac{4\pi}{\sqrt{p}} \int_0^{\infty} e^{-K^* t} \, t^{n+\frac{1}{2}} \; f(n_2,i;t) \; dt$$

where $K^* = \underline{k}_a / \underline{k}_b$

The f functions are linear combinations of the $\zeta_{n,m}$.

$$f(n_2,i;t) \; = \; \sum_{j=0}^{i} \frac{2j+1}{2} \, R_j^i \, \zeta_{n,j} \, (1,t;p)$$

and $$R_j^i \; = \int_0^{\pi} P_j(\cos\theta) \cos^i\theta \sin\theta \, d\theta \; = \; \frac{2^{j+1} \; i! \; [(i+j)/2]!}{[(i-j)/2]! \; (k+j+1)!}$$

This final integration of the J integrals can be performed numerically or with the help of tables of the zeta functions prepared by the National Physical Laboratory (1952), or by the Z method described in detail in Barnett and Coulson (1951). The last method is not immediately recommendable as it is indeed a lengthy procedure compared to the other methods now available. All the integrals which we require (except the exchange) are tabulated in the article and will be referred to when needed.

3·4 Spot values using various methods.

The various methods were tried and compared for spot values of the parameters for the coulomb integral $\int 2s\, 2s\ 1/r_{12}\ 2s\, 2s\ dt$ and the two electron nuclear attraction integral $\int 2s_a\ 1/r_{a_{2s}b}\ 2s_a\ dt$. The parameter values were

$$R = 2, \quad k = k_a = k'_a = k_b = k'_b = 2{\cdot}5$$

1. The coulomb integral

a) The method of Roothaan

Using the form of the integral in the paper,

$$C = (2s_a 2s'_a :: 2s_b 2s'_b) = (1+\tau_a)^{\frac{5}{2}} (1-\tau_a)^{\frac{5}{2}} (1+\tau_b)^{\frac{5}{2}} (1-\tau_b)^{\frac{5}{2}} \quad (3S_a : 3S_b)$$

but $\tau_a = \tau_b = 0$

$$\therefore \quad C = (3S_a : 3S_b)$$

$$= k/\rho \left[1 - \left(1 + \frac{419}{256}\rho + \frac{163}{128}\rho^2 + \frac{119}{192}\rho^3 + \frac{5}{24}\rho^4 + \frac{1}{20}\rho^5 + \frac{1}{120}\rho^6 + \frac{1}{1200}\rho^7\right)e^{-2\rho} \right]$$

Now $\rho = Rk = 5$ and $e^{-10} = 0{\cdot}00004539993$

$$\therefore \quad C = \tfrac{1}{2}\left[1 - (597{\cdot}16411)\,(0{\cdot}00004539993) \right]$$

$$= \underline{0{\cdot}4864444}.$$

Some time after the computation had been done, Roothaan (1955) published a set of tables of integrals and the integral was computed from these, the result being identical i.e. 0·4864444.

b) <u>The method of Barnett and Coulson.</u>

Abstracting from the paper

$$\underline{k}_a = \tfrac{1}{2}(k_a + k'_a) \qquad \underline{k}_b = \tfrac{1}{2}(k_b + k'_b)$$

$$C = (2s_a 2s_a :: 2s_b 2s_b) = N_c(2s2s2s2s)\int_0^\infty t^{\frac{1}{2}}\, g_c(2s2s2s2s:t)\, dt$$

$$= \frac{1}{238}\left[\frac{2\cdot 5^{20}}{5\ R}\right]^{\frac{1}{2}} \frac{1}{2\cdot 5^9}\int_0^\infty t^{\frac{1}{2}}\, j_5(K^*t)\,\zeta_{0,3}(1,t,2\underline{k}_bR)\, dt$$

$$= 0\cdot 002745033\int_0^\infty t^{\frac{1}{2}}\, j_5(K^*t)\,\zeta_{0,3}(1,t,2\underline{k}_bR)\, dt$$

Put $2\underline{k}_bR = T = 10,$

$$\zeta_{0,3}(1,t;T) = (t^2 + T^2)\zeta_{0,1}(1,t;T) - 2tT\zeta_{1,1}(1,t;T)$$

But the National Physical Laboratory Zeta function tables are given in terms of the Chi functions related thus:

$$\zeta_{n,m} = \chi_{m,n} / 2\sqrt{tT} \quad \text{(Note the suffix order change.)}$$

$$\therefore\ C = 0\cdot 002745035\int_0^\infty j_5(K^*t)\left[(t^2+T^2)\chi_{1,0}/2\sqrt{T} - t\sqrt{T}\,\chi_{1,1}\right] dt$$

But $K^* = \underline{k}_a/\underline{k}_b = 1$

and $j_5(t) = 24 - (24 + 18t + 6t^2 + t^3)\, e^{-t}$

Integrating now using Simpson's Rule

$$= \frac{h}{3}\left[f(0) + f(n) + 2\left\{f(2) + f(4) + \ldots + f(n-2)\right\} + 4\left\{f(1) + f(3) + \ldots + f(n-1)\right\}\right]$$

$$\therefore\ C = 0\cdot 002745035\sum N(i)\left[f(i)_{1,0} - f(i)_{1,1}\right]$$

$N(i)$, $f(i)_{1,0}$ and $f(i)_{1,1}$ have been set down in Table 3·1.

Table 3·1 Simpson's Rule.

i	N(i)	$f(i)_{1,0}$	$f(i)_{1,1}$
1	1·33	0·098613122	0·006175143
2	0·66	0·558208056	0·118980473
3	1·33	0·013388666	0·781797333
4	0·66	6·140884300	3·37964540
5	1·33	17·0801802	11·709253
6	0·66	44·5080424	35·215518
7	1·33	109·234047	94·939156
8	0·66	248·914205	229·68950
9	1·33	301·712941	479·537937
10	0·66	756·35667	733·66602
11	1·33	616·00554	593·70663
12	0·66	375·61360	356·11449
13	1·33	205·28721	188·35077
14	0·66	102.86438	92.994966
15	1·33	49·858987	43·824770
16	0·66	23·440258	19·997588
17	1·33	10·768605	8·9069370
18	0·66	4·8577343	3·8928070
19	1·33	2·1588965	1·6756053
20	0·66	0·9475454	0·7122081
21	1·33	0·4114532	0·2995267
22	0·66	0·1770124	0·1248319
23	1·33	0·0755321	0·0516185
24	0·33	0·0319961	0·0211982

$$\therefore \quad C = 0{\cdot}002745035\left[1{\cdot}3\dot{3}(88{\cdot}71521) + 0{\cdot}6\dot{6}(88{\cdot}47195) + 0{\cdot}3\dot{3}(0{\cdot}01079788)\right]$$

$$= \underline{0{\cdot}4866169.}$$

c) The method of Kopineck (1950) after Kotani.

It must be observed first of all that whereas we are using atomic units this article employs the ordinary c.g.s. system and therefore to compare results the appropriate modifications have to be made. On consideration it is seen that $Ze^2/2a_0 = k$, and the integral in his notation is C_{ssss}. On comparison of the formulae (Kopineck , 1950,p.423) with the corresponding equations of Roothaan it is immediately obvious that they are identical and so it is not surprising that we find using the tables the value

$$C = 5(0{\cdot}097289) = \underline{0{\cdot}486445.}$$

2. The two electron nuclear attraction integral.

a) The method of Roothaan.

From the paper,

$$V_2 = Z(2s_a2s_a) = Z(1+\tau)^{\frac{5}{2}}(1-\tau)^{\frac{5}{2}}(k/\rho)\left[1 - (1 + 1{\cdot}5\rho + \rho^2 + 0{\cdot}3\dot{3}\rho^3)\, e^{-2\rho}\right]$$

but $\tau = 0$ and $\rho = kR = 5.$

$$\therefore \quad V_2 = Z/R\left[1 - (1 + 1{\cdot}5\rho + \rho^2 + 0{\cdot}3\dot{3}\rho^3)\, e^{-2\rho}\right]$$

$$V_2 = Z/2\left[1 - (75{\cdot}1)(0{\cdot}0000453999)\right] = 0{\cdot}49829\ Z.$$

b) The method of Barnett and Coulson.

$$V_2 = Z(2s_a 2s_a) = Z/12 \ (k_a^5 \, k_a'^5)^{\frac{1}{2}} \, \underline{k}_a^{-4} \, (2\underline{k}_a R)^{-1} \ j_3(2\underline{k}_a R)$$

$$\text{but} \quad k_a = k_a' = \underline{k}_a = k$$

$$\therefore \quad V_2 = (Z/24R)\left[24 - (24 + 18s + 6s^2 + s^3)\, e^{-s}\right]$$

where $s = 2kR$

$$= 0{\cdot}0208\dot{3} \ (24 - 0{\cdot}0819016) \ Z = 0{\cdot}49829 \ Z.$$

c) The method of Kopineck.

Taking the same precautions as in 1c), we find that

$$V_2 = K_{ss} = 5(0{\cdot}099659)Z = 0{\cdot}49829 \ Z$$

From the above examples we are able to gauge the work required in each of the methods. The numerical tables available although helpful for rough checking are not very suitable for our problem since the effort of accurate interpolation outweighs the effort required to calculate from the basic formulae.

The method of Kopineck suffers further from the disadvantage as mentioned previously of assuming all the k_i equal which is not always so. As far as the coulomb integrals are concerned it appears that the Roothaan method is on the whole faster than the Barnett and Coulson method when a desk machine is used. It is possible that with an electronic machine such as the I.B.M. 626 as recommended by Dr Barnett, it would be faster and more efficient to use his method for <u>all</u> the integrals including the exchange when the auxiliary zeta functions had been prepared in advance. With the limited facilities available the Roothaan method was chosen. The nuclear attraction integrals have been computed by both methods with good agreement.

3·5 The Overlap Integrals.

It is logical to start with the overlap integrals appearing as they do as a factor in all the other integrals. Once again they are:

$$
\begin{aligned}
\int a_1 b_1 \, dt &= (\mathrm{I}) &&= \int 1s_a \, 1s_b \, dt &&= (1s1s) \\
\int a_3 b_3 \, dt &= (\mathrm{II}) &&= \int 2s_a \, 2s_b \, dt &&= (2s2s) \\
\int a_5 b_5 \, dt &= (\mathrm{III}) &&= \int 2p_{za} 2p_{zb} dt &&= (2p_z 2p_z) \\
\int a_7 b_7 \, dt &= (\mathrm{IV}) &&= \int 2p_{xa} 2p_{xb} dt &&= (2p_x 2p_x) \\
\int a_9 b_9 \, dt &= (\mathrm{V}) &&= \int 2p_{ya} 2p_{yb} dt &&= (2p_y 2p_y) \\
\int a_1 b_3 \, dt &= (\mathrm{VI}) &&= \int 1s_a \, 2s_b \, dt &&= (1s2s) \\
\int a_1 b_5 \, dt &= (\mathrm{VII}) &&= \int 1s_a \, 2p_{zb} dt &&= (1s2p_z) \\
\int a_3 b_5 \, dt &= (\mathrm{VIII}) &&= \int 2s_a \, 2p_{zb} dt &&= (2s2p_z)
\end{aligned}
$$

But we defined

$$2s = H\,2s' - H'\,1s'$$

$$
\begin{aligned}
\therefore \quad \int a_3 b_3 \, dt &= (\mathrm{II}) = H^2(2s'2s') - 2HH'(1s'2s') + H'(1s'1s') \\
\int a_1 b_3 \, dt &= (\mathrm{VI}) = H(1s2s') - H'(1s1s') \\
\int a_3 b_5 \, dt &= (\mathrm{VIII}) = H(2s'2p_z) - H'(1s'2p_z)
\end{aligned}
$$

The actual form and parameter values of the wave functions represented by the ns and np are those stated in chapter 2. In all the integrals except $(1s'2s')$, $(1s2s')$, $(1s1s')$, $(2s'2p_z)$, and $(1s'2p_z)$

$$k_a = k_b, \quad \text{that is } \tau = 0.$$

We can use the spacial form noted by Roothaan for these cases and their evaluation presents no difficulty: $\rho = kR$.

$$(1s1s) = (1 + \rho + 0\cdot\dot{3}\rho^2)\, e^{-\rho} \qquad (k = 9\cdot66 \text{ and } 8\cdot97)$$

$$(2s2s) = (1 + \rho + 0\cdot\dot{4}\rho^2 + 0\cdot\dot{1}\rho^3 + 0\cdot0\dot{2}\rho^4)\, e^{-\rho} \qquad (k = 2\cdot934)$$

$$(2p_z2p_z) = (-1 - \rho - 0\cdot2\rho^2 + 0\cdot1\dot{3}\rho^3 + 0\cdot0\dot{6}\rho^4)\, e^{-\rho} \qquad (k = 2\cdot88)$$

$$(2p_x2p_x) = (2p_y2p_y) = (1 + \rho + 0\cdot4\rho^2 + 0\cdot0\dot{6}\rho^3)\, e^{-\rho} \qquad (k = 2\cdot88)$$

The other integrals however require further consideration.

$$(1s'2s') = \frac{(1-\tau^2)^{\frac{1}{2}}}{\sqrt{3}\,\tau\rho}\Big[-(1-K)\Big\{2(1+K)(2-3K) + (1-2K)\rho_a\Big\}e^{-\rho_a}$$
$$+(1+K)\Big\{2(1-K)(2-3K) + 4(1-K)\rho_b + \rho_b^2\Big\}e^{-\rho_b}\Big]$$

$k_a = 8\cdot97 \qquad k_b = 2\cdot934 \qquad \therefore\ \underline{k} = 5\cdot952$

$\rho_a = Rk_a \quad \rho_b = Rk_b \qquad \tau = 0\cdot50705645 \qquad K = 1\cdot2396117$

$$\therefore\ (1s'2s') = 0\cdot98142968/\rho\Big[-0\cdot2396117\Big\{-7\cdot6990464 - 1\cdot479223\rho_a\Big\}e^{-\rho_a}$$
$$+2\cdot2396117\Big\{0\cdot823706 - 0\cdot9584468\rho_b + \rho_b^2\Big\}e^{-\rho_b}\Big]$$

Now $(1s2s) = H(1s2s') - H'(1s1s')$

$$(1s2s') = \frac{H(1-\tau^2)^{\frac{1}{2}}}{\sqrt{3}\,\tau\rho}\Big[-(1-K)\Big\{2(1+K)(2-3K) + (1-2K)\rho_a\Big\}e^{-\rho_a}$$
$$+(1+K)\Big\{2(1-K)(2-3K) + 4(1-K)\rho_b + \rho_b^2\Big\}e^{-\rho_b}\Big]$$

$k_a = 9\cdot66 \qquad k_b = 2\cdot934 \qquad \therefore\ \underline{k} = 6\cdot297$

$\rho_a = Rk_a \quad \rho_b = Rk_b \qquad \tau = 0\cdot5340638 \qquad K = 1\cdot20325$

$$\therefore\ H(1s2s') = 0\cdot9496128/\rho\Big[0\cdot20325\Big\{-7\cdot0933634 - 1\cdot4065\rho_a\Big\}e^{-\rho_a}$$
$$+ 2\cdot20325\Big\{0\cdot65436338 - 0\cdot8130\rho_b + \rho_b^2\Big\}e^{-\rho_b}\Big]$$

$$H'(1s1s') = \frac{H'(1-\tau^2)^{\frac{1}{2}}}{\tau\rho}\left[-(1-K)\left\{2(1+K) + \rho_a\right\}e^{-\rho a} + (1+K)\left\{2(1-K) + \rho_b\right\}e^{-\rho b}\right]$$

$k_a = 9·66$ $\qquad$ $k_b = 8·97$ $\qquad$ $.'. \ \underline{k} = 9·315$

$\tau = 0·037037$ $\qquad$ $K = 13·5185$

$$.'. \ H'(1s1s') = 6·8533015/\rho\left[12·5185(29·03704 + \rho_a)e^{-\rho a} + 14·5185(-25·03704 + \rho_b)e^{-\rho b}\right]$$

$$(1s2p_z) = \frac{1}{\tau\rho}\left(\frac{1+\tau}{1-\tau}\right)^{\frac{1}{2}}\left[-(1-K)^2\left\{6(1+K)(1+\rho_a) + 2\rho_a^2\right\}e^{-\rho a} + (1+K)\left\{6(1-K)^2(1+\rho_b) + 4(1-K)\rho_b^2 + \rho_b^3\right\}e^{-\rho b}\right]$$

$k_a = 9·66$ $\qquad$ $k_b = 2·88$ $\qquad$ $\tau = 0·5406699$

$K = 1·1951136$

$$.'. \ (1s2p_z) = 0·08616385/R^2\left[-0·03806952\left\{13·170682(1+\rho_a) + 2\rho_a^2\right\}e^{-\rho a} + 2·1951136\left\{0·2284159(1+\rho_b) - 0·7804544\rho_b^2+\rho_b^3\right\}e^{-\rho b}\right]$$

Now $(2s2p_z) = H(2s'2p_z) - H'(1s'2p_z)$

For $H(2s'2p_z)$ the values of k_a and k_b are $2·934$ and $2·88$ respectively. By taking $k_a = k_b = 2·88$ the error involved is small and for simplicity this will be used.

$$.'. \ H(2s'2p_z) = 0·86380838R\,(1 + \rho + 0·46\rho^2 + 0·13\rho^3)\,e^{-\rho}$$

For $H'(1s'2p_z)$, $k_a = 8·97$, $k_b = 2·88$, $\tau = 0·5139241$, $K = 1·2298684$.

$$.'. \ 2H'(1s'2p_z) = 0·024836799/R^2\left[-0·052839\left\{13·37921(1+\rho_a) + 2\rho_a^2\right\}e^{-\rho a} + 2·2298684\left\{0·317037(1+\rho_b) - 0·919474\rho_b^2 + \rho_b^3\right\}e^{-\rho b}\right]$$

Referring to the appropriate tables in the appendix it only remains to tabulate the values of these integrals and their squares (Table 3·2) prior to the calculation of L itself. This is a summation of such magnitude and monotony that in my estimation its execution would serve no other purpose in this context than to emphasize the drop-in-the-ocean contribution to the whole project.

Using the special relation for $R = 0$ from the Roothaan paper the overlap integral $(1s_a 2s_b)$ was calculated and found to be zero, which is to be expected since the model has degenerated into an atomic or one centred problem, the wave functions of which were made accurately orthonormal at the start.

In computing the integral it must be remembered that the 2s function is a difference: the integral in question then reads

$H(1s_a 2s_b') \quad - \quad H'(1s_a 1s_b')$ in which the k_i are respectively

9·66, 2·934 $\qquad$ 9·66, 8·97

$R = 0$, the integral is

$$\tfrac{1}{2}H\left[3(1+\tau_1)^3(1-\tau_1)^5\right]^{\frac{1}{2}} - H'\left[(1+\tau_2)^3(1-\tau_2)^3\right]^{\frac{1}{2}}$$

but $\tau_1 = 0{\cdot}5340638 \qquad \tau_2 = 0{\cdot}057037$

$\therefore$ the integral $= 0{\cdot}2533832 - 0{\cdot}2533832 = 0$

An interesting paradox shows up if one assumes the electron wave functions orthonormal on each atom, and orthogonal but not normalised between the atoms which at first sight seems a plausible assumption.

Table 3·2a The two centre overlap integrals.

Table 3·2b The squares of the overlap integrals.

R	0·5	1·0	1.5	2·0	2·5
(1s 1s)	·10867352	·0026642	$\cdot 0^{4}4554$	$\cdot 0^{6}59$	$\cdot 0^{8}7$
(2s'2s')	·89408150	·64961006	·39025920	·20070410	·09157488
(1s'2s')	·25458360	·12992826	·04825710	·01547367	·00458498
(1s'1s')	·13746748	·00467877	$\cdot 0^{3}10727$	$\cdot 0^{5}204$	$\cdot 0^{7}3$
(2s 2s)	·83992890	·63317250	·39594451	·20854980	·09646060
$(2p_z 2p_z)$	-·51406132	·12531822	·24916075	·26931950	·15704398
$(2p_x 2p_x)$	·82168894	·49339873	·24152444	·10326578	·04017914
$(2p_y 2p_y)$	·82168894	·49339873	·24152444	·10326578	·04017914
(1s 2s')	·24049321	·12150248	·04467961	·01424341	·00420299
(1s 1s')	·03137440	·00090941	$\cdot 0^{4}1787$	$\cdot 0^{6}29$	
(1s 2s)	·20911383	·12059307	·04466174	·01424512	·00420299
$(1s\ 2p_z)$	·33207299	·19179437	·07521080	·02484623	·00756098
$(2s'2p_z)$	·58940338	·53022696	·42701015	·25980125	·13245637
$(1s'2p_z)$	·09051750	·05432557	·02132749	·00710024	·00217107
$(2s\ 2p_z)$	·29888588	·47590139	·40568264	·25270101	·13028530

$(1s\ 1s\ )^2$	·01180991	$\cdot 0^{5}710$	$\cdot 0^{8}2$		
$(2s\ 2s\ )^2$	·70548056	·40090712	·15677171	·04549314	·00930465
$(2p_z 2p_z)^2$	·26425771	·01504773	·06208113	·07253300	·02466281
$(2p_x 2p_x)^2$	·67517264	·24344232	·05833445	·01066382	·00161436
$(1s\ 2s\ )^2$	·04373067	·01454263	·00199467	·00020236	$\cdot 0^{4}1766$
$(1s\ 2p_z)^2$	·11027247	·03678508	·00565666	·00061733	$\cdot 0^{4}5717$
$(2s\ 2p_z)^2$	·08933277	·22648213	·16457840	·06585780	·01697426

3·0	3·5	4·0	4·5	5·0
·03812420	·01476527	·00540370	·00188758	·00063454
·00129389	$\cdot 0^{3}35305$	$\cdot 0^{4}9408$	$\cdot 0^{4}2460$	$\cdot 0^{5}635$
·04043270	·01575683	·00578512	·00202517	$\cdot 0^{3}68181$
·07658085	·03525098	·01329435	·00500516	·00178795
·01459505	·00502915	·00166339	·00053312	$\cdot 0^{3}16576$
·01459505	·00502915	·00166339	·00053312	$\cdot 0^{3}16576$
·00118266	$\cdot 0^{3}32198$	$\cdot 0^{4}8566$	$\cdot 0^{4}2238$	$\cdot 0^{5}577$
·00118266	$\cdot 0^{3}32198$	$\cdot 0^{4}8566$	$\cdot 0^{4}2238$	$\cdot 0^{5}577$
·00218924	$\cdot 0^{3}61305$	$\cdot 0^{3}16762$	$\cdot 0^{4}4509$	$\cdot 0^{4}1192$
·05980818	·02471424	·00954762	·00550596	·00122846
$\cdot 0^{3}63067$	$\cdot 0^{3}17702$	$\cdot 0^{4}4272$	$\cdot 0^{4}1506$	$\cdot 0^{5}546$
·05917751	·02453722	·00949889	·00548090	·00122500

·00165885	$\cdot 0^{3}24828$	$\cdot 0^{4}3347$	$\cdot 0^{5}410$	$\cdot 0^{6}46$
·00586465	·00110565	$\cdot 0^{3}17674$	$\cdot 0^{4}2505$	$\cdot 0^{5}320$
$\cdot 0^{3}21296$	$\cdot 0^{4}2529$	$\cdot 0^{5}277$	$\cdot 0^{6}28$	$\cdot 0^{7}5$
$\cdot 0^{5}140$	$\cdot 0^{6}10$	$\cdot 0^{8}7$		
$\cdot 0^{5}479$	$\cdot 0^{6}38$	$\cdot 0^{7}5$		
·00550200	$\cdot 0^{3}602075$	$\cdot 0^{4}9025$	$\cdot 0^{4}1218$	$\cdot 0^{5}150$

In this case there are only five different terms (I) (II) (III) (IV) and (V) instead of the eight in the completely non-orthonormal case which we have just treated. The total overlap integral then reads

$$L = \left[(0) - 2\sum_{i=1}^{5} (i) + 2\sum_{j \neq i=1}^{5} (i)(j) - \dots + 2(I)(II)(III)(IV)(V) \right]$$

and the numerical values for the internuclear separations of 0·5, 1·0 and 1·5 atomic units are respectively -0·9548, -0·3249, +0·4026.

But the overlap integral L is a positive definite quantity hence the paradox. Such an example serves to illustrate the danger of false assumptions over oversimplification which in this case is the assumption of orthogonality of the wave functions between different atoms. In fact the overlap integrals neglected there are of prime importance.

3·6 The Method of Roothaan and the Kinetic Energy Integrals.

In chapter 2 we saw that the kinetic energy integral was

$$T\,L = 2\sum_{v,w=1}^{5} \int a_w \nabla_w^{2} b_v \; dt_w \cdot L_{w,v}$$

$$= 2\sum_{v,w=1}^{5} (a_w \, T \, b_v) \cdot L_{w,v}$$

As was stated in section 3·2 these integrals can be expressed as functions of the overlap integrals. Some of the integrals are symmetric in the k_i in which case $\tau = 0$. The modified and simpler form of the overlap integrals can therefore be used again.

Focussing our attention on the $(a_v\ T\ b_v)$ the different integrals occurring are

$(1s\ T\ 1s)$

$(1s\ T\ 2s) = H\ (1s\ T\ 2s') - H'\ (1s\ T\ 1s')$

$(1s\ T\ 2p_z)$

$(2s\ T\ 2s) = H^2(2s'T\ 2s') - 2HH'(1s'T\ 2s') + H'^2(1s'T\ 1s')$

$(2s\ T\ 2p_z) = H\ (2s'T\ 2p_z) - H'\ (1s'T2p_z)$

$(2p_zT\ 2p_z)$

$(2p_xT\ 2p_x)$

$(2p_yT\ 2p_y)$

The numerical values of the integrals are in Table 3·3 at the end of the section.

$$(1s_aT\ 1s_b) = 9{\cdot}66^2\left[(1s_a1s_b) - 2\sqrt{2}\ (0s_a1s_b)\right]$$

$$= 93{\cdot}3156\ (\ -1 - \rho + \rho^2/3\ )\ e^{-\rho}$$

where $\rho = kR = 9{\cdot}66R$

$$H^2(2s_a'T\ 2s_b') = H^2(2{\cdot}934)^2\left[(2s_a2s_b) - 4(1s_a2s_b)/\sqrt{3} + 2\sqrt{2}\ (0s_a2s_b)/\sqrt{3}\ \right]$$

$$= H^2 8{\cdot}608356\ (-\ 1/3 - \rho/3 - \rho^3/9 + \rho^4/45)\ e^{-\rho}$$

where $\rho = kR = 2{\cdot}934R$

$$H'^2(1s_a'T\ 1s_b') = H'^2(8{\cdot}97)^2\left[(1s_a1s_b) - 2\sqrt{2}\ (0s_a1s_b)\right]$$

$$= H'^2\ 80{\cdot}4609\ \ (\ -1 - \rho + \rho^2/3)\ e^{-\rho}$$

where $\rho = kR = 8{\cdot}97R$

$$(2p_{za}T\,2p_{zb}) = 2{\cdot}88^2\left[(2p_{za}2p_{zb}) - 4(1p_{za}2p_{zb})/\sqrt{3}\right]$$

$$= 8{\cdot}2944\ (1 + \rho - \rho^2/5 - 0{\cdot}5\dot{3}\rho^3 + \rho^4/30)\ e^{-\rho}$$

where $\rho = kR = 2{\cdot}88\ R$

$$(2p_{xa}T2p_{xb}) = (2p_{ya}T2p_{yb}) = 2{\cdot}88^2\left[(2p_{xa}2p_{xb}) - 4(1p_{xa}2p_{xb})/\sqrt{3}\right]$$

$$= 8{\cdot}2944\ (-1 - \rho - 0{\cdot}2\dot{6}\rho^2 + 0{\cdot}0\dot{6}\rho^3)\ e^{-\rho}$$

WHERE $\rho = kR = 2{\cdot}88\ R$

$$2HH'(1s_a'T\,2s_b') = 5{\cdot}952^2(1+\tau)^2\ 2HH'\left[(1s_a2s_b) - 2\sqrt{2}\ (0s_a2s_b)\right]$$

$$= 5{\cdot}952^2(1+\tau)^2\ 2HH'\ (1-\tau^2)^{\frac{1}{2}}/\sqrt{3}\ \tau\rho$$

$$\Big[-(1-K)\left\{2(1+K)(2-3K) + (1-2K)\rho_a - 2(1-2K)\right\} e^{-\rho a}$$

$$+ \left\{2(1-K)(1+K-3K^2) + 4(1-K)K\rho_b - (K-1)\rho_b^2\right\} e^{-\rho b}\Big]$$

where $\rho = 5{\cdot}952\ R$, $\tau = 0{\cdot}507056$, $K = 1{\cdot}2396117$,

$k_a = 8{\cdot}97$, $k_b = 2{\cdot}934.$

$$H\ (1s_a\ T\ 2s_b') = 6{\cdot}297^2(1+\tau)^2\ H\ \ (1-\tau^2)^{\frac{1}{2}}/\sqrt{3}\ \tau\rho$$

$$\Big[-(1-K)\left\{2(1+K)(2-3K) + (1-2K)\rho_a - 2(1-2K)\right\} e^{-\rho a}$$

$$+ \left\{2(1-K)(1+K-3K^2) + 4(1-K)K\rho_b - (K-1)\rho_b^2\right\} e^{-\rho b}$$

where $\rho = 6{\cdot}297\ R$, $\tau = 0{\cdot}534064$, $K = 1{\cdot}203249$,

$k_a = 9{\cdot}66$, $k_b = 2{\cdot}934.$

$$H'\ (1s_a\ T\ 1s_b') = 9{\cdot}315^2(1+\tau)^2\ H'\left[(1s_a1s_b) - 2\sqrt{2}\ (0s_a1s_b)\right]$$

$$= 9{\cdot}315^2(1+\tau)^2 H\frac{(1-\tau^2)^{\frac{1}{2}}}{\tau\rho}\left[-(1-K)(2K+\rho_a)\,e^{-\rho a} + (1-K)(2K-\rho_b)\,e^{-\rho b}\right]$$

where $\rho = 9{\cdot}315\ R$, $\tau = 0{\cdot}037037$, $K = 13{\cdot}5185185$,

$k_a = 9{\cdot}66$, $k_b = 8{\cdot}97$

Table 3·3 The two centre Kinetic Energy Integrals.

R	0·5	1·0	1·5	2·0	2·5
$(1s_a T\ 1s_b)$	1·450600	·1217025	·00259058	$\cdot 0^{4}3952$	$\cdot 0^{6}48$
$H^2(2s' T\ 2s')$	-2·293916	-1·221628	-·3546182	·04227098	·1072861
$2HH'(1s' T 2s')$	-·7253902	-·1108354	·0313347	·02390421	·0097023
$H'^2(1s' T\ 1s')$	·0713564	·0111156	$\cdot 0^{3}3415$	$\cdot 0^{5}74$	$\cdot 0^{6}14$
$(2s\ T\ 2s)$	-1·497169	-1·099679	-·3656113	·01837419	·0975840
$(2p_z T\ 2p_z)$	1·865380	-3·829663	-3·287528	-1·701630	-·6913899
$(2p_x T\ 2p_x)$	-5·489845	-2·094721	-·5429582	-·0749377	·0177049
$(2p_y T\ 2p_y)$	-5·489845	-2·094721	-·5429582	-·0749377	·0177049
$H(1s\ T\ 2s')$	-1·337433	-·1898562	·0571952	·0421985	·01695188
$H'(1s\ T\ 1s')$	·3683153	·0309009	$\cdot 0^{3}6577$	$\cdot 0^{4}100$	$\cdot 0^{6}1$
$(1s\ T\ 2s)$	-1·705748	-·2207571	·0565374	·0421885	·01695176
$(1s\ T\ 2p_z)$	-5·242079	-·9914017	·0085469	·0551538	·02626378
$H\ (2s' T\ 2p_z)$	-1·877745	-2·303885	-1·028964	-·2495887	·02815286
$H'(1s' T\ 2p_z)$	-1·496443	-·2244417	$\cdot 0^{3}7256$	·0153643	·00745671
$(2s\ T\ 2p_z)$	-·3813018	-2·079443	-1·029689	-·2649530	·02069614

3·0	3·5	4·0	4·5	5·0
$\cdot 0^{3}6$				
·0759595	·03967883	·0176857	·007116538	·00266247
·0037423	$\cdot 0^{3}98575$	$\cdot 0^{3}2829$	$\cdot 0^{4}7813$	$\cdot 0^{4}2101$
$\cdot 0^{3}2$				
·0722167	·03869308	·0174023	·007058408	·00264146
−·0239920	−·07346632	−·0199572	−·004694501	$-\cdot 0^{3}8568$
·0197361	·0104645	·0044482	·001687915	$\cdot 0^{3}5935$
·0197361	·0104645	·0044482	·001687915	$\cdot 0^{3}5935$
·0056385	·0017066	$\cdot 0^{3}4886$	$\cdot 0^{3}13805$	$\cdot 0^{4}3618$
·0056385	·0017066	$\cdot 0^{3}4886$	$\cdot 0^{3}13805$	$\cdot 0^{4}3618$
·0094155	·0029964	$\cdot 0^{3}8926$	$\cdot 0^{3}25534$	$\cdot 0^{4}7076$
·0687757	·0470944	·0240921	·0106379	·00425925
·0026951	$\cdot 0^{3}86154$	$\cdot 0^{3}27655$	$\cdot 0^{4}7379$	$\cdot 0^{4}2047$
·0660806	·0462328	·0238155	·0105641	·0042388

$$
\begin{aligned}
(1s_a\ T\ 2p_{zb}) &= 6{\cdot}27^2(1+\tau)^2\left[(1s_a2p_{zb}) - 2\sqrt{2}\,(0s_a2p_{zb})\right]\\
&= 6{\cdot}27^2(1+\tau)^2\sqrt{(1+\tau)/(1-\tau)}\ \ 1/\tau\rho^2\\
&\qquad\Big[-(1-K)^2\left\{(6K+2)(1+\rho_a) + 2\rho_a^2\right\}e^{-\rho a}\\
&\qquad\ +(1-K)^2\left\{(6K+2)(1+\rho_b) + 4(1-K)K\rho_b^2 + (K-1)\rho_b^3\right\}e^{-\rho b}\Big]
\end{aligned}
$$

where $\rho = 6{\cdot}27\ R$, $\tau = 0{\cdot}5406699$, $K = 1{\cdot}1951156$,

$k_a = 9{\cdot}66$, $k_b = 2{\cdot}88$.

$$
\begin{aligned}
H'(1s_a'\ T\ 2p_{zb}) &= 5{\cdot}925^2(1+\tau)^2H'\left[(1s_a2p_{zb}) - 2\sqrt{2}\,(0s_a2p_{zb})\right]\\
&= 5{\cdot}925^2(1+\tau)^2\sqrt{(1+\tau)/(1-\tau)}\ \ H'/\tau\rho^2\\
&\qquad\Big[-(1-K)^2\left\{(6K+2)(1+\rho_a) + 2\rho_a^2\right\}e^{-\rho a}\\
&\qquad\ +(1-K)^2\left\{(6K+2)(1+\rho_b) + 4(1-K)K\rho_b^2 + (K-1)\rho_b^3\right\}e^{-\rho b}\Big]
\end{aligned}
$$

where $\rho = 5{\cdot}925\ R$, $\tau = 0{\cdot}51592405$, $K = 1{\cdot}2298684$,

$k_a = 8{\cdot}97$, $k_b = 2{\cdot}88$.

$$
\begin{aligned}
H(2s_a'\ T\ 2p_{zb}) &= 2{\cdot}88^2\left[(2s_a2p_{zb}) - 4(1s_a2p_{zb})/\sqrt{3} + 2\sqrt{2}\,(0s_a2p_{zb})/\sqrt{3}\right]\\
&= 2{\cdot}88^2\ \rho/30\sqrt{3}\left[-5 - 5\rho - 15\rho^2 + 2\rho^3\right]e^{-\rho}
\end{aligned}
$$

where $\rho = k\,R = 2{\cdot}88\ R$.

3·7 The Potential energy V_2.

From chapter 2 we recall,

$$
V_2L = -4\sum_{i,i'=1}^{5} Z\int\left[a_i\frac{1}{r_{a_ib}}a_{i'}\,L_{Z\ ii'} + a_i\frac{1}{r_{a_ib}}b_{i'}\,L_{Z\ ii'}\right]dt_i
$$

These integrals go under a variety of names: Roothaan classes them as two electron and one electron integrals respectively; while Barnett and Coulson designate the first one by one electron coulomb integral and the second by resonance integral.

1. The integrals $\int a_1 \ 1/r_{a_1 b} \ a_{1'} \, dt_1$.

The description of these by Roothaan as two electron integrals looks erroneous at first sight. The justification lies in the acceptance of the nuclear charge Z as a negative electron charge distribution. The evaluation was carried out independently by both methods in many cases and the results agreed. This is only to be expected, however, for a closer examination of the final formulae in each method shows that they are in fact identical although they were reached by different ways.

The different integrals are:

$Z(1s_a 1s_a)$

$Z(2s_a 2s_a) = H^2 Z(2s'_a 2s'_a) - 2HH' Z(1s'_a 2s'_a) + H'^2 Z(1s'_a 1s'_a)$

$Z(2p_{za} 2p_{za})$

$Z(2p_{xa} 2p_{xa})$

$Z(2p_{ya} 2p_{ya})$

$Z(1s_a 2s_a) = H Z(1s_a 2s'_a) - H' Z(1s_a 1s'_a)$

$Z(1s_a 2p_{za})$

$Z(2s_a 2p_{za}) = H Z(2s'_a 2p_{za}) - H' Z(1s'_a 2p_{za})$

In most cases the Roothaan formula (R) and the Barnett and Coulson formula (BC) will be given (in simplified form when $k_a = k'_a$)

to enable the comparison between the two to be made. The Roothaan parameters are $\rho = kR$ and τ, while those of Barnett and Coulson are $s = 2\rho$ and $\underline{k}$.

$$Z(1s_a 1s_a) = 1/R \left[1 - (1+\rho)e^{-2\rho}\right] \qquad (R)$$

$$= 1/2R \left[2 - (2+s)e^{-s}\right] \qquad (BC)$$

where $\rho = \underline{k}\,R = 9{\cdot}66\ R$

$$Z(2s'_a 2s'_a) = 1/R \left[1 - (1 + 3\rho/2 + \rho^2 + \rho^3/3)e^{-2\rho}\right] \qquad (R)$$

$$= 1/24R \left[24 - (24 + 18s + 6s^2 + s^3)e^{-s}\right] \qquad (BC)$$

where $\rho = \underline{k}\,R = 2{\cdot}934\ R$

$$Z(1s'_a 2s'_a) = \tfrac{1}{2}\sqrt{3}\,(1+\tau)^{3/2}(1-\tau)^{5/2}/R \left[1 - (1 + 4\rho/3 + 2\rho^2/3)e^{-2\rho}\right]$$

$$= 0{\cdot}04555813/R \left[6 - (6 + 8\rho + 4\rho^2)e^{-2\rho}\right] \qquad (R)$$

$$= \tfrac{1}{2}\,(k_a^3 k_a'^5/3)^{\frac{1}{2}}\,\underline{k}^{-3}\,s^{-1} \left[6 - (6 + 4s + s^2)e^{-s}\right]$$

$$= 0{\cdot}04555813/R \left[6 - (6 + 4s + s^2)e^{-s}\right] \qquad (BC)$$

where $\rho = \underline{k}\,R = 5{\cdot}952\ R$, $\qquad \tau = 0{\cdot}50705645$,

$k_a = 8{\cdot}97 \qquad\qquad k'_a = 2{\cdot}934$.

$$Z(1s'_a 1s'_a) = 1/R \left[1 - (1+\rho)e^{-2\rho}\right]$$

where $\rho = \underline{k}\,R = 8{\cdot}97\ R$

$$Z(2p_{za} 2p_{za}) = 1/R \left[1 - (1 + 3\rho/2 + \rho^2 + \rho^3/3)e^{-2\rho}\right]$$

$$+ 3\underline{k}/\rho^3 \left[1 - (1 + 2\rho + 2\rho^2 + 4\rho^3/3 + 2\rho^4/3 + 2\rho^5/9)e^{-2\rho}\right] \quad (R)$$

$$= 0{\cdot}003767602/R^3 \left[96 + 8s^2 - (96+96s+56s^2+22s^3+6s^4+s^5)e^{-s}\right] \quad (BC)$$

where $\rho = \underline{k}\,R = 2{\cdot}88\ R$

The numerical results are collected together in table 3·4.

$$Z(2p_{xa}2p_{xa}) = Z(2p_{ya}2p_{ya}) = 1/R\left[1 - (1 + 3\rho/2 + \rho^2 + \rho^3/3)e^{-2\rho}\right]$$

$$- 3\underline{k}/2\rho^3\left[1 - (1 + 2\rho + 2\rho^2 + 4\rho^3/3 + 2\rho^4/3 + 2\rho^5/9)e^{-2\rho}\right] \quad \text{(R)}$$

$$= 0{\cdot}007535204/R^3\left[-24 + 4s^2 + (24+24s+8s^2+s^3)e^{-s}\right] \quad \text{(BC)}$$

$$Z(1s_a2s'_a) = \tfrac{1}{2}(k_a^3k_a'^5/3)^{\frac{1}{2}}\,\underline{k}^{-3}\,s^{-1}\left[6 - (6 + 4s + s^2)e^{-s}\right]$$

$$= 0{\cdot}04064065/R\left[6 - (6 + 4s + s^2)e^{-s}\right]$$

where $s = 12{\cdot}594\,R$

$$Z(1s_a1s'_a) = (k_a^3k_a'^3)^{\frac{1}{2}}\,\underline{k}^{-2}\,s^{-1}\left[2 - (2 + s)e^{-s}\right]$$

$$= 0{\cdot}49897155/R\left[2 - (2 + s)e^{-s}\right]$$

where $s = 18{\cdot}65\,R$

$$Z(1s_a2p_{za}) = \tfrac{1}{2}(k_a^3k_a'^5)^{\frac{1}{2}}\,\underline{k}^{-3}\,s^{-2}\left[8 - (8 + 8s + 4s^2 + s^3)e^{-s}\right]$$

$$= 0{\cdot}00545154/R^2\left[8 - (8 + 8s + 4s^2 + s^3)e^{-s}\right]$$

where $s = 12{\cdot}54\,R$

$Z(1s'_a2p_{za})$ similarly

$$= 0{\cdot}006473485/R^2\left[8 - (8 + 8s + 4s^2 + s^3)e^{-s}\right]$$

where $s = 11{\cdot}85\,R$

$$Z(2s'_a2p_{za}) = (k_a^5k_a'^5/3)^{\frac{1}{2}}\,\underline{k}^{-4}(2s)^{-2}\left[40 - (40+40s+20s^2+6s^3+s^4)e^{-s}\right]$$

$$= 0.012529302/R^2\left[40 - (40+40s+20s^2+6s^3+s^4)e^{-s}\right]$$

where $s = 5{\cdot}76\,R.$

Table 3·4 The Integrals $Z(a_i a_{i'})$.

R	0·5	1·0	1·5	2·0	2·5
$Z(1s\ 1s)$	1·999256	1·0000000	·66666667	·50000000	·40000000
$H^2Z(2s'2s')$	1·423832	1·0112857	·71384994	·53940410	·43187273
$-2HH'Z(1s'2s')$	·2803222	·14420833	·09615995	·07212005	·05769604
$H'^2Z(1s'1s')$	·1288880	·06446799	·04297866	·03223399	·02578718
$Z(2s\ 2s)$	1·272398	·93154511	·66066864	·49951805	·39996389
$Z(2p_z 2p_z)$	1·554883	1·1283312	·75391409	·54357074	·42301973
$Z(2p_x 2p_x)$	1·173670	·83384722	·61366494	·47742141	·38842733
$Z(2p_y 2p_y)$	1·173670	·83384722	·61366494	·47742141	·38842733
$HZ(1s\ 2s')$	·4957236	·25332323	·16891246	·12667691	·10134152
$-H'Z(1s\ 1s')$	·5066981	·25347752	·16898502	·12673877	·10139102
$Z(1s\ 2s\ )$	−·0109745	−·00015429	$-{\cdot}0^{4}8256$	$-{\cdot}0^{4}6186$	$-{\cdot}0^{4}4950$
$Z(1s\ 2p_z)$	·1553924	·04355945	·01938312	·01090308	·00697797
$HZ(2s'2p_z)$	·1362116	·05369588	·02391409	·01193856	·00860921
$-H'Z(1s'2p_z)$	·1281989	·09539469	·05374430	·03158791	·02034899
$Z(2s\ 2p_z)$	·0580128	−·04169881	−·02983021	−·01964935	−·01173978

3·0	3·5	4·0	4·5	5·0
·33333333	·28571429	·25000000	·22222222	·20000000
·35992156	·30850625	·26994311	·23994944	·21595455
·04808003	·04121145	·03606002	·03205335	·02884302
·02146933	·01841943	·01611699	·01432622	·01289359
·33330866	·28571429	·24999999	·22222222	·20000000
·34671963	·29414952	·25565141	·22619137	·20289353
·32663542	·28149632	·24717432	·22023764	·19855324
·32663542	·28149632	·24717432	·22023764	·19855324
·08445127	·07238683	·06333846	·05630084	·05067076
·08449252	·072422154	·063369386	·05632834	·05069551
−·0^{4}4125	−·0^{4}3535	−·0^{4}3093	−·0^{4}2750	−·0^{4}2475
·00484581	·00356019	·00272577	·00215369	·00174450
.00597862	·00439246	·00336298	·00265717	·00215230
·01414279	·01039155	·00795611	·00628631	·00509191
−·00816417	−·00599909	−·00459515	−·00362914	−·00293961

2. The Integrals $\int a_i \; 1/r_{a_i b} \, b_{i'} \, dt$.

Barnett and Coulson call these resonance integrals and list them in terms of the zeta functions. I consider this method of integration on a desk machine long compared with the Roothaan method, and therefore only the latter was employed. When detailing the integrals we must note that since there is no longer symmetry, $Z(1s_a 2s_b) \neq Z(2s_a 1s_b)$. We have:

$Z(1s_a 1s_b)$

$Z(2s_a 2s_b) = H^2 Z(2s'_a 2s'_b) - HH' Z(1s'_a 2s'_b) - HH' Z(2s'_a 1s'_b) + H'^2 Z(1s'_a 1s'_b)$

$Z(2p_{za} 2p_{zb})$

$Z(2p_{xa} 2p_{xb})$

$Z(2p_{ya} 2p_{yb})$

$Z(1s_a 2s_b) = HZ(1s_a 2s'_b) - H'Z(1s_a 1s'_b)$

$Z(2s_a 1s_b) = HZ(2s'_a 1s_b) - H'Z(1s'_a 1s_b)$

$Z(1s_a 2p_{zb})$

$Z(2p_{za} 1s_b)$

$Z(2s_a 2p_{zb}) = HZ(2s'_a 2p_{zb}) - H'Z(1s'_a 2p_{zb})$

$Z(2p_{za} 2s_b) = HZ(2p_{za} 2s'_b) - H'Z(2p_{za} 1s'_b)$

$Z(1s_a 1s_b) = 9{\cdot}66(1 + \rho)e^{-\rho}$

where $\rho = \underline{k} R = 9{\cdot}66 R$

$Z(2s'_a 2s'_b)H^2 = \frac{1}{2}H^2 \, 2{\cdot}934 \, (1 + \rho + 4\rho^2/9 + \rho^3/9)e^{-\rho}$

where $\rho = \underline{k} R = 2{\cdot}934 R$

$$HH'Z(1s_a'2s_b') = 5{\cdot}952HH'(1+\tau)(1-\tau^2)^{\frac{1}{2}}/\sqrt{3}\ \tau\rho\ \Big[-(1-K)(1-2K)e^{-\rho_a}$$
$$+\Big\{(1-K)(1-2K) + 2(1-K)\rho_b + \rho_b^2\Big\}e^{-\rho_b}\Big]$$
$$= 2{\cdot}3232765/\rho\Big[-(1-K)(1-2K)e^{-\rho_a} + \Big\{(1-K)(1-2K) + 2(1-K)\rho_b + \rho_b^2\Big\}e^{-\rho_b}\Big]$$

WHERE $\rho = kR = 5{\cdot}952R$, $\tau = 0{\cdot}50705645$, $K = 1{\cdot}2396117$,

$k_a = 8{\cdot}97$ $k_b = 2{\cdot}934$.

$$HH'Z(2s_a'1s_b') = 5{\cdot}952HH'(1+\tau)(1-\tau^2)^{\frac{1}{2}}/\sqrt{3}\ \tau\rho\ \Big[-(1-K)\Big\{2(1+K) + \rho_a\Big\}e^{-\rho_a}$$
$$+ (1+K)\Big\{2(1-K) + \rho_b\Big\}e^{-\rho_b}\Big]$$
$$= 2{\cdot}3232765/\rho\Big[-(1-K)\Big\{2(1+K) + \rho_a\Big\}e^{-\rho_a} + (1+K)\Big\{2(1-K) + \rho_b\Big\}e^{-\rho_b}\Big]$$

where $\rho = 5{\cdot}952R$, $\tau = 0{\cdot}50705645$, $K = 1{\cdot}2396117$,

$k_a = 2{\cdot}934$, $k_b = 8{\cdot}97$.

$$H'^2Z(1s_a'1s_b') = H'^2\ 8{\cdot}97(1+\rho)e^{-\rho}$$

where $\rho = 8{\cdot}97R$

$$Z(2p_{za}2p_{zb}) = \tfrac{1}{2}\ 2{\cdot}88\ \Big[-1 - \rho + \rho^3/3\Big]e^{-\rho}$$

where $\rho = 2{\cdot}88\ R$

$$Z(2p_{xa}2p_{xb}) = Z(2p_{ya}2p_{yb}) = \tfrac{1}{2}\ 2{\cdot}88\Big[1 + \rho + \rho^3/3\Big]e^{-\rho}$$

where $\rho = 2{\cdot}88\ R$

$$HZ(1s_a2s_b') = 6{\cdot}297\ H\ (1+\tau)(1-\tau^2)^{\frac{1}{2}}/\sqrt{3}\ \tau\rho\ \Big[-(1-K)(1-2K)e^{-\rho_a}$$
$$+\Big\{(1-K)(1-2K) + 2(1-K)\rho_b + \rho_b^2\Big\}e^{-\rho_b}\Big]$$

where $\rho = 6{\cdot}297\ R$, $\tau = 0{\cdot}534064$, $K = 1{\cdot}203249$,

$k_a = 9{\cdot}66$, $k_b = 2{\cdot}934$.

Table 3·5 contains the numerical values of the integrals.

$$H'Z(1s_a 1s'_b) = H'\ 9{\cdot}315(1+\tau)(1-\tau^2)^{\frac{1}{2}}/\tau\rho \left[-(1-K)e^{-\rho a} + \left\{(1-K) + \rho_b\right\}e^{-\rho b}\right]$$

where $\rho = 9{\cdot}315\ R$, $\tau = 0{\cdot}037037$, $K = 13{\cdot}5185$,

$k_a = 9{\cdot}66$, $k_b = 8{\cdot}97$.

$H'Z(1s'_a 1s_b)$ as above but with $k_a = 8{\cdot}97$, $k_b = 9{\cdot}66$.

$$HZ(2s'_a 1s_b) = 6{\cdot}297H(1+\tau)(1-\tau^2)^{\frac{1}{2}}/\sqrt{3}\tau\rho \left[-(1-K)\left\{2(1+K) + \rho_a\right\}e^{-\rho a} + (1+K)\left\{2(1-K) + \rho_b\right\}e^{-\rho b}\right]$$

where $\rho = 6{\cdot}297\ R$, $\tau = 0{\cdot}534064$, $K = 1{\cdot}203249$

$k_a = 2{\cdot}934$, $k_b = 9{\cdot}66$.

$$Z(1s_a 2p_{zb}) = 6{\cdot}27(1+\tau)\sqrt{(1+\tau)/(1-\tau)}\ 1/\tau\rho^2 \left[-2(1-K)^2(1+\rho_a)\ e^{-\rho a} + \left\{2(1-K)^2(1+\rho_b) + 2(1-K)\rho_b^2 + \rho_b^3\right\}e^{-\rho b}\right]$$

where $\rho = 6{\cdot}27\ R$, $\tau = 0{\cdot}5406699$, $K = 1{\cdot}1951136$,

$k_a = 9{\cdot}66$, $k_b = 2{\cdot}88$.

$H'Z(1s'_a 2p_{zb})$ as above but with $k_a = 8{\cdot}97$, $k_b = 2{\cdot}88$,

$\rho = 5{\cdot}925\ R$, $\tau = 0{\cdot}51392405$, $K = 1{\cdot}2298684$.

$$Z(2p_{za} 1s_b) = 6{\cdot}27(1+\tau)\sqrt{(1-\tau)/(1+\tau)}\ 1/\tau\rho^2 \left[-(1-K)\left\{2(1+K)(1+\rho_a) + \rho_a^2\right\}e^{-\rho a} + (1+K)\left\{2(1-K)(1+\rho_b) + \rho_b^2\right\}e^{-\rho b}\right]$$

where $\rho = 6{\cdot}27$, $\tau = 0{\cdot}5406699$, $K = 1{\cdot}1951136$,

$k_a = 2{\cdot}88$, $k_b = 9{\cdot}66$.

$H'Z(2p_{za} 1s'_b)$ as above but with $k_a = 2{\cdot}88$, $k_b = 8{\cdot}97$,

$\rho = 5{\cdot}925\ R$, $\tau = 0{\cdot}51392405$, $K = 1{\cdot}2298684$.

$HZ(2s'_a 2p_{zb}) = 2{\cdot}88\rho/2\sqrt{3}\ (1 + \rho + \rho^2/3)e^{-\rho}$ where $\underline{k} = 2{\cdot}88$.

$HZ(2p_{za} 2s'_b) = 2{\cdot}88\rho/6\sqrt{3}\ (1 + \rho + \rho^2)e^{-\rho}$ where $\underline{k} = 2{\cdot}88$.

Table 3•5 The Integrals $Z(a_1 b_{1'})$.

R	0•5	1•0	1•5	2•0	2•5
$Z(1s\ 1s)$	•44981031	•00656883	$\cdot 0^{4}7623$	$\cdot 0^{6}80$	$\cdot 0^{8}7$
$H^2Z(2s'2s')$	1•3786535	•89025343	•45612091	•19989138	•07860761
$-HH'Z(1s'2s')$	•32146982	•15683517	•05620644	•01764402	•00515507
$-HH'Z(2s'1s')$	•41705564	•11427464	•02802882	•00665948	•00156299
$H'^2Z(1s'1s')$	•03576266	$\cdot 0^{3}75320$	$\cdot 0^{4}1116$	$\cdot 0^{6}18$	$\cdot 0^{8}2$
$Z(2s\ 2s)$	•67589083	•61987682	•37189694	•17558806	•07188955
$Z(2p_z 2p_z)$	-•49282962	•32988734	•49879931	•25857544	•12495722
$Z(2p_x 2p_x)$	1•0681654	•53708058	•22102944	•08085637	•02759211
$Z(2p_y 2p_y)$	1•0681654	•53708058	•22102944	•08085637	•02759211
$HZ(1s\ 2s')$	1•2507004	•59674984	•21282345	•06660568	•01942134
$-H'Z(1s\ 1s')$	•13358460	•00246986	$\cdot 0^{4}3660$	$\cdot 0^{6}49$	$\cdot 0^{8}7$
$Z(1s\ 2s)$	1•0971194	•59427938	•21278685	•06660518	•01942135
$HZ(2s'1s)$	1•0288814	•11750235	•02133998	•00430177	$\cdot 0^{3}90689$
$-H'Z(1s'1s)$	•11345500	•01002567	$\cdot 0^{4}8036$	$\cdot 0^{6}62$	$\cdot 0^{8}8$
$Z(2s\ 1s)$	•91542640	•10747668	•02125962	•00431115	$\cdot 0^{3}90688$
$Z(1s\ 2p_z)$	1•8516364	•97856999	•36282598	•11715475	•03516017
$Z(2p_z 1s)$	•95301579	•07193294	•01205095	•00239767	$\cdot 0^{3}50802$
$HZ(2s'2p_z)$	•92271704	•92789660	•57279802	•27938582	•11831111
$-H'Z(1s'2p_z)$	•47791212	•25622628	•09564868	•03099967	•00932505
$Z(2s\ 2p_z)$	•44480492	•67167032	•47714934	•24838615	•10698606
$HZ(2p_z 2s')$	•44336305	•56668796	•39676825	•20872617	•09292776
$-H'Z(2p_z 1s')$	•32856164	•02517352	•00413913	$\cdot 0^{3}82076$	$\cdot 0^{3}17371$
$Z(2p_z 2s)$	•11480141	•54151444	•39262912	•20790541	•09275405

3·0	3·5	4·0	4·5	5·0
·02860043	,00980765	·00521472	·00101570	$\cdot 0^{3}51145$
·00142678	$\cdot 0^{3}39050$	$\cdot 0^{3}10344$	$\cdot 0^{4}2694$	$\cdot 0^{5}693$
$\cdot 0^{3}36430$	$\cdot 0^{4}3482$	$\cdot 0^{4}1969$	$\cdot 0^{5}456$	$\cdot 0^{5}106$
·02680886	·00933253	·00309160	$\cdot 0^{3}98420$	$\cdot 0^{3}30347$
·05230713	·01993416	·00710736	·00241449	$\cdot 0^{3}78651$
·00879377	·00271259	$\cdot 0^{3}81151$	$\cdot 0^{3}23732$	$\cdot 0^{4}6784$
·00879377	·00271259	$\cdot 0^{3}81151$	$\cdot 0^{3}23732$	$\cdot 0^{4}6784$
·00541992	·00146669	$\cdot 0^{3}38843$	$\cdot 0^{3}101124$	$\cdot 0^{4}2598$
·00541992	·00146669	$\cdot 0^{3}38843$	$\cdot 0^{3}101124$	$\cdot 0^{4}2598$
$\cdot 0^{3}19614$	$\cdot 0^{4}4308$	$\cdot 0^{5}956$	$\cdot 214.10^{-5}$	$\cdot 0^{6}48$
$\cdot 0^{3}19614$	$\cdot 0^{4}4308$	$\cdot 0^{5}956$	$\cdot 0^{5}214$	$\cdot 0^{6}48$
·01003669	·00280593	$\cdot 0^{3}76343$	$\cdot 0^{3}20457$	$\cdot 0^{4}5595$
$\cdot 0^{3}11131$	$\cdot 0^{4}2489$	$\cdot 0^{5}602$	$\cdot 0^{5}129$	$\cdot 0^{6}30$
·04557816	·01640260	·00560807	·00184307	$\cdot 0^{3}58600$
·00267934	$\cdot 0^{3}74618$	$\cdot 0^{3}203191$	$\cdot 0^{4}5448$	$\cdot 0^{4}1437$
·04289882	·01565642	·00540488	·00179059	$\cdot 0^{3}57163$
·03709355	·01370707	·00478334	·00159958	$\cdot 0^{3}51482$
$\cdot 0^{4}3803$	$\cdot 0^{5}849$	$\cdot 0^{5}192$	$\cdot 0^{6}44$	$\cdot 0^{6}10$
·03705553	·01369858	·00478142	·001599139	$\cdot 0^{3}51472$

3·8 The Coulomb Integrals.

As was pointed out in section 3·4 when spot values of the integrals were computed the labour involved in the Barnett and Coulson evaluation is considerable when only a desk machine is available. Early on in this project several attempts were made to use the original Z method as outlined in Barnett and Coulson (1951a) but the great number of auxiliary functions and tables which had to be calculated and constructed proved the method uneconomic and time consuming.

The coulomb integrals are those appearing in the summation

$$C = 4\sum_{ii'jj'=1}^{5} C(a_i b_j :: a_{i'} b_{j'}) \quad \text{or} \quad 4\sum C(a_i a_{i'} :: b_j b_{j'})$$

to facilitate comparison with Roothaan. This totals 625 terms, but the number of different integrals is reduced since the atoms centred on a and b are symmetric and identical resulting in $(a_i a_i :: b_j b_j) = (a_j a_j :: b_i b_i)$. Besides many of the integrals are zero on integration of the angular component leaving in all 36 different integrals of which we have chosen 14.

$C_1 = (1s_a\ 1s_a :: 1s_b\ 1s_b)$

$C_2 = (1s_a\ 1s_a :: 2s_b\ 2s_b)$

$C_3 = (1s_a\ 1s_a :: 2p_{zb} 2p_{zb})$

$C_4 = (1s_a\ 1s_a :: 2p_{xb} 2p_{xb})$

$C_5 = (1s_a\ 1s_a :: 2p_{yb} 2p_{yb})$

$C_6 = (2s_a\ 2s_a :: 2s_b\ 2s_b)$

$C_7 = (2s_a\ 2s_a :: 2p_{zb} 2p_{zb})$

$C_8 = (2s_a\ 2s_a :: 2p_{xb} 2p_{xb})$

$C_9 = (2s_a\ 2s_a :: 2p_{yb} 2p_{yb})$

$C_{10} = (2p_{za} 2p_{za} :: 2p_{zb} 2p_{zb})$

$C_{11} = (2p_{za} 2p_{za} :: 2p_{xb} 2p_{xb})$

$C_{12} = (2p_{za} 2p_{za} :: 2p_{yb} 2p_{yb})$

$C_{13} = (2p_{xa} 2p_{xa} :: 2p_{xb} 2p_{xb})$

$C_{14} = (2p_{xa} 2p_{xa} :: 2p_{yb} 2p_{yb})$

We must note too that the 2s function, as defined in chapter 2, is the difference of two terms,

$$2s = H\,2s' - H'\,1s'$$

where $H = 1{\cdot}039$, $H' = 0{\cdot}2559$.

The integrals thus affected are C_2, C_6, C_7, C_8, and C_9

$$\begin{aligned} C_2 &= (\,1s_a\,1s_a : (\,H\,2s'_b - H'\,1s'_b\,)(\,H\,2s'_b - H'\,1s'_b\,)\,) \\ &= H^2(1s_a1s_a:2s'_b2s'_b) - 2HH'(1s_a1s_a:1s'_b2s'_b) + H'^2(1s_a1s_a:1s'_b1s'_b) \\ &= H^2\,C_{2.1} - 2HH'\,C_{2.2} + H'^2\,C_{2.3} \end{aligned}$$

This follows since there is only one centre of integration involved on the right hand side of the colon; i.e.

$$(1s_a1s_a:1s'_b2s'_b) = (1s_a1s_a:2s'_b1s'_b)$$

$$\begin{aligned} C_6 &= ((H2s'_a - H'1s'_a)(H2s'_a - H'1s'_a) : (H2s'_b - H'1s'_b)(H2s'_b - H'1s'_b)) \\ &= H^4(2s'_a2s'_a:2s'_b2s'_b) - 4H^3H'(2s'_a2s'_a:1s'_b2s'_b) + 2H^2H'^2(2s'_a2s'_a:1s'_b1s'_b) \\ &\quad + 4H^2H'^2(1s'_a2s'_a:1s'_b2s'_b) - 4HH'^3(1s'_a1s'_a:1s'_b2s'_b) + H'^4(1s'_a1s'_a:1s'_b1s'_b) \\ &= H^4\,C_{6.1} - 4H^3H'\,C_{6.2} + 2H^2H'^2\,C_{6.3} \\ &\qquad + 4H^2H'^2\,C_{6.4} - 4HH'^3\,C_{6.5} + H'^4\,C_{6.6} \end{aligned}$$

taking into account the reason given above, and because the value of the integral is not altered by complete interchange of the centre of integration; i.e.

$$(a_ia_i:b_jb_j) = (b_jb_j:a_ia_i).$$

$$
\begin{aligned}
C_7 &= \left((H2s'_a - H'1s'_a)\,(H2s'_a - H'1s'_a) : 2p_{zb}2p_{zb} \right) \\
&= H^2(2s'_a2s'_a:2p_{zb}2p_{zb}) - 2HH'(1s'_a2s'_a:2p_{zb}2p_{zb}) + H'^2(1s'_a1s'_a:2p_{zb}2p_{zb}) \\
&= H^2\,C_{7.1} - 2HH'\,C_{7.2} + H'^2\,C_{7.3}
\end{aligned}
$$

$$
\begin{aligned}
C_8 &= H^2(2s'_a2s'_a:2p_{xb}2p_{xb}) - 2HH'(1s'_a2s'_a:2p_{xb}2p_{xb}) + H'^2(1s'_a1s'_a:2p_{xb}2p_{xb}) \\
&= H^2\,C_{8.1} - 2HH'\,C_{8.2} + H'^2\,C_{8.3}
\end{aligned}
$$

$$
\begin{aligned}
C_9 &= H^2(2s'_a2s'_a:2p_{yb}2p_{yb}) - 2HH'(1s'_a2s'_a:2p_{yb}2p_{yb}) + H'^2(1s'_a1s'_a:2p_{yb}2p_{yb}) \\
&= H^2\,C_{9.1} - 2HH'\,C_{9.2} + H'^2\,C_{9.3}
\end{aligned}
$$

The wave functions of $2p_x$ and $2p_y$ are identical except for the ϕ component which is $\cos\phi$ in one and $\sin\phi$ in the other. In these integrals they always appear as

$$\int_0^{2\pi} \cos^2\phi \qquad \text{or} \qquad \int_0^{2\pi} \sin^2\phi$$

which give the same result. The following integrals then are equal,

$$C_4 = C_5 \qquad C_{8.1} = C_{9.1} \qquad C_{8.2} = C_{9.2}$$

$$C_{8.3} = C_{9.3} \qquad C_{11} = C_{12}.$$

Each of these integrals is tabulated as a function of the Roothaan charge distributions e.g. $(1S_a:3S_b)$ whose coefficients are

$$(1+\tau_a)^{c/2}(1-\tau_a)^{d/2}(1+\tau_b)^{e/2}(1-\tau_b)^{f/2}$$

which is abbreviated to (cdef). In many cases the τ_a and τ_b are $= 0$.

Table 3·6. The Coulomb integrals in terms of the charge distributions.

$C_1 = (1s_a\,1s_a : 1s_b\,1s_b) = (3333)\,(1S_a : 1S_b)$

$C_{2.1} = (1s_a\,1s_a : 2s'_b\,2s'_b) = (3355)\,(1S_a : 3S_b)$

$C_{2.2} = (1s_a\,1s_a : 1s'_b\,1s'_b) = (3335)\,\tfrac{1}{2}\sqrt{3}\,(1S_a : 2S_b)$

$C_{2.3} = (1s_a\,1s_a : 1s'_b\,1s'_b) = (3333)\,(1S_a : 1S_b)$

$C_3 = (1s_a\,1s_a : 2p_{zb}2p_{zb}) = (3355)\left[(1S_a : 3S_b) + 3(1S_a : 3D\Sigma)\right]$

$C_4 = (1s_a\,1s_a : 2p_{xb}2p_{xb}) = (3355)\left[(1S_a : 3S_b) - \tfrac{3}{2}(1S_a : 3D\Sigma_b)\right]$

$C_{6.1} = (2s'_a\,2s'_a : 2s'_b\,2s'_b) = (5555)\,(3S_a : 3S_b)$

$C_{6.2} = (1s'_a\,2s'_a : 2s'_b\,2s'_b) = (3555)\,\tfrac{1}{2}\sqrt{3}\,(2S_a : 3S_b)$

$C_{6.3} = (1s'_a\,1s'_a : 2s'_b\,2s'_b) = (3355)\,(1S_a : 3S_b)$

$C_{6.4} = (1s'_a\,2s'_a : 1s'_b\,2s'_b) = (3535)\,\tfrac{3}{4}(2S_a : 2S_b)$

$C_{6.5} = (1s'_a\,1s'_a : 1s'_b\,2s'_b) = (3335)\,\tfrac{1}{2}\sqrt{3}\,(1S_a : 2S_b)$

$C_{6.6} = (1s'_a\,1s'_a : 1s'_b\,1s'_b) = (3333)\,(1S_a : 1S_b)$

$C_{7.1} = (2s'_a\,2s'_a : 2p_{zb}2p_{zb}) = (5555)\left[(3S_a : 3S_b) + 3(3S_a : 3D\Sigma_b)\right]$

$C_{7.2} = (1s'_a\,2s'_a : 2p_{zb}2p_{zb}) = (3555)\,\tfrac{1}{2}\sqrt{3}\left[(2S_a : 3S_b) + 3(2S_a : 3D\Sigma_b)\right]$

$C_{7.3} = (1s'_a\,1s'_a : 2p_{zb}2p_{zb}) = (3355)\left[(1S_a : 3S_b) + 3(1S_a : 3D\Sigma_b)\right]$

$C_{8.1} = (2s'_a\,2s'_a : 2p_{xb}2p_{xb}) = (5555)\left[(3S_a : 3S_b) - \tfrac{3}{2}(3S_a : 3D\Sigma_b)\right]$

$C_{8.2} = (1s'_a\,2s'_a : 2p_{xb}2p_{xb}) = (3555)\,\tfrac{1}{2}\sqrt{3}\left[(2S_a : 3S_b) - \tfrac{3}{2}(2S_a : 3D\Sigma_b)\right]$

$C_{8.3} = (1s'_a\,1s'_a : 2p_{xb}2p_{xb}) = (3355)\left[(1S_a : 3S_b) - \tfrac{3}{2}(1S_a : 3D\Sigma_b)\right]$

$C_{10} = (2p_{za}2p_{za} : 2p_{zb}2p_{zb}) = (5555)\left[(3S_a : 3S_b) + 3(3S_a : 3D\Sigma_b) + 3(3D\Sigma_a : 3S_b)\right.$
$\left. + 9(3D\Sigma_a : 3D\Sigma_b)\right]$

$C_{11} = (2p_{za}2p_{za} : 2p_{xb}2p_{xb}) = (5555)\left[(3S_a : 3S_b) - \tfrac{3}{2}(3S_a : 3D\Sigma_b) + 3(3D\Sigma_a : 3S_b)\right.$
$\left. - \tfrac{9}{2}(3D\Sigma_a : 3D\Sigma_b)\right]$

$C_{13} = (2p_{xa}2p_{xa} : 2p_{xb}2p_{xb}) = (5555)\left[(3S_a : 3S_b) - \tfrac{3}{2}(3S_a : 3D\Sigma_b) - 3/2(3D\Sigma_a : 3S_b)\right.$
$\left. + 9/4(3D\Sigma_a : 3D\Sigma_b) + 27/4(3D\ _a : 3D\Delta_b)\right]$

$C_{14} = (2p_{xa}2p_{xa} : 2p_{yb}2p_{yb}) = (5555)\left[(3S_a : 3S_b) - \tfrac{3}{2}(3S_a : 3D\Sigma_b) - 3/2(3D\Sigma_a : 3S_b)\right.$
$\left. + 9/4(3D\Sigma_a : 3D\Sigma_b) - 27/4(3D\Delta_a : 3D\Delta_b)\right]$

Proceeding now to the details of the calculation. In each case the parameters and the formulae will be given, the main numerical values being collected in Table 3·12 at the end of the section. Subsidiary tables will be inserted at the appropriate places for the calculation of integrals which are the sum or difference of charge distributions.

k values will be given in preference to $\rho = k R$.

$$C_1 = (1S_a:1S_b) = 1/R\left[1 - (1 + 11/8\,\rho + 3\rho^2/4 + \rho^3/6)\,e^{-2\rho}\right]$$

where $\tau = 0$, $\underline{k} = k_a = k'_a = k_b = k'_b = 9{\cdot}66$

$$\begin{aligned} C_{2\cdot1} = (1S_a:3S_b) = 1/R\Big[1 &- (1-K)^3\left\{(1-5K-4K^2)/16 - K\rho_a/8\right\}e^{-2\rho a} \\ &- (1+K)^2\left\{(15-22K-15K^2-4K^3)/16 + 3(3-3K+K^2)\rho_b/8 + (2-K)\rho_b^2/4 \right. \\ &\left. + \rho_b^3/12\right\}e^{-2\rho b}\Big] \end{aligned}$$

where $\underline{k} = 6{\cdot}297$, $k_a = k'_a = 9{\cdot}66$, $k_b = k'_b = 2{\cdot}934$,

$\tau_a = \tau_b = 0$, $\tau = 0{\cdot}534064$, $K = 1{\cdot}203249$.

$$\begin{aligned} C_{2\cdot2} = \tfrac{1}{2}\sqrt{3}\,(1+\tau_b)\,(1-\tau_b)\,(1S_a:2S_b) = \\ 0{\cdot}2733493/R\Big[1 &- (1-K)^2\left\{(1-K-K^2)/4 + (1-2K)\rho_a/12\right\}e^{-2\rho a} \\ &- (1+K)^2\left\{(3-3K+K^2)/4 + (2-K)\rho_b/3 + \rho_b^2/6\right\}e^{-2\rho b}\Big] \end{aligned}$$

where $\underline{k} = 7{\cdot}806$, $k_a = k'_a = 9{\cdot}66$, $k_b = 8{\cdot}97$, $k'_b = 2{\cdot}934$,

$\tau_a = 0$, $\tau_b = 0{\cdot}50705645$, $\tau = 0{\cdot}2375096$, $K = 2{\cdot}223933$.

$$\begin{aligned} C_{2\cdot3} = (1S_a:1S_b) = 1/R\Big[1 &- (1-K)^2\left\{(2+K)/4 + \rho_a/4\right\}e^{-2\rho a} \\ &- (1-K)^2\left\{(2+K)/4 + \rho_b/4\right\}e^{-2\rho b}\Big] \end{aligned}$$

where $\underline{k} = 9{\cdot}315$, $k_a = k'_a = 9{\cdot}66$, $k_b = k'_b = 8{\cdot}97$

$\tau_a = \tau_b = 0$, $\tau = 0{\cdot}037037$, $K = 13{\cdot}5185185$.

$$C_3 = (1S_a{:}3S_b) + 3(1S_a{:}3D\Sigma_b)$$

$$C_4 = (1S_a{:}3S_b) - \tfrac{3}{2}(1S_a{:}3D\Sigma_b)$$

These two integrals can be done together, Table 3·7: let us put

$$C_1^* = (1S_a{:}3S_b) = 1/R\Big[1 - (1-K)^3\Big\{\frac{(1-5K-4K^2)}{16} - \frac{K}{8}\rho_a\Big\}e^{-2\rho_a}$$
$$- (1+K)^2\Big\{\frac{(15-22K-15K^2-4K^3)}{16} + \frac{3(3-3K+K^2)}{8}\rho_b + \frac{(2-K)}{4}\rho_b^2 + \frac{\rho_b^3}{12}\Big\}e^{-2\rho_b}\Big]$$

and

$$C_2^* = (1S_a{:}3D\Sigma_b) = \frac{\underline{k}}{(1-\tau)^2\,\rho^3}\Big[1 - (1-K)^4\Big\{\frac{(3+2K)}{16}(1+2\rho_a) + \frac{(7+4K)}{24}\rho_a^2 + \frac{\rho_a^3}{12}\Big\}e^{-2\rho_a}$$
$$-(1+K)^2\Big\{\frac{(15-16K+9K^2-2K^3)}{16}(1+2\rho_b) + \frac{(37-42K+21K^2-4K^3)}{24}\rho_b^2$$
$$+ \frac{(11-10K+3K^2)}{12}\rho_b^3 + \frac{(2-K)}{6}\rho_b^4 + \rho_b^5/18\Big\}e^{-2\rho_b}\Big]$$

where $\underline{k} = 6{\cdot}27$, $k_a = k'_a = 9{\cdot}66$, $k_b = k'_b = 2{\cdot}88$

$\tau_a = \tau_b = 0$, $\tau = 0{\cdot}5406699$, $K = 1{\cdot}1951136$.

$$C_{6.2} = \tfrac{1}{2}\sqrt{3}\,(1+\tau_a)\,(1-\tau_a)\,(2S_a{:}3S_b)$$
$$= 0{\cdot}2735495/R\Big[1 - (1-K)^3\Big\{\frac{(11-19K-44K^2-20K^3)}{48} + \frac{(1-5K-4K^2)}{12}\rho_a - \frac{K\rho_a^2}{12}\Big\}e^{-2\rho_a}$$
$$-(1+K)^2\Big\{\frac{(57-22K-39K^2+56K^3-20K^4)}{48} + \frac{(6+K-8K^2+4K^3)}{8}\rho_b$$
$$+ \frac{(1+K-K^2)}{4}\rho_b^2 + \frac{(1+2K)}{36}\rho_b^3\Big\}e^{-2\rho_b}\Big]$$

where $\underline{k} = 4{\cdot}443$, k_a 0 $8{\cdot}97$, $k'_a = k_b = k'_b = 2{\cdot}934$,

$\tau_a = 0{\cdot}50705645$, $\tau_b = 0$, $\tau = 0{\cdot}33963538$, $K = 1{\cdot}6419847$.

$$C_{6.1} = (3S_a{:}3S_b) = 1/R\Big[1 - (1 + 1{\cdot}636719\rho + 1{\cdot}273437\rho^2 + 0{\cdot}619791\rho^3$$
$$+ 0{\cdot}2083\rho^4 + 0{\cdot}05\rho^5 + {\cdot}0083\rho^6 + {\cdot}0^3 7936\rho^7)\,e^{-2\rho}\Big]$$

where $\underline{k} = k_a = k'_a = k_b = k'_b = 2{\cdot}934$, $\tau = 0$

Table 3·7

R	$(1S_a:3S_b)$	$3(1S_a:3D_b)$	C_3	C_4
0·5	1·2003613	·21961869	1·4199800	1·0905520
1·0	·9229069	·18748947	1·1103964	·82916217
1·5	·6595653	·09232755	·75189287	·61340155
2·0	·4993964	·04397964	·54337607	·47740661
2·5	·3999519	·02505093	·42500283	·38842644
3·0	·33332968	·01338858	·34671826	·32663539
3·5	·28571421	·00843538	·29414549	·28149233
4·0	·25000000	·00565137	·25565137	·24717432
4·5	·22222222	·00396915	·22619137	·22023765
5·0	·20000000	·00289353	·20289353	·19855325

Table 3·8

R	$(3S_a:3S_b)$	$3(3S_a:3D_b)$	$C_{7.1}$	$C_{8.1}$
0·5	·97416412	·02318900	·99735312	·96256962
1·0	·80658959	·05574962	·86233899	·77871459
1·5	·63057602	·05402348	·68459950	·60356428
2·0	·49409836	·05632542	·55042588	·47593575
2·5	·39915401	·02182930	·42098331	·38823941
3·0	·33322498	·01322141	·34644649	·32661428
3·5	·28570158	·00841497	·29411655	·28149414
4·0	·24999862	·00564908	·25564770	·24717418
4·5	·22222222	·00396891	·22619113	·22023777
5·0	·20000000	·00289349	·20289349	·19855325

$$C_{6.3} = (1S_a:3S_b) = 1/R \Big[1 - (1-K)^3 \Big\{ (1-5K-4K^2)/16 - K\rho_a/8 \Big\} e^{-2\rho a}$$
$$- (1+K)^2 \Big\{ \frac{(15-22K-15K^2-4K^3)}{16} + \frac{3(3-3K+K^2)}{8}\rho_b + \frac{(2-K)}{4}\rho_b^2 + \rho_b^3 \Big\} e^{-2\rho b} \Big]$$

where $\underline{k} = 5{\cdot}952$, $k_a = k_a' = 8{\cdot}97$, $k_b = k_b' = 2{\cdot}934$,

$\tau_a = \tau_b = 0$, $\tau = 0{\cdot}50705645$, $K = 1{\cdot}2396117$.

$$C_{6.4} = 0{\cdot}75(1+\tau_a)^3(1-\tau_a)^5 \ (2S_a:2S_b)$$
$$= 0{\cdot}07471982/R \Big[1 - (1 + 1{\cdot}5416\rho + 1{\cdot}083\rho^2 + 4\rho^3/9 + \rho^4/9 + 2\rho^5/135) e^{-2\rho} \Big]$$

where $\underline{k} = 5{\cdot}952$, $k_a = k_b = 8{\cdot}97$, $k_a' = k_b' = 2{\cdot}934$,

$\tau_a = \tau_b = 0{\cdot}50705645$, $\tau = 0$

$$C_{6.5} = \tfrac{1}{2}\sqrt{3}\ (1+\tau_b)^{\frac{3}{2}}(1-\tau)^{\frac{5}{2}}(1S_a:2S_b)$$
$$= 0.2733493/R \Big[1 - (1-K)^2 \Big\{ 0{\cdot}25(1-K-K^2) + (1-2K)\rho_a/12 \Big\} e^{-2\rho a}$$
$$- (1+K)^2 \Big\{ \frac{(3-3K+K^2)}{4} + \frac{(2-K)}{3}\rho_b + \rho_b^2/6 \Big\} e^{-2\rho b} \Big]$$

where $\underline{k} = 7{\cdot}461$, $k_a = k_a' = 8{\cdot}97$, $k_b = 8{\cdot}97$, $k_b' = 2{\cdot}934$,

$\tau_a = 0$, $\tau_b = 0{\cdot}50705645$, $\tau = 0{\cdot}2022517$, $K = 2{\cdot}5732929$.

$$C_{6.6} = (1S_a:1S_b) = 1/R \Big[1 - (1 + 1{\cdot}375\rho + 0{\cdot}75\rho^2 + \rho^3/6)\ e^{-2\rho} \Big]$$

where $\underline{k} = k_a = k_a' = k_b = k_b' = 8{\cdot}97$, $\tau = 0$.

$$C_{7.1} = (3S_a:3S_b) + 3(3S_a:3D\Sigma_b)$$
$$C_{8.1} = (3S_a:3S_b) - \tfrac{5}{2}(3S_a:3D\Sigma_b)$$

These two integrals can be computed concurrently (see table 3·8) since the parameters are the same:

$k_a = k_a' = 2{\cdot}934$, $k_b = k_b' = 2{\cdot}88$, $\therefore\ \tau = 0{\cdot}0092879$.

It is seen that the value of τ is very small. By putting

$$\tau = \tau_a = \tau_b = 0, \quad \text{and} \quad \underline{k} = 2{\cdot}88,$$

it was confirmed that the error incurred by such a step at $R = 1{\cdot}0$ is in the region of $0{\cdot}0002$ in 0.2750 or less than $0{\cdot}1\%$. Taking therefore,

$$C_1^* = (3S_a:3S_b) = 1/R\Big[1 - (1 + 1{\cdot}636718\rho + 1{\cdot}2734375\rho^2 + {\cdot}61979166\rho^3$$
$$+ {\cdot}2083\rho^4 + {\cdot}05\rho^5 + {\cdot}0083\rho^6 + {\cdot}0^3 79365\rho^7)\, e^{-2\rho}\Big]$$

$$C_2^* = (3S_a:3D\Sigma_b) = \underline{k}/R^3\Big[1 - (1 + 2\rho + 2\rho^2 + 4\rho^3/3 + 2\rho^4/3 + {\cdot}253277\rho^5$$
$$+ {\cdot}086111\rho^6 + {\cdot}0226191\rho^7 + {\cdot}004497\rho^8 + {\cdot}0^3 52910\rho^9\, e^{-2\rho}\Big]$$

$$C_{7.2} = \tfrac{1}{2}\sqrt{3}\,(1+\tau_a)^{\frac{5}{2}}(1-\tau_a)^{\frac{5}{2}}\Big[(2S_a:3S_b) + 3(2S_a:3D\Sigma_b)\Big]$$
$$C_{3.2} = \tfrac{1}{2}\sqrt{3}\,(1+\tau_a)^{\frac{5}{2}}(1-\tau_a)^{\frac{5}{2}}\Big[(2S_a:3S_b) - \tfrac{3}{2}(2S_a:3D\Sigma_b)\Big]$$

Again these integrals will be done together by putting

$$C_1^* = (2S_a:3S_b) = 1/R\Big[1 - (1-K)^3\Big\{\frac{(11-19K-44K^2-20K^3)}{48} + \frac{(1-5K-4K^2)}{12}\rho_a - \frac{K\rho_a^2}{12}\Big\}e^{-2\rho_a}$$
$$-(1+K)^2\Big\{\frac{(37-22K-39K^2+56K^3-20K^4)}{48} + \frac{(6+K-8K^2+4K^3)}{8}\rho_b$$
$$+\frac{(1+K-K^2)}{4}\rho_b^2 + \frac{(1+2K)}{36}\rho_b^3\Big\}\, e^{-2\rho_b}\Big]$$

$$C_2^* = (2S_a:3D\Sigma_b) = \underline{k}/(1-\tau)^2\rho^3\Big[1 - (1-K)^4\Big\{(19+26K+10K^2)(1+2\rho_a)/48$$
$$+ \frac{(49+60K+20K^2)}{72}\rho_a^2 + \frac{(11+8K)}{36}\rho_a^3 + \rho_a^4/18\Big\}e^{-2\rho_a}$$
$$-(1+K)^2\Big\{\frac{(29-8K-53K^2+54K^3-10K^4)}{48}(1+2\rho_b) + \frac{(79-10K-93K^2+80K^3-20K^4)}{72}\rho_b^2$$
$$+ \frac{(7+2K-9K^2+4K^3)}{12}\rho_b^3 + \frac{(1+K-K^2)}{6}\rho_b^4 + \frac{(1+2K)}{54}\rho_b^5\Big\}\, e^{-2\rho_b}\Big]$$

where $\underline{k} = 4{\cdot}416$, $k_a = 8{\cdot}97$, $k_a' = 2{\cdot}934$, $k_b = k_b' = 2{\cdot}88$

$\tau_a = {\cdot}50705645$, $\tau_b = 0$ $\tau = {\cdot}3478261$, $K = 1{\cdot}611413$.

The numerical results are in Table 3·9.

$$C_{7.3} = (1S_a:3S_b) + 3(1S_a:3D\Sigma_b)$$

$$C_{8.3} = (1S_a:3S_b) - \frac{3}{2}(1S_a:3D\Sigma_b)$$

Let us put

$$C_1^* = 1/R\Big[1 - (1-K)^3\Big\{(1-5K-4K^2)/16 - K\rho_a/8\Big\}e^{-2\rho_a} - (1+K)^2\Big\{\frac{(15-22K-15K^2-4K^3)}{16} + 3\frac{(5-3K+K^2)}{8}\rho_b + \frac{(2-K)}{4}\rho_b^2 + \frac{\rho_b^3}{12}\Big\}e^{-2\rho_b}\Big]$$

$$C_2^* = (1S_a:3D\Sigma_b) = \frac{\underline{k}}{(1-\tau)^2\rho^3}\Big[1 - (1-K)^4\Big\{\frac{(5+2K)}{16}(1+2\rho_a) + \frac{(7+4K)}{24}\rho_a^2 + \frac{\rho_a^3}{12}\Big\}e^{-2\rho_a}$$
$$-(1+K)^2\Big\{\frac{(13-16K+9K^2-2K^3)}{16}(1+2\rho_b) + \frac{(37-42K+21K^2-4K^3)}{24}\rho_b^2$$
$$+ \frac{(11-10K+3K^2)}{12}\rho_b^3 + \frac{(2-K)}{6}\rho_b^4 + \frac{\rho_b^5}{18}\Big\}e^{-2\rho_b}\Big]$$

where $\underline{k} = 5{\cdot}925$, $k_a = k_a' = 8{\cdot}97$, $k_b = k_b' = 2{\cdot}88$,

$\tau_a = \tau_b = 0$, $\tau = 0{\cdot}51392405$, $K = 1{\cdot}2298684$.

The numerical results have been collected in Table 3·10

For C_{10}, C_{11}, C_{13} and C_{14} we must first compute the five auxiliary charge distributions which will be

$$C_1^* = (3S_a:3S_b)$$

$C_2^* = (3S_a:3D\Sigma_b)$ both of which have already been calculated for the same parameters in the integrals $C_{7.1}$ and $C_{8.1}$ and will not be given here again.

$$C_3^* = (3D\Sigma_a:3D\Sigma_b) = 6\underline{k}/\rho^5\Big[1 - (1+2\rho+2\rho^2+4\rho^3/3+2\rho^4/3+{\cdot}26614\rho^5+{\cdot}087847\rho^6$$
$$+{\cdot}024658\rho^7+{\cdot}00626102\rho^8+{\cdot}0015873\rho^9+{\cdot}0^3 3821\rho^{10}+{\cdot}0^4 588\rho^{11})\,e^{-2\rho}\Big]$$

Table 3·9

R	$g(2S_a:3S_b)$	$3g(2S_a:3D\Sigma_b)$	$C_{7.2}$	$C_{8.2}$
0·5	·33496568	·03949539	·37446112	·31521799
1·0	·24917312	·04359175	·29276497	·22737724
1·5	·17971925	·02402136	·20374061	·16770862
2·0	·13644229	·01188409	·14832638	·13050025
2·5	·10932011	·00628789	·11560825	·10617617
3·00911	·09111488	·00365864	·09477353	.08928556
3·5	·07809968	·00230572	·08040540	·07694682
4·0	·06833752	·00154479	·06988211	·06756493
4·5	·06074429	·00108497	·06182925	·06020181
5·0	·05466986	$·0^3 79094$	·05546080	·05427439

Table 3·10

R	$(1S_a:3S_b)$	$3(1S_a:3D\Sigma_b)$	$C_{7.3}$	$C_{8.3}$
0·5	1·2788808	·21494612	1·49382692	1·1714078
1·0	·92673793	·18609296	1·11283088	·83369145
1·5	·65972162	·09213219	·75185381	·61365552
2·0	·49940039	·04395904	·54335943	·47742087
2·5	·39995176	·02304906	·42300082	·38842723
3·0	·33332965	·01338842	·34671807	·32663544
3·5	·28571428	·00843369	·29414965	·28149660
4·0	·25000000	·00565137	·25565137	·24717432
4·5	·22222222	·00396915	·22619137	·22023765
5·0	·20000000	·00289353	·20289353	·19855324

g = 0·2733493.

$$C_4^* = (3D\Delta_a:3D\Delta_b) = \underline{k}/\rho^5\Big[1 - (1+2\rho+2\rho^2+4\rho^3/3+2\rho^4/3+{\cdot}2635416\rho^5+{\cdot}082638\rho^6$$
$$+{\cdot}01964286\rho^7+{\cdot}0031746\rho^8+{\cdot}0^3 26455\rho^9)\,e^{-2\rho}\Big]$$

$C_5^* = (3D\Sigma_a:3S_b) = (3S_a:3D\Sigma_b)$ for this case of $\tau = 0$ and where for the above five integrals

$$\tau = 0, \quad \underline{k} = k_a = k'_a = k_b = k'_b = 2{\cdot}88.$$

Only the C^* integrals will be listed in Table 3·11; the main integrals will be found in Table 3·12 at the end of the section.

$$C_{10} = C_1^* + 6C_2^* + 9C_3^*$$
$$C_{11} = C_1^* + \tfrac{3}{2}C_2^* - \tfrac{9}{2}C_3^*$$
$$C_{13} = C_1^* - 3C_2^* + \tfrac{9}{4}C_3^* + \tfrac{27}{4}C_4^*$$
$$C_{14} = C_1^* - 3C_2^* + \tfrac{9}{4}C_3^* - \tfrac{27}{4}C_4^*$$

Table 3·11

R	$(3S_a:3S_b)$	$3(3S_a:3D_b)$	$9(3D_a:3D_b)$	$27/4\,(3D_a:3D_b)$
0·5	·97416411	·02513900	·02405564	·04479681
1·0	·80658939	·05574962	$-{\cdot}0^4 4764$	·02040467
1·5	·65057602	·05402348	·010449536	·00744535
2·0	·49409356	·03652543	·01021074	·00259173
2·5	·39915401	·02182930	·00591436	${\cdot}0^3 96247$
3·0	·33522491	·01322147	·00294449	${\cdot}0^3 40007$
3·5	·23570163	·00841497	·00145950	${\cdot}0^3 18293$
4·0	·24999362	·00564903	${\cdot}0^3 76258$	${\cdot}0^4 9456$
4·5	·22222222	·00396391	${\cdot}0^3 42495$	${\cdot}0^4 5319$
5·0	·20000000	·00289349	${\cdot}0^3 25113$	${\cdot}0^4 3139$

Table 3·12. The Coulomb Integrals: numerical values.

R	0·5	1·0	1·5	2·0	2·5
C_1	1·994397	·9999991	·6666666	·5000000	·4000000
$C_{2.1}$	1·2995731	·9320728	·6605563	·4995001	·3999619
$C_{2.2}$	·53262021	·2752383	·1822325	·1366747	·1093397
$C_{2.3}$	1·9925632	·9999983	·6666666	·5000000	·4000000
C_3	1·4199802	1·110396	·7518929	·5433761	·4230028
C_4	1·0905521	·8291622	·6134016	·4774066	·3884264
$C_{6.1}$	·98964013	·8146839	·6333183	·4947777	·3992862
$C_{6.2}$	·33907392	·2504649	·1799506	·1364737	·1093236
$C_{6.3}$	1.2959186	·9313683	·6604621	·49949052	·3999611
$C_{6.4}$	·13425320	·0745215	·0498115	·03735990	·0298879
$C_{6.5}$	·50155890	·2731719	·1822522	·1366747	·1093397
$C_{6.6}$	1·9905155	·9999969	·6666666	·5000000	·4000000
$C_{7.1}$	·99735312	·8623390	·6845995	·5504238	·4209833
$C_{7.2}$	·37446107	·2927649	·2037406	·1483264	·11560821
$C_{7.3}$	1·4938269	1·1128309	·7518538	·5433594	·42300083
$C_{8.1}$	·96256962	·7787146	·6035643	·4759357	·3882394
$C_{8.2}$	·31521800	·2273773	·1677036	·1305002	·1061762
$C_{8.3}$	1·1714077	·8336915	·6136555	·4774209	·3884272
C_{10}	1·0445983	·9180410	·7490726	·5769599	·4487275
C_{11}	·97373082	·8344882	·6523629	·5071557	·4071112
C_{13}	1·00178581	·7712326	·5866103	·4629174	·3797659
C_{14}	·91219219	·7304232	·5717196	·4577339	·3778410

3·0	3·5	4·0	4·5	5·0
·33333333	·28571428	·25000000	·22222222	·20000000
·33333052	·28571428	·25000000	·22222222	·20000000
·09111643	·07809863	·06833733	·06074429	·05466986
·33333333	·28571428	·25000000	·22222222	·20000000
·34671826	·29414542	·25565137	·22619137	·20289553
·32665539	·28149231	·24717436	·22023765	·19855325
·33324616	·28570461	·24999999	·22222222	·20000000
·09111522	·07809971	·06833732	·06074429	·05466986
·33333051	·28571428	·25000000	·22222222	·20000000
·02490661	·02134952	·01867995	·01660440	·01494596
·09111643	·07809863	·06833732	·06074429	·05466986
·33333333	·28571428	·25000000	·22222222	·20000000
·34644644	·29411657	·25564773	·22619112	·20289549
·09477353	·08040540	·06988211	·06182925	·05546082
·34671807	·29414965	·25565137	·22619137	·20289553
·32661422	·28149413	·24717411	·22023777	·19855325
·08928556	·07694682	·06756495	·06020181	·05427439
·32665544	·28149660	·24717432	·22023765	·19855324
·36261233	·30399104	·26205936	·23058502	·20603812
·33836345	·28917944	·25244193	·22399421	·20132122
·32113963	·27783444	·24463476	·21841273	·19720068
·32033951	·27746863	·24445742	·21830653	·19713792

3·9 The Hybrid Integrals.

While taking the hybrid integrals as a particular case it was intended to make a completely general approach to the computation of molecular integrals in a method applicable to the smaller type of electronic machine. Although the hybrid, coulomb and other integrals will be produced as 'by-products' of the exchange integral project now under consideration for the I B M type 704 electronic machine, it is often desirable to compute the integrals without going to the expense of applying the exchange type programme.

Examination shows that there are two principal functions occurring, viz. the $j_n(r)$ and $\zeta\,(r,R)$.

The $j_n(r)$ are simple polynomial type functions (see table 3·15) basically

$$e^{-r}(b_0 + b_1 r + b_2 r^2 + \ldots\ldots\ldots\ldots + b_m r^m)$$

while the $\zeta\,(r,R)$ are most adequately described in Barnett and Coulson(1951)

All the ζ_{mn} can be computed from the ζ_{on}

$$\zeta_{on}(1,r,R) = \gamma_n(1,r,R) = I_{n+\frac{1}{2}}(r)\, K_{n+\frac{1}{2}}(R) \quad \text{for} \quad r \leqslant R$$

$$= I_{n+\frac{1}{2}}(R)\, K_{n+\frac{1}{2}}(r) \quad \text{for} \quad r > R$$

where $I_{n+\frac{1}{2}}$ and $K_{n+\frac{1}{2}}$ are the well known bessel functions of the first and second kind respectively of imaginary argument and half integral order

$$I_{n+\frac{1}{2}}(r) = \frac{1}{\sqrt{2\pi r}} \quad e^{r}\sum_{j=0}^{n} \frac{(n+j)!}{j!\,(n-j)!\,2^j}\left(\frac{-1}{r}\right)^j \quad + (-1)^{n+1} e^{-r}\sum_{j=0}^{n} \frac{(n+j)!}{j!\,(n-j)!\,2^j}\left(\frac{1}{r}\right)^j$$

$$K_{n+\frac{1}{2}}(r) = (\pi/2r)^{\frac{1}{2}} e^{-r} \sum_{j=0}^{n} \frac{(n+j)!}{j!(n-j)!2^j} \left(\frac{1}{r}\right)^j$$

All the molecular except the exchange integrals arising from consideration of the first two electron orbits can be reduced to some function of the γ_n where n ranges from -1 to 4. It is expedient to compute not the $\gamma_n(r,R)$ themselves but $2\sqrt{rR}\,\gamma_n(r,R)$ and these are shown in table 3·14.

Table 3·13

Values of $j_n(r)$ for the first two orbits.

$$j_1(r) = 2 - (2+r)e^{-r}$$

$$j_2(r) = 6 - (6+4r+r^2)e^{-r}$$

$$j_3(r) = 24 - (24+18r+6r^2+r^3)e^{-r}$$

$$j_4(r) = 8 - (8+8r+4r^2+r^3)e^{-r}$$

$$j_5(r) = 40 - (40+40r+20r^2+6r^3+r^4)e^{-r}$$

$$j_6(r) = \frac{2}{3}\left[144 - (144+144r+72r^2+6r^3+6r^4+r^5)e^{-r}\right] + \frac{1}{3}r^2\left[24 - (24+18r+6r^2+r^3)e^{-r}\right]$$

$$j_7(r) = 144 - (144+144r+72r^2+6r^3+6r^4+r^5)e^{-r}$$

$$j_8(r) = \frac{1}{6}r^2\left[24 - (24+18r+6r^2+r^3)e^{-r}\right] - \frac{1}{6}\left[144 - (144+144r+72r^2+24r^3+6r^4+r^5)e^{-r}\right]$$

Figure 3·3

The general scheme of evaluation of the hybrid integrals

$$\begin{tikzcd}
\text{I} & & e^{\pm kr}(b_o \mp b_1 r^{\pm 1} + b_2 r^{\pm 2} \mp b_3 r^{\pm 3} + \dots\dots\dots) \arrow[dl] \arrow[dr] & & \text{I} \\
\text{IIa} & j_n(r) \arrow[d] & & \gamma_n^+ \text{ and } \gamma_n^- \arrow[d] & \text{IIb} \\
\text{IIIa} & K\, j_n(r)\, t^m\, e^{-k\Delta t} \arrow[ddddr] & & \gamma_n(r,R) \arrow[d] & \text{IIIb} \\
 & & & p_n(r,R) \arrow[d] & \text{IV} \\
 & & & q_n(r,R) \arrow[d] & \text{V} \\
 & & & \text{the several functions of } \gamma,\ p, \text{ and } q \arrow[dl] & \text{VI} \\
\text{VII} & & \text{The Hybrid Integrals} & & \text{VII}
\end{tikzcd}$$

Table 3·14

γ_n for the first two orbits: initial values are for $r \leq R$
latter values for $r > R$

$$2\sqrt{rR}\ \gamma_{-1}(r,R) = (e^{r} + e^{-r})\ e^{-R}$$
$$= (e^{R} + e^{-R})\ e^{-r}$$

$$2\sqrt{rR}\ \gamma_{0}(r,R) = (e^{r} - e^{-r})\ e^{-R}$$
$$= (e^{R} - e^{-R})\ e^{-r}$$

$$2\sqrt{rR}\ \gamma_{1}(r,R) = \left[e^{r}(1-\frac{1}{r}) + e^{-r}(1+\frac{1}{r})\right] e^{R}(1+1/R)$$
$$= \left[e^{R}(1-\frac{1}{R}) + e^{-R}(1+1/R)\right] e^{r}(1+\frac{1}{r})$$

$$2\sqrt{rR}\ \gamma_{2}(r,R) = \left[e^{r}(1-\frac{3}{r}+\frac{3}{r^2}) - e^{-r}(1+\frac{3}{r}+\frac{3}{r^2})\right] e^{-R}(1+\frac{3}{R}+\frac{3}{R^2})$$
$$= \left[e^{R}(1-\frac{3}{R}+\frac{3}{R^2}) - e^{-R}(1+\frac{3}{R}+\frac{3}{R^2})\right] e^{-r}(1+\frac{3}{r}+\frac{3}{r^2})$$

$$2\sqrt{rR}\ \gamma_{3}(r,R) = \left[e^{r}(1-\frac{6}{r}+\frac{15}{r^2}-\frac{15}{r^3}) + e^{-r}(1+\frac{6}{r}+\frac{15}{r^2}+\frac{15}{r^3})\right] e^{-R}(1+\frac{6}{R}+\frac{15}{R^2}+\frac{15}{R^3})$$
$$= \left[e^{R}(1-\frac{6}{R}+\frac{15}{R^2}-\frac{15}{R^3}) + e^{-R}(1+\frac{6}{R}+\frac{15}{R^2}+\frac{15}{R^3})\right] e^{-r}(1+\frac{6}{r}+\frac{15}{r^2}+\frac{15}{r^3})$$

$$2\sqrt{rR}\ \gamma_{4}(r,R) = \left[e^{r}(1-\frac{10}{r}+\frac{45}{r^2}-\frac{105}{r^3}+\frac{105}{r^4}) - e^{-r}(1+\frac{10}{r}+\frac{45}{r^2}+\frac{105}{r^3}+\frac{105}{r^4})\right]$$
$$\left[e^{-R}(1+\frac{10}{R}+\frac{45}{R^2}+\frac{105}{R^3}+\frac{105}{R^4})\right]$$
$$= \left[e^{R}(1-\frac{10}{R}+\frac{45}{R^2}-\frac{105}{R^3}+\frac{105}{R^4}) - e^{-R}(1+\frac{10}{R}+\frac{45}{R^2}+\frac{105}{R^3}+\frac{105}{R^4})\right]$$
$$\left[e^{-r}(1+\frac{10}{r}+\frac{45}{r^2}+\frac{105}{r^3}+\frac{105}{r^4})\right]$$

The most general function embracing both j and γ types is

$$e^{\pm kr}(b_0 \mp b_1 r^{\pm 1} + b_2 r^{\pm 2} \mp b_3 r^{\pm 3} + \dots\dots)$$

Several hybrid integrals were taken as illustrations and the general scheme for their evaluation is shown in figure 3·3.

In chapter 2 we wrote the hybrid integral symbolically

$$\begin{aligned} I_s &= I_s(a_i a_j :: a_{i'} b_{j'}) \\ &= N'_s \int_0^\infty K\, j_n(r)\; t^m\, e^{-k\Delta t}\; g(\zeta_{mn}(t,T)\,)\, dt \end{aligned}$$

which follows from Barnett and Coulson (1951a) on redefinition of terms. Since the ζ_{mn} are all greater by $2\sqrt{tT}$, this factor must be absorbed: therefore $N_1 = 2\sqrt{T}\, N'_s$ and the $t^{\frac{1}{2}}$ is no longer explicit. The g function of the above paper is split up in such a way that it is here a function of ζ_{mn} only. K is the factor unity or $k_4 R$: the argument of j_n is $r = 2k_a t/k_4$ and $k = k_3/k_4$. Table 3·15 shows the various integrals.

I The general function

$$e^{\pm kr}\,(b_0 \mp b_1 r^{\pm 1} + b_2 r^{\pm 2} + b_3 r^{\pm 3} + \ldots\ldots\ldots\ldots)$$

The computation in this section was performed on an I.B.M. 602A mechanical calculator and all work in subsequent sections on the I.B.M.626 type electronic machine. The initial quantities b_i, r, and $e^{\pm k\Delta r}$, were introduced into the machine which for each increment of r first formed the exponential by multiplication of the previous and the initial values. r was generated by simple addition of the Δr while the polynomial was built up in a cyclic process: finally the polynomial was multiplied by the exponential and the result punched on cards. It had been hoped to include a step to produce the $1/r$ in the same programme but this proved to be beyond the programme capacity of the machine. Consequently the polynomial of the inverse of r was done by reversing the order of the b_i,

Table 3.15

s	$a_i a_j a_{i'} b_{j'}$	$2\sqrt{T}\,N_i$	K	n	r	m	k	function of $\mathcal{J}_{mn}(t,T)$	T
+ 1	1s 1s 1s 1s	1	1	1	2t	0	1	p_o	8.97 9.66
+ 2	1s 1s 2s'2s'	1/3	1	1	6.585t	1	1	q_o	2.934
+ 3	$1s1s2_{px}2_{px}$	1/3	1	1	6.7083t	2	1	p_o-p_2	2.88
- 4.1	$1s1s2p_z2p_z$	1	1	1	6.7083t	2	1	$p_o-2/3(p_o-p_2)$	2.88
+ 4.2		1	2.88	1	6.7083t	1	1	p_1	2.88
+ 5	1s'2s'1s'2s'	0.095846	1	2	4.0573t	0	3.0573	q_o	2.934
+ 6	1s'2s'2s'2s'	0.030372	1	2	4.0573t	1	1	q_o	2.934
+ 7	$1s'2s'2p_x2p_x$	0.030372	1	2	$4.1\dot{3}t$	2	1	p_o-p_2	2.88
- 8.1	$1s'2s'2p_z2p_z$	0.0911164	1	2	$4.1\dot{3}t$	2	1	$p_o-2/3(p_o-p_2)$	2.88
+ 8.2		0.0911164	2.88	2	$4.1\dot{3}t$	1	1	p_1	2.88
+ 9	2s'2s'2s'2s'	1/36	1	3	2t	1	1	q_o	2.934
+ 10	$2s'2s'2p_x2p_x$	1/36	1	3	2.0375t	2	1	p_o-p_2	2.88
- 11.1	$2s'2s'2p_z2p_z$	1/12	1	3	2.0375t	2	1	$p_o-2/3(p_o-p_2)$	2.88
+ 11.2		1/12	2.88	3	2.0375t	1	1	p_1	2.88
+ 12.1	$2p_z2p_z2p_z2p_z$	1/8	2.88	8	2t	-1	1	p_1	2.88
+ 12.2		1/8	2.88	7	2t	-1	1	$\frac{1}{2}[p_1-2/5(p_1-p_3)]$	2.88
- 12.3		1/8	1	8	2t	0	1	$p_o-2/3(p_o-p_2)$	2.88
- 12.4		1/8	1	7	2t	0	1	$\frac{1}{2}[p_o-4/5(p_o-p_2)-\frac{8}{35}(p_2-p_4)]$	2.88

generating the positive power polynomial, and dividing that by the highest power of r appearing in the series. A detailed description of the machine technique will be found in Appendix II. The evaluation was carried out at intervals of 0·2 in the range 0 to 6·0 where it was considered that the integral would be negligible.

IIa The $j_n(r)$ functions.

They were simply obtained by subtracting the polynomials of section I from constants and in some cases multiplying by a further constant and power of r.

IIIa The $K\, j_n(r)\, t^m\, e^{-k\Delta t}$ functions.

The required powers of t multiplied by K where necessary were punched on the respective j cards and by merging with cards containing the exponential a simple multiplication procedure was sufficient to obtain the functions.

IIb The γ_n^+ and γ_n^- functions.

Referring to the table of γ functions it is evident that the technique of section I leads to a convenient definition of γ^+ and γ^-

$$\gamma^+(r) = e^{-kr}/r^m \quad (b_0 r^m + b_1 r^{m-1} + b_2 r^{m-2} + \ldots\ldots + b_m)$$

$$\gamma^-(r) = e^{kr}/r^m \quad (b_0 r^m - b_1 r^{m-1} + b_2 r^{m-2} - \ldots\ldots (-)^m b_m)$$

The functions were computed for the variable t in the range 0(0·2)6·0 and for the constants T.

IIIb The $\gamma_n(t,T)$ functions.

To proceed to the γ_n functions it is necessary to split t into the two ranges $0 < t < T$ and $T < t$ and multiply the γ^+ and γ^- as required from the γ table.

IV The $p_n(t,T)$ functions.

The higher order zeta functions are found from the γ's by convenient recurrence formulae: in the case of the p functions the following were used

$$
\begin{aligned}
p_{-1} &= (T+1)\,\gamma_{-1} - t\,\gamma_0 \\
p_0 &= (T+1)\,\gamma_0 - t\,\gamma_{-1} \\
p_1 &= (tT/3)(\gamma_0 - \gamma_2) \\
p_2 &= (tT/5)(\gamma_1 - \gamma_3) \\
p_3 &= (tT/7)(\gamma_2 - \gamma_4) \\
p_4 &= -7(t/T + T/t)\gamma_3 + 5\gamma_2 + 9\gamma_4 + p_2
\end{aligned}
$$

All the equations were easily handled on the machine using card programming.

V The only q_n appearing in the list of integrals is q_0 the relation for which is

$$
q_0 = (tT/1)(p_{-1} - p_1) - p_0
$$

VI The several functions of γ, p and q.

These several functions are listed in column 10 of table 3·15 and their simple form presents no difficulties in their computation.

VII The Hybrid Integrals.

The values of the hybrid integrals at the incremental points are then simple products of sections IIIa and VI and of N'_s. In many cases it was found that at $t = 6\cdot0$ the integrand had not reached negligible proportions and therefore allowance for the cut off in the final integration will have to be made. Since the maximum of the integrand does not necessarily occur at any of the incremental points, Simpson's integration rule will not be valid. However for comparison such an integration was carried out.

Results:

It was a sufficiently major undertaking to compute the 12 selected hybrid integrals for one value of R (R = 1 was the value chosen). Table 5·16 shows the results of the Simpson Rule integration which in every case agreed with a series of planimeter readings on the graphed points. From the form of the graphs it was clear that the cut off error was very small except of course for I_1($T = 9\cdot66$ and $8\cdot97$) where the maximum of the integrand was not reached.

The curve of the integrands was not smooth since the maxima of the component functions (IIIa and VI of figure 5·5) did not coincide. This resulted in a tendency for the fairly sharp peaks to separate and to lower the accuracy of the integration procedure. To resolve the difficulty the interval of integration would require to be smaller by a factor of two or five and the integration to extend over the range $t = 0$ to at least 2·5T. To conclude then we see that the scheme is at least workable.

Time has prevented a comparison with the recently published method for dealing with hybrid integrals by Rüdenberg, Roothaan and Jaunzemis (1956) and Roothaan (1956). By defining a new auxiliary function introduced specifically to deal with the hybrid integrals they show how it can be extended to incorporate all the other integrals except the exchange type.

Table 3·16 The Hybrid integrals I_s

s	T	I_s
1	9·66	0·004687
1	8·97	0·008402
2	2·934	2·461766
3	2·88	1·566199
4·1	2·88	1·351311
4·2	2·88	1·727393
4	2·88	0·376082
5	2·934	0·554096
6	2·934	7·121793
7	2·88	4·624013
8·1	2·88	4·106656
8·2	2·88	5·107131
8	2·88	1·000475
9	2·934	22·698220
10	2·88	15·845195
11·1	2·88	14·970620
11·2	2·88	17·508591
11	2·88	2·537968
12·1	2·88	10·229633
12·2	2·88	2·273757
12·3	2·88	9·071743
12·4	2·88	2·329946
12	2·88	1·101701

Chapter 4.

The Exchange Integrals.

By far the most difficult type of integral to compute in molecular potential work is the exchange integral. The general form from Chapter 2 is

$$\int a_i a_j \frac{1}{r_{12}} b_{j'} b_{i'} \, dt \qquad \ldots\ldots(4.1)$$

and if we write the general form of the wave function as

$$D \; r^{n-1} \; e^{-kr} \; P$$

where D is a numerical coefficient defined later; n is the orbital quantum number and P is a spherical function, we can expand equation (4.1) to

$$\int \mathcal{D} \exp(-k_1 r_{a1} - k_2 r_{b1} - k_3 r_{a2} - k_4 r_{b2}) \; r^{n1-1} r^{n2-1} r^{n3-1} r^{n4-1} \left(\frac{1}{r_{12}}\right) dt$$

see figure 4·2.

Several different methods have been expounded in the quest to evaluate integrals of the kind.

1. The method of Kopineck
2. The method of Rüdenberg
3. The method of Barnett and Coulson.

As was mentioned in chapter 3 there is a similarity between the first two methods.

4·1 The method of Kopineck.

H. J. Kopineck (1950 et seq.) and H. Preuss (1954) have published a series of papers in which they treat various two centred integrals associated with the first two electron shells. It is noted once more however that there is a severe restriction on the generality of this work since it is assumed that

$$k_1 = k_2 = k_3 = k_4$$

as defined in an earlier chapter. The results follow the series of Japanese papers (Kotani, Amemiya and Simose, 1938, 1940) and include corrections of the latter. Use is made of the Neumann expansion of $1/r$ in elliptical coordinates and the integrals are listed in terms of the functions $W^{v}_{\tau}(m,n;\alpha)$ with numerical coefficients. It is erroneously asserted in the third paper (Kopineck, 1952) that

$$W^{M}_{l}(n,\bar{n}) = \phi^{Ml}_{n\bar{n}}(\alpha,\bar{\alpha})$$

where the ϕ function is from the paper of Rüdenberg (see below) whose notation has been substituted. On examination of the results it is seen that the equivalence should read

$$\phi^{Ml}_{n\bar{n}} = (-1)^{M}(l-M)!\,W^{M}_{l}/(l+M)!$$

It is obvious that the lack of generality makes the method of little practical use and does not justify further consideration here.

4·2 The method of Rüdenberg (1951).

A brief outline will be presented here to avoid continual reference to the original paper. The general form of the integral

$$\int a_i a_j \; 1/r_{12} \; b_{j'} b_{i'} \, dt$$

is represented thus $(a_i b_{i'} :: a_j b_{j'})$.

As in the Kopineck scheme, $1/r_{12}$ is expressed as a function of both centres a and b by the Neumann (1878) expansion which is unfortunately not a closed form.

The wave functions of each electron are treated as charge distributions

$$(a_i b_{i'} :: a_j b_{j'}) = (\Omega_i :: \Omega_j) = (\Omega :: \bar{\Omega})$$

where Ω are the charge distributions, and as in the paper a bar is used over symbols referring to electron 2.

Of the Legendre functions included there are the normalised Legendre functions

$$\mathcal{P}_l^m(\cos\theta) = \left[\frac{(2l+1)\ (l-m)!}{2(l+m)!}\right]^{\frac{1}{2}} P_l^m(\cos\theta)$$

The associated Legendre polynomials

$$P_l^m(\cos\theta) = \sin^m\theta\ P_l^{(m)}(\cos\theta)$$

$$P_l^{(m)}(\cos\theta) = d^m/d(\cos\theta)^m \quad P_l(\cos\theta)$$

where $P_l(\cos\theta)$ are the Legendre polynomials and $P_l^{(m)}(\cos\theta)$ are intermediate functions. The direct relation between the associated Legendre polynomials is

$$P_l^m(t) = (1 - t^2)^{\frac{1}{2}t} \quad d^m/dt^m\, P_l(t)$$

The nodeless Slater wave functions when normalised can be written

$$D_n\, r^{n-1}\, e^{-kr} \mathcal{P}_l^m(\cos\theta) \begin{cases} 1/\ 2 & (m = 0,\ l+1 \leqslant n\ ) \\ \cos m\phi & \\ \sin m\phi & (1 \leqslant m \leqslant l, \quad l+1 \leqslant n\ ) \end{cases}$$

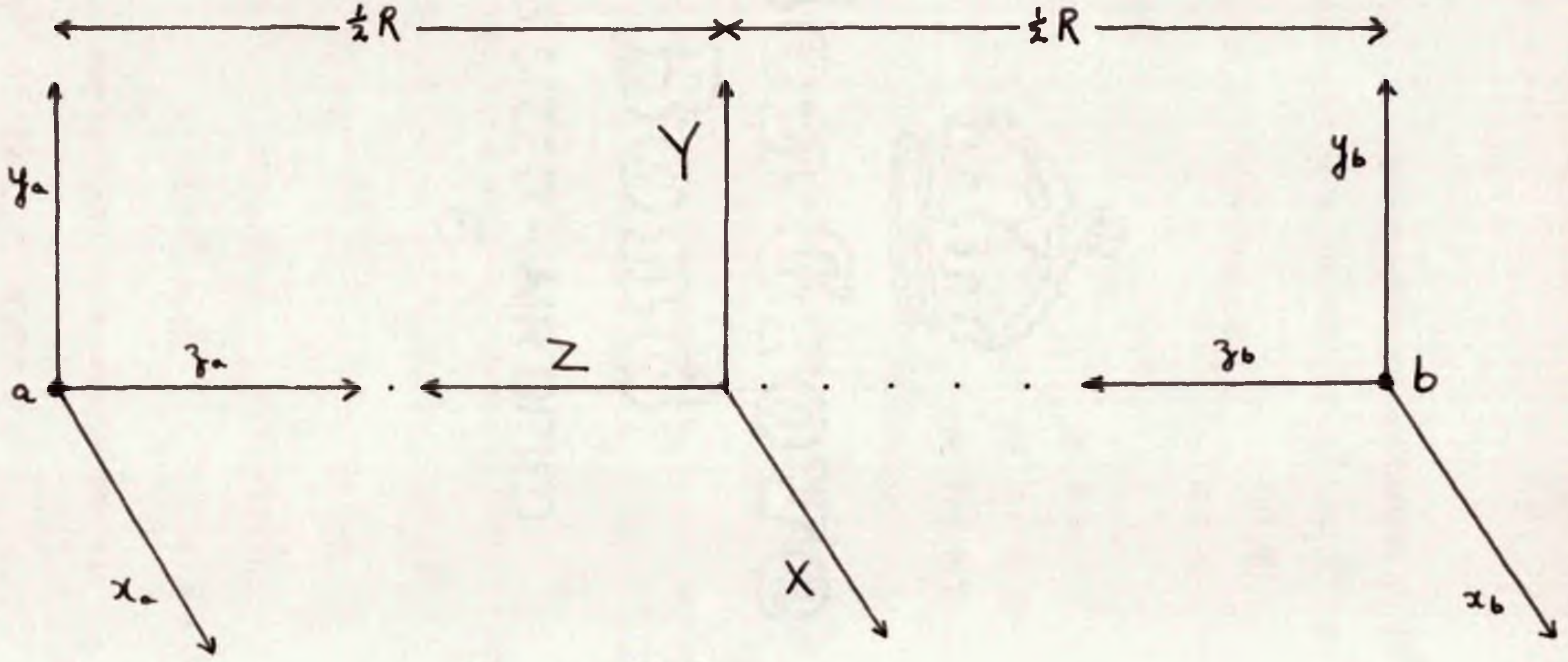

Figure 4·1

where $$D_n = (2k)^{n+\frac{1}{2}} / \left[\pi(2n)!\right]^{\frac{1}{2}}$$

From figure 4·1 we see that the polar coordinates are

$$x_a = x_b = X \qquad y_a = y_b = Y \qquad d = (X + Y)^{\frac{1}{2}}$$

$$\phi_a = \phi_b = \phi = \cos^{-1}(X/d) = \sin^{-1}(Y/d)$$

$$z_a = \tfrac{1}{2}R - Z \qquad z_b = \tfrac{1}{2}R + Z$$

$$\cos\theta_a = z_a / r_a \qquad \cos\theta_b = z_b / r_b$$

The charge distributions are products of pairs of the Slater functions. Using the identities

$$\cos m\phi \cos m'\phi = \tfrac{1}{2}\cos(m+m')\phi + \tfrac{1}{2}\cos(m-m')\phi$$

$$\sin m\phi \sin m'\phi = -\tfrac{1}{2}\cos(m+m')\phi + \tfrac{1}{2}\cos(m-m')\phi$$

$$\sin m\phi \cos m'\phi = \tfrac{1}{2}\sin(m+m')\phi + \tfrac{1}{2}\sin(m-m')\phi$$

the general charge distributions are simple linear combinations of

$$D_n D_{\bar{n}}\, r_a^{n-1}\, r_b^{\bar{n}-1} \exp(-k_a r_a - k_b r_b)\, P_l^m(\cos\theta_a)\, P_l^m(\cos\theta_b) \begin{cases} \cos(m+m')\phi \\ \sin(m+m')\phi \\ \cos|m-m'|\phi \\ \sin|m-m'|\phi \end{cases}$$

which are of the form

$$D \exp(-k_a r_a - k_b r_b)\, p(z_a, r_a, z_b, r_b)\, d^{2q}\, d^M \begin{cases} \cos M\phi \\ \sin M\phi \end{cases}$$

where 2q is an even number, D depends on k_a and k_b, M is zero or a positive integer and p is a homogeneous polynomial in (z_a, r_a, z_b, r_b).

Transforming to elliptic coordinates (ξ, η)

$$r_a = \tfrac{1}{2}R(\xi - \eta) \qquad r_b = \tfrac{1}{2}R(\xi + \eta) \qquad 1 \leqslant \xi \leqslant \infty$$

$$d = \tfrac{1}{2}R\left[(\xi^2 - 1)(1 - \eta^2)\right]^{\frac{1}{2}} \qquad Z = \tfrac{1}{2}R\xi\eta \qquad -1 \leqslant \eta \leqslant 1$$

the charge distributions become

$$K\, w(\xi, \eta) \exp(\alpha\xi + \beta\eta) \cdot (\xi^2 - 1)^{\frac{1}{2}M}(1 - \eta^2)^{\frac{1}{2}M} \begin{cases} \cos M\phi \\ \sin M\phi \end{cases}$$

where $\alpha = \tfrac{1}{2}R\,(k_a + k_b)$ $\qquad \beta = \tfrac{1}{2}R\,(k_a - k_b)$

$$K = R^{-3}\,(Rk_a)^{n+\frac{1}{2}}\,(Rk_b)^{n+\frac{1}{2}}$$

$w(\xi, \eta)$ is a polynomial in ξ, η whose coefficients are real numbers. The constants w_{nj} are related to $w(\xi, \eta)$ by

$$\tfrac{1}{2}\pi\left[\tfrac{1}{2}(1 - \delta_{M0})\right]^{\frac{1}{2}}(\xi^2 - \eta^2)\, w(\xi, \eta) = \sum_{n=0}^{N}\sum_{j=0}^{J} w_{jn}\, \xi^n \eta^j$$

and are listed for the various charge distributions on pages 1462 - 1466 of the paper.

The nomenclature is such that when $M = 0$ the charge distribution is of the Σ^+ type; $M = 1$, it is Π type; and $M = 2$ it is Δ type.

For a given value of M the charge distributions form the basis of an irreducible representation of the two dimension rotation reflection group $C_{\infty v}$ and so the exchange integrals will be different from zero only if both distributions in the integral have the same value of M.

Let the first electron occupy the charge distribution

$$K\, w(\zeta, \eta)\exp(-\alpha\zeta + \beta\eta) \cdot (\zeta^2 - 1)^{\frac{1}{2}M}(1 - \eta^2)^{\frac{1}{2}M} \cos M\phi$$

the second electron having the same distribution but with $\bar{K}$, $\bar{w}$, $\bar{\alpha}$ and $\bar{\beta}$, while $1/r_{12}$ is expanded by the Neumann series

$$\frac{R}{r_{12}} = 4\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} (-1)^m \frac{(l-|m|)!}{(l+|m|)!} P_l^m(\zeta_1)\, Q_l^m(\zeta_2)\mathcal{P}_l^{|m|}(\eta_1)\mathcal{P}_l^{|m|}(\eta_2) \exp(im\phi_1 - im\phi_2)$$

where Q^m are the associated Legendre functions of the second kind and where $\zeta_1 < \zeta_2$. Now, in elliptic coordinates the volume element is

$$dt = (\tfrac{1}{2}R)^3 (\zeta^2 - \eta^2)\, d\zeta\, d\eta\, d\phi$$

so that the exchange integrals assume the form

$$A = R^{-1}(Rk_a)^{n_a+\frac{1}{2}}(Rk_b)^{n_b+\frac{1}{2}}(R\bar{k}_a)^{\bar{n}_a+\frac{1}{2}}(R\bar{k}_b)^{\bar{n}_b+\frac{1}{2}} \sum_{l=M}^{\infty} I = \mathcal{R} \sum_{l=M}^{\infty} I$$

in which $$I = \sum_{n=0}^{N} \sum_{\bar{n}=0}^{\bar{N}} w_n^l(\beta)\, \bar{w}_{\bar{n}}^l(\bar{\beta})\, \phi_{n\bar{n}}^{Ml}(\alpha, \bar{\alpha})$$

with $$\phi_{n\bar{n}}^{Ml}(\alpha, \bar{\alpha}) = (-1)^M \frac{(l-M)!}{(l+M)!} \int_1^{\infty} d\zeta\, Q_l^M(\zeta)\, (\zeta^2 - 1)^{\frac{1}{2}M} \cdot$$

$$\left\{\left[e^{-\alpha\zeta}\zeta^n \int_1^{\zeta} dx\, P_l^M(x)(x^2-1)^{\frac{1}{2}M} e^{-\bar{\alpha}x} x^{\bar{n}}\right] + \left[e^{-\bar{\alpha}\zeta}\zeta^{\bar{n}} \int_1^{\zeta} dx\, P_l^M(x)(x^2-1)^{\frac{1}{2}M} e^{-\alpha x} x^n\right]\right\}$$

$$w_n^l(\beta) = \sum_{j=0}^{J} w_{nj} B_j^{Ml}(\beta) \qquad\qquad w_{\bar{n}}^l(\bar{\beta}) = \sum_{j=0}^{J} \bar{w}_{\bar{n}j} B_j^{Ml}(\bar{\beta})$$

$$B_j^{Ml}(\beta) = \left[\frac{2l+1}{2} \frac{(l-M)!}{(l+M)!}\right]^{\frac{1}{2}} \int_{-1}^{1} d\eta\, P_l^M(\eta)(1-\eta^2)^{\frac{1}{2}M} e^{-\beta\eta} \eta^j \qquad \ldots\ldots(4\cdot2)$$

Therefore it is found that

$$A = \mathcal{R} \sum_{l=0}^{\infty} \sum_{n=0}^{N} \sum_{\bar{n}=0}^{\bar{N}} \sum_{j=0}^{J} w_{nj}\, B_{j}^{Ml}(\beta) \sum_{\bar{j}=0}^{\bar{J}} \bar{w}_{\bar{n}\bar{j}}\, B_{j}^{Ml}(\bar{\beta}) \quad \phi_{n\bar{n}}^{Ml}(\alpha,\bar{\alpha})$$

The upper limits N, $\bar{N}$, J, $\bar{J}$ are determined by the values of the w_{nj} all of which are zero due to the delta function except those listed - loc. cit. page 1462 - 6. The distinction between n_a, n_b, n and N should be noted. N is the upper limit of the running index n in the summation while n_a and n_b are the principal quantum numbers in the various charge distributions. It is seen that in the

Σ^{+} type distribution, $n_a + n_b = N$

Π type distribution, $n_a + n_b = N + 1$

Δ type distribution, $n_a + n_b = N + 2$

The problem is reduced to the calculation of the $B_{j}^{Ml}(\beta)$ and the $\phi_{n\bar{n}}^{Ml}(\alpha,\bar{\alpha})$ functions. The latter are independent of the charge distributions except for the symmetry characteristic M.

By studying the equation for the $B(\beta)$ functions it is seen that

$$B_{j}^{Ml}(-\beta) = (-1)^{j+l+M}\, B_{j}^{Ml}(\beta)$$

These two facts enable us to make a further simplification : consider the charge distributions

$$(a_i b_j) \quad \text{and} \quad (a_j b_i).$$

These will give rise to two different polynomials $w(\zeta,\eta)$ and $w'(\zeta,\eta)$ which by definition of the various quantities will satisfy the relation

$$w'(\zeta,\eta) = w(\zeta,-\eta)$$

but $$\tfrac{1}{2}\pi\left[\tfrac{1}{2}(1+\delta_{Mo})\right]^{\frac{1}{2}}(\zeta^2-\eta^2)\;w(\zeta,\eta) = \sum_{n=0}^{N}\sum_{j=0}^{J} w_{nj}\,\zeta^n\eta^j$$

$$\therefore\quad w'_{nj} = (-1)^j\, w_{nj}$$

It follows from the above equations that

$$w'^{\,l}_{n}(\beta) = (-1)^{l+M}\, w^{l}_{n}(-\beta)$$

Finally,

$$(a_i b_j) = (-1)^{l+M}\,(a_j b_i).$$

The $B_j^{Ml}(\beta)$ Functions.

The argument of the B functions is $\beta = \frac{1}{2}R(k_a - k_b)$ and it is necessary to consider its different ranges in the calculation of the B's. Roughly speaking the range division is

1. $\beta = 0$
2. $\beta < 0{\cdot}5$
3. $\beta > 0{\cdot}5$

1. $\beta = 0$

It is clear that such B functions will be constant for all values of R, the internuclear separation, and so we can tabulate the results once and for all. From equation (4·2)

$$(1-t^2)^{\frac{1}{2}M}\, e^{\beta t}\, t^j = \sum_{l=M}^{\infty} B_j^{Ml}(\beta)\,\mathcal{P}_{\ell}^{M}(t) \qquad \text{.........(4.3)}$$

$$\therefore\quad e^{\beta t}\, t^j = \sum_{l=M}^{\infty}\left[\frac{(l-M)!}{(l+M)!}\right]^{\frac{1}{2}} B_j^{Ml}(\beta)\,\mathcal{P}_{\ell}^{(M)}(t) \qquad \text{....(4·4)}$$

when $\beta = 0$, we get

$$B^{Ml}_{j}(0) = \left[\frac{(l+M)!}{(l-M)!}\right]^{\frac{1}{2}} \frac{j!}{(j+M)!} \quad B^{ol}_{j+M}(0)$$

by differentiation of

$$t^{j} = \sum_{l=0}^{\infty} B^{ol}_{j}(0)\,\mathcal{P}_{l}(t)$$

from equation (4·3) and comparing with equations (4·2) and (4·4), we have

$$B^{ol}_{j}(0) = \sqrt{2(2l+1)} \;\; \tfrac{1}{2}\int_{-1}^{1} P_{l}(t)\, e^{\beta t}\, t^{j}\, dt \qquad \text{.......(4.5)}$$

Now, the integral can easily be evaluated (Whitaker and Watson,1950, p.310)

$$\tfrac{1}{2}\int_{-1}^{1} P_{l}(t)\, e^{\beta t}\, t^{j}\, dt = 2^{l} \frac{j!}{(j+l+1)!} \; \frac{(\frac{1}{2}(j+l))!}{(\frac{1}{2}(j-l))!}$$

for $j-l \geqslant 0$ and even; otherwise it is zero for all other j values.

$$\therefore \; B^{ol}_{j}(0) = \sqrt{2(2l+1)} \;\; 2^{l} \frac{j!}{(j+l+1)!} \; \frac{(\ \frac{1}{2}(j+l)\ )!}{(\ \frac{1}{2}(j-l)\ )!}$$

for $j-l \geqslant 0$ and even

$$= 0 \quad \text{otherwise}$$

$$B^{1l}_{j}(0) = \sqrt{\frac{(l+1)!}{(l-1)!}} \; \frac{j!}{(j+1)!} \quad B^{ol}_{j+1}(0)$$

$$= \sqrt{\frac{(l+1)!}{(l-1)!}} \;\; 2^{l} \; \frac{j!\sqrt{2(2l+1)}}{(j+l+2)!} \;\; \frac{(\ \frac{1}{2}(j+l+1)\ )!}{(\ \frac{1}{2}(j-l+1)\ )!}$$

for $j-l+1 \geqslant 0$ and even

$$= 0 \quad \text{otherwise}$$

$$B_j^{2l}(0) = 2^l \sqrt{\frac{(l+2)!}{(l-2)!}} \; \frac{j!\sqrt{2(2l+1)}}{(j+l+3)!} \; \frac{(\frac{1}{2}(j+l+2))!}{(\frac{1}{2}(j-l+2))!}$$

for $j-l+1 \geqslant 0$ and even

$= 0$ otherwise.

Table of $B_j^{0l}(0)$ values

$l \rightarrow$ $j \downarrow$	0	1	2	3	4	5
0	1·4142135					
1	0	0·8164666				
2	0·4714045	0	0·42163701			
3	0	0·4898980	0	0·21380899		
4	0·2828427	0	0·36140315	0	0·10774960	
5	0	0·3499271	0	0·23756554	0	0·05414621
6	0·2020305	0	0·30116929	0	0·14693127	0

Table of $B_j^{1l}(0)$ values

$l \rightarrow$ $j \downarrow$	0	1	2	3	4	5
0	0	1·1547004				
1	0	0	0·51639778			
2	0	0·23094012	0	0·24688536		
3	0	0	0·22131333	0	0·12046772	
4	0	0·09897434	0	0·16459024	0	0·039514203
5	0	0	0·12295185	0	0·10951610	0

Table of $B_j^{21}(0)$ values

	0	1	2	3	4	5
0	0	0	1·03279557			
1	0	0	0	0·39036002		
2	0	0	0·14754222	0	0·170367078	
3	0	0	0	0·13012001	0	0·07846551
4	0	0	0·04918074	0	0·09292749	0

2. $\beta < 0{\cdot}5$.

When $\beta = 0{\cdot}5$ the coefficient of the 6th term is 10^{-6} times the coefficient of the 1st term. Writing

$$d/d\beta \,.\, B_j^{Ml}(\beta) = B_{j+1}^{Ml}(\beta)$$

we can use the Taylor expansion

$$B_j^{Ml}(\beta) = B_j^{Ml}(\beta_o + h) = \sum_{k=0}^{\infty} \frac{h^k}{k!} B_{j+k}^{Ml}(\beta_o)$$

For small values of β therefore,

$$B_j^{Ml}(\beta) = \sum_{k=0}^{\infty} \frac{\beta^K}{k!} B_{j+k}^{Ml}(0)$$

In this method it would seem useful to have a table of $\beta^k/k!$ values. This in fact was done before starting the computation.

3. $\beta > 0{\cdot}1$.

When β is greater than about 0·5 the series given above does not converge rapidly enough for quick calculation. Therefore the present method, which overlaps the previous, is adopted.

Using a Legendre recurrence relation we get

$$B^{Ml}_{j+1}(\beta) = a_M(l)\; B_j^{M(l-1)}(\beta) + a_M(l+1)\; B_j^{M(l+1)}(\beta)$$

where $a_M(l) = a_o(l)\left[1 - (M/l)^2\right]^{\frac{1}{2}}$ and $a_o(l) = (4 - 1/l^2)^{-\frac{1}{2}}$

These $a_M(l)$ functions are constants for all values of β and R and are listed in the table below.

Table of $a_M(l)$ values.

l	$a_o(l)$	l	$a_1(l)$	l	$a_2(l)$
0	0·0	0	0·0	0	0·0
1	0·5773502	1	0·0	1	0·0
2	0·51639777	2	0·447213585	2	0·0
3	0·50709254	3	0·478091431	3	0·377964462
4	0·50395263	4	0·487950038	4	0·436435778
5	0·50251891	5	0·492365958	5	0·460566189
6	0·50174520	6	0·494727435	6	0·473049910
7	0·50128041	7	0·496138937	7	0·480384461
8	0·50097943	8	0·497050123	8	0·485071249
9	0·50077340	9	0·497672606	9	0·488252082
10	0·50062617	10	0·498116751	10	0·490511459
11	0·50051732	11	0·498444775	11	0·492174777
12	0·50043459	12	0·498693943	12	0·493435157

Now, $$B_o^{ol}(\beta) = \left[2(2l+1)\right]^{\frac{1}{2}} b_o^l(\beta)$$

and $$b_o^l(\beta) = \tfrac{1}{2}\int_{-1}^{1} P_l(t)\, e^{\beta t}\, dt \qquad \text{from equation } (4{\cdot}5)$$

$$= (\pi/2\beta)^{\frac{1}{2}}\, I_{l+\frac{1}{2}}(\beta) \qquad \ldots\ldots (4{\cdot}6)$$

which is the Bessel function of purely imaginary argument and half integral order (Watson, 1952). Besides,

$$B_o^{Ml}(\beta) = \frac{1}{\beta^M}\left[\frac{(l+M)!}{(l-M)!}\right]^{\frac{1}{2}} B_o^{ol}(\beta)$$

$$b_o^o = \frac{1}{\beta}\sinh\beta \qquad\qquad b_o^1 = \frac{1}{\beta}(\cosh\beta - b_o^o).$$

The Bessel function recurrence relation

$$(2l+1)\, b_o^l = \beta\,(b_o^{l-1} - b_o^{l+1})$$

is valid but with it errors due to differencing effects increase rapidly and it is advisable to start at the greatest value of l with

$$b_o^l = \frac{(2l+3)}{\beta}\, b_o^{l+1} + b_o^{l+2}$$

and descending to lower l values. In practice, however, the recurrence relations are not very consistent and we must unfortunately revert to a laborious series calculation.

Split β into the ranges (a) $\beta < 1$ and (b) $\beta > 1$

(a) When β is small we can use the infinite series

$$I_{l+\frac{1}{2}}(\beta) = \pi^{-\frac{1}{2}}(2\beta)^{l+\frac{1}{2}} \sum_{t=0}^{\infty} \frac{(l+t)!}{t!(2l+2t+1)!}\, \beta^{2t}$$

$$\therefore \quad b_o^l(\beta) = (2\beta)^l\, \beta^{2t} \sum_{t=0}^{\infty} \frac{(l+t)!}{t!(2l+2t+1)!}$$

from equation (4·6).

(b) When β is no longer small we cannot use the infinite series expansion for $I_{l+\frac{1}{2}}$: instead we must employ

$$I_{l+\frac{1}{2}}(\beta) = (2\pi\beta)^{-\frac{1}{2}}\left[e^{\beta}\sum_{t=0}^{l}\frac{(l+t)!(-\beta)^{-t}}{t!(l-t)!\;2^{t}} + (-1)^{l+1}e^{-\beta}\sum_{t=0}^{l}\frac{(l+t)!(\beta)^{-t}}{t!(l-t)!\;2^{t}}\right]$$

and therefore

$$b_o^{l}(\beta) = -\frac{1}{2\beta}\left[e^{\beta}\sum_{t=0}^{l}\frac{(l+t)!(-\beta)^{-t}}{t!(l-t)!\;2^{t}} + (-1)^{l+1}e^{-\beta}\sum_{t=0}^{l}\frac{(l+t)!(\beta)^{-t}}{t!(l-t)!\;2^{t}}\right]$$

Examples of this type of expansion have already been given in chapter 3 when dealing with the Hybrid integrals. It was found (see numerical examples later) that the error incurred was small if the expansions were calculated for selected values of l viz. $l = 0,1,4,5,8,9,$ while the values of the $b_o^{l}(\beta)$ between these were filled in using recurrence relations. Using these recurrence formulae more than twice led to errors greater than could be tolerated in the calculation.

Having constructed a table of the $b_o^{l}(\beta)$ we can proceed to the $B_J^{Ml}(\beta)$ which are, from the functions listed previously;

$$B_o^{ol}(\beta) = \sqrt{2(2l+1)}\;\; b_o^{l}(\beta)$$

$$B_1^{ol}(\beta) = a_o(l)\, B_o^{ol-1} + a_o(l+1)\, B_o^{ol+1}$$

$$B_2^{ol}(\beta) = a_o(l)\, B_1^{ol-1} + a_o(l+1)\, B_1^{ol+1}$$

$$B_3^{ol}(\beta) = a_o(l)\, B_2^{ol-1} + a_o(l+1)\, B_2^{ol+1}$$

and so on

$$B_0^{1l}(\beta) = \frac{1}{\beta}\sqrt{\frac{(l+1)!}{(l-1)!}}\; B_0^{0l}(\beta)$$

$$B_1^{1l}(\beta) = a_1(l)\, B_0^{1l-1} + a_1(l+1)\, B_0^{1l+1}$$

$$B_2^{1l}(\beta) = a_1(l)\, B_1^{1l-1} + a_1(l+1)\, B_1^{1l+1}$$

and so on.

$$B_0^{2l}(\beta) = \frac{1}{\beta}\sqrt{\frac{(l+2)!}{(l-2)!}}\; B_0^{0l}(\beta)$$

$$B_1^{2l}(\beta) = a_2(l)\, B_0^{2l-1} + a_2(l+1)\, B_0^{2l+1}$$

$$B_2^{2l}(\beta) = a_2(l)\, B_1^{2l-1} + a_2(l+1)\, B_1^{2l+1}$$

and so on.

The $\phi_{n\bar{n}}^{Ml}(\alpha,\bar{\alpha})$ Functions.

Partial integration of the ϕ function and introduction of

$$P_l^M(x)\frac{d}{dx}Q_l^M(x) - Q_l^M(x)\frac{d}{dx}P_l^M(x) = \frac{(-1)^M}{(1-x^2)}\;\frac{(l+M)!}{(l-M)!}$$

results in

$$\phi_{n\bar{n}}^{Ml}(\alpha,\bar{\alpha}) = \int_1^\infty \frac{d\zeta(\zeta^2-1)^{-1}}{\left[P_l^M(\zeta)\right]^2}\left[\int_1^\zeta P_l^M(x)\,(x^2-1)^{\frac{1}{2}M}e^{-\alpha x}\,x^n\,dx\int_1^\zeta P_l^M(\bar{x})\,(\bar{x}^2-1)^{\frac{1}{2}M}e^{-\bar{\alpha}\bar{x}}\,\bar{x}^{\bar{n}}\,d\bar{x}\right]$$

It is remarked that all the $\phi_{n\bar{n}}^{Ml}$ are positive.

Let us take the simplest case; viz. ϕ_{00}^{00}

$$\phi_{00}^{00}(\alpha,\bar{\alpha}) = \int_1^\infty d\zeta/(\zeta^2-1)\left[\int_1^\zeta e^{-\alpha x}\,dx\int_1^\zeta e^{-\bar{\alpha}\bar{x}}\,d\bar{x}\right]$$

$$= \int_1^\infty d\zeta/(\zeta^2-1)\left\{\frac{1}{\alpha\bar{\alpha}}\left[-e^{-a} + e^{-a\zeta}\right]\left[-e^{-\bar{a}} + e^{-\bar{a}\zeta}\right]\right\}$$

$$= \frac{1}{a\bar{a}}\int_1^\infty e^{-a-\bar{a}}\, d\zeta\left[\frac{1}{\zeta^2-1} + \frac{\frac{1}{2}e^{-(a+\bar{a})(\zeta-1)}}{\zeta-1} - \frac{\frac{1}{2}e^{-(a+\bar{a})(\zeta-1)}}{\zeta+1}\right.$$

$$\left.\frac{-\frac{1}{2}e^{-\bar{a}(\zeta-1)}}{\zeta-1} + \frac{\frac{1}{2}e^{-\bar{a}(\zeta-1)}}{\zeta+1} - \frac{\frac{1}{2}e^{-a(\zeta-1)}}{\zeta-1} + \frac{\frac{1}{2}e^{-a(\zeta-1)}}{\zeta+1}\right]$$

Following Jahnke and Emde (1933) we shall define

$$-\ E_i(-x) = \int_x^\infty \frac{e^{-t}}{t}\, dt > 0 \qquad \infty > x > 0$$

and use this in the integral evaluation. Besides it is convenient to expand

$$E_i(x) = C + \ln|x| + \sum_{n=1}^{\infty} \frac{x^n}{n.n!}$$

at the lower limit $\zeta = 1$, so that the infinities at that point will cancel. C is Euler's constant (= 0·577215665).

Further, we use the notation

$$\mathcal{E}(x) = \tfrac{1}{2}\left[C + \ln 2x - e^{2x} E_i(-2x)\right]$$

and find that $\phi^{oo}_{oo}(a,\bar{a})$ reduces to

$$\phi^{oo}_{oo}(a,\bar{a}) = \frac{e^{-a-\bar{a}}}{a\bar{a}}\left\{\mathcal{E}(a) + \mathcal{E}(a) - \mathcal{E}(a+a)\right\}$$

We shall introduce

$$G_o(a) = e^{-a}\,\mathcal{E}(a)$$

$$G_n(a) = (-1)^n\,(d^n/da^n)\,G_o(a)$$

which lead directly to

$$G_0(a) = \tfrac{1}{2} e^{-a}\left[C + \ln 2a - e^{2a} E_1(-2a)\right]$$

$$G_1(a) = \tfrac{1}{2} e^{-a}\left[C + \ln 2a + e^{2a} E_1(-2a)\right]$$

$$G_n(a) = G_{n-2}(a) - A_{n-2}(a)$$

and

$$A_0(a) = (1/a)\, e^{-a}$$

$$A_n(a) = \int_1^{\infty} e^{-at}\, t^n\, dt = (-1)^n (d^n/da^n)\, A_0(a)$$

giving the recurrence relation

$$A_n(a) = nA_{n-1}(a) + e^{-a}$$

and

$$A_{n\bar{n}}(a\bar{a}) = (-1)^{n+\bar{n}} \left(\partial^{n+\bar{n}}/\partial a^n \partial \bar{a}^{\bar{n}}\right) \frac{e^{-a-\bar{a}}}{a\bar{a}\,(a + \bar{a})}$$

the recurrence relation for which being

$$A_{n\bar{n}} = \frac{1}{\alpha + \bar{a}}\left[nA_{n-1,\bar{n}} + \bar{n}A_{n,\bar{n}-1} + A_n(a)\, A_{\bar{n}}(\bar{a})\right]$$

where

$$A_{00} = \frac{1}{a + \bar{a}}\, A_0(a)\, A_0(\bar{a})$$

Finally we can write

$$\phi^{00}_{00}(a,\bar{a}) = \frac{1}{a\bar{a}}\left[e^{-a}\, G_0(\bar{a}) + e^{-\bar{a}}\, G_0(a) - G_0(a + \bar{a})\right]$$

Now,

$$\phi^{00}_{n\bar{n}} = (-1)^{n+\bar{n}} \left(\partial^{n+\bar{n}}/\partial a^n \partial \bar{a}^{\bar{n}}\right) \phi^{00}_{00}$$

which gives the recurrence relation

$$\phi^{oo}_{n\bar{n}} = \frac{1}{\alpha\bar{\alpha}}\left[\bar{\alpha}n\phi_{n-1,\bar{n}} + \alpha\bar{n}\phi_{n,\bar{n}-1} - n\bar{n}\phi_{n-1,\bar{n}-1} + e^{-\alpha}\,G_{\bar{n}}(\bar{\alpha}) + e^{-\bar{\alpha}}\,G_n(\alpha) - G_{n+\bar{n}}(\alpha+\bar{\alpha})\right]$$

To obtain the $\phi^{ol}_{n\bar{n}}$ we shall define

$$\phi^{oo}_{n\bar{n}} = \varphi^{o}_{n\bar{n}} \quad \text{and} \quad \phi^{ol}_{nn} = \left[(2l-1)/\,l^2\right]\varphi^{l}_{n\bar{n}} \qquad l \geq 1$$

Rüdenberg proves

$$\varphi^{l}_{n\bar{n}} = (b_{l-2}/b_{l-1})\,\varphi^{l-2}_{n\bar{n}} + \psi^{l-1}_{n\bar{n}} \qquad l \geq 2$$

and

$$\psi^{l}_{n\bar{n}} = \psi^{l-2}_{n\bar{n}} + b_l\varphi^{l}_{n+1,\bar{n}+1} + b_{l-2}\varphi^{l-2}_{n+1,\bar{n}+1} - b_{l-1}\left[\varphi^{l-1}_{n+2,\bar{n}} + \varphi^{l-1}_{n,\bar{n}+2}\right]$$

where $b_o = 1$ and $b_l = 4 - (1/l^2)$ $\quad l \geq 1$

The method of evaluation is from the $\varphi^{l}_{n\bar{n}}$ to the $\psi^{l}_{n\bar{n}}$ whence to the $\varphi^{l+1}_{n\bar{n}}$ For $l = 0,1$ we must add the following

$$\varphi^{1}_{n\bar{n}} = \psi^{o}_{n\bar{n}}$$

$$\psi^{1}_{n\bar{n}} = 3\varphi^{1}_{n+1,\bar{n}+1} + \varphi^{1}_{n,\bar{n}} - \varphi^{o}_{n+1,\bar{n}+1} - \varphi^{o}_{n+2,\bar{n}} - \varphi^{o}_{n,\bar{n}+2} + A_n(\alpha)\,A_{\bar{n}+1}(\bar{\alpha}) + A_{n+1}(\alpha)\,A_{\bar{n}}(\bar{\alpha})$$

$$\psi^{o}_{n,\bar{n}} = \varphi^{o}_{n+1,\bar{n}+1} - A_n(\alpha)\,A_{\bar{n}}(\bar{\alpha}) - A_{n,\bar{n}}(\alpha,\bar{\alpha})$$

We have then,

$$\phi^{o1}_{n\bar{n}}(\alpha,\bar{\alpha}) = \phi^{oo}_{n+1,\bar{n}+1}(\alpha,\bar{\alpha}) - A_n(\alpha)A_{\bar{n}}(\bar{\alpha}) - A_{n\bar{n}}(\alpha,\bar{\alpha})$$

$$4\phi^{02}_{n\bar{n}}(a,\bar{a}) = 9\phi^{01}_{n+1,\bar{n}+1}(a,\bar{a}) + \phi^{00}_{n\bar{n}}(a,\bar{a}) + 3\left[A_n(a)A_{\bar{n}+1}(\bar{a}) + A_{n+1}(a)A_{\bar{n}}(\bar{a})\right]$$
$$- 3\left[\phi^{00}_{n+2,\bar{n}}(a,\bar{a}) + \phi^{00}_{n,\bar{n}+2}(a,\bar{a}) + A_n(a)A_{\bar{n}}(\bar{a}) + A_{n\bar{n}}(a,\bar{a})\right]$$

$$9\phi^{03}_{n\bar{n}}(a,\bar{a}) = 25\phi^{02}_{n+1,\bar{n}+1} + 9\phi^{01}_{n\bar{n}} + 5\phi^{00}_{n+1,\bar{n}+1} - 15\left[\phi^{01}_{n+2,\bar{n}} + \phi^{01}_{n,\bar{n}+2}\right]$$

$$48\phi^{04}_{n\bar{n}} = 147\phi^{03}_{n+1,\bar{n}+1} + 55\phi^{02}_{n\bar{n}} + 63\phi^{01}_{n+1,\bar{n}+1} - 105\left[\phi^{02}_{n+2,\bar{n}} + \phi^{02}_{n,\bar{n}+2}\right] + 7\phi^{00}_{n\bar{n}}$$

$$125\phi^{05}_{n\bar{n}} = 405\phi^{04}_{n+1,\bar{n}+1} + 161\phi^{03}_{n\bar{n}} + 225\phi^{02}_{n+1,\bar{n}+1} - 315\left[\phi^{03}_{n+2,\bar{n}} + \phi^{03}_{n,\bar{n}+2}\right]$$
$$- 36\phi^{01}_{n\bar{n}}$$

for $l \geq 4$ there is the general formula

$$l^2(2l-5)\,\phi^{0l}_{n\bar{n}} = (2l-5)(2l-1)^2\,\phi^{0l-1}_{n+1,\bar{n}+1}$$
$$+\left[(2l-5)(l-1)^2 + (2l-1)(l-2)^2\right]\phi^{0l-2}_{nn}$$
$$+ (2l-1)(2l-5)^2\,\phi^{0l-3}_{n+1,\bar{n}+1}$$
$$- (2l-1)(2l-3)(2l-5)\left[\phi^{0l-2}_{n+2,\bar{n}} + \phi^{0l-2}_{n,\bar{n}+2}\right]$$
$$- (2l-1)(l-3)^2\,\phi^{0l-4}_{n\bar{n}}$$

Having obtained the $\phi^{0l}_{n\bar{n}}$ we can proceed to the $\phi^{Ml}_{n\bar{n}}$ by means of the recurrence relations which are derived in the Rüdenberg paper, viz.

$$\phi^{(M+1)l}_{n\bar{n}} = \phi^{Ml}_{n+1,\bar{n}+1} - \frac{(l+M)}{(2l+1)}\,\phi^{M(l-1)}_{n\bar{n}} - \frac{(l+1-M)}{(2l+1)}\,\phi^{M(l+1)}_{n\bar{n}}$$

or specifically,

$$\phi^{1l}_{n\bar{n}} = \phi^{ol}_{n+1,\bar{n}+1} - \frac{l}{2l+1}\phi^{o,l-1}_{n\bar{n}} - \frac{l+1}{2l+1}\phi^{o,l+1}_{n\bar{n}}$$

$$\phi^{2l}_{n\bar{n}} = \phi^{1l}_{n+1,\bar{n}+1} - \frac{l+1}{2l+1}\phi^{1,l-1}_{n\bar{n}} - \frac{l}{2l+1}\phi^{1,l+1}_{n\bar{n}}$$

and so on.

Numerical Procedure.

The evaluation of $B^{Ml}_{j}(\beta)$ and $\phi^{Ml}_{n\bar{n}}(\alpha,\bar{\alpha})$ present such a formidable problem of computation that a clear cut programme of action is essential. For each atomic separation R, the parameters α, $\bar{\alpha}$, β, $\bar{\beta}$, n, $\bar{n}$, and M should be tabulated; then for the $B(\beta)$ and $\phi(\alpha)$ we have the respective programmes.

The $B(\beta)$ Functions.

1. List the different $B(\beta)$ functions required.
2. Group the various β values occurring according to their ranges as defined previously.
3. $\beta = 0$. The values of $B(0)$ are constant and are already tabulated.
4. β $0{\cdot}5$
    - a) tabulate $\beta^k/k!$
    - b) tabulate $B^{ol}_{j}(\beta)$
    - c) tabulate $B^{1l}_{j}(\beta)$
    - d) tabulate $B^{2l}_{j}(\beta)$
5. β $0{\cdot}1$. The $a_M(l)$ are constant for all values of R and are already tabulated.
    - a) Evaluate the $b_o(\beta)$ functions

for 1) the range $0{\cdot}1 < \beta < 1$

2) the range $1 < \beta$

b) Tabulate all the $b_o^1(\beta)$ values thus obtained.

c) Tabulate the $B_j^{M1}(\beta)$.

The $\phi(\alpha,\bar{\alpha})$ Functions.

1. Tabulate e^{-y}, $2y$, $-e^{2y}E_1(-2y)$, $\ln 2y$, e^{2y} for $y = \alpha, \bar{\alpha}, \alpha + \bar{\alpha}$.

e^{-y} = antilog($-y.\ 0{\cdot}4342945$), similarly e^{2y} = antilog($2y.\ 0{\cdot}4342945$).

<u>NOTE:</u> The common logarithms are denoted by 'log' and the natural or Naperian logarithms by 'ln'. At least seven figures must be taken because the final results are very small differences and are liable to be meaningless unless this precaution is observed. Chamber's seven figure Mathematical Tables (Chambers, 1943) were used.

In the tabulation of $-e^{2y}\,E_1(-2y)$, we can use the British Association tables (Cambridge, 1951) for $-E_1(-y)$ in the range $y < 15$. When $y > 15$ the infinite series expansion is useful:

$$-e^{x}\,E_1(-x) = \frac{1}{x} - \frac{1}{x^2} + \frac{2!}{x^3} - \frac{3!}{x^4} + \ldots\ldots$$

2. Tabulate $A_i(\alpha)$, $A_i(\bar{\alpha})$, $A_i(\alpha + \bar{\alpha})$ to i = 9, 9, and 16 respectively.

3. Tabulate $G_i(\alpha)$, $G_i(\bar{\alpha})$, $G_i(\alpha + \bar{\alpha})$ to i = 9, 9, and 18 respectively. The maximum values of i quoted above are chosen where it was found that the differencing effects in the recurrence formula began to be noticeable.

4. Evaluate $A_{n\bar{n}}(a,\bar{a})$ by means of the scheme

	$a + \bar{a}$	$A_o(\bar{a})$	$A_1(\bar{a})$	$A_2(\bar{a})$	$A_3(\bar{a})$	.....
	n	0	1	2	3	
$A_o(a)$	0					
$A_1(a)$	1					
$A_2(a)$	2					

5. Evaluate $\phi^{oo}_{n\bar{n}}(a,\bar{a})$ from the scheme

	$a\bar{a}$	$e^{-a}\ G_o(\bar{a})$	$e^{-a}\ G_1(\bar{a})$	$e^{-a}\ G_2(\bar{a})$	$e^{-a}\ G_3(\bar{a})$
	na				
$e^{-\bar{a}}\ G_o(a)$					
$e^{-\bar{a}}\ G_1(a)$					
$e^{-\bar{a}}\ G_2(a)$					

$G_o(a+\bar{a})$

$G_1(a+\bar{a})$

$G_2(a+\bar{a})$

$G_3(a+\bar{a})$

6. Tabulate $\phi^{o1}_{n\bar{n}}(a,\bar{a})$

7. Tabulate $\phi^{o2}_{n\bar{n}}(a,\bar{a})$

8. Tabulate $\phi^{o3}_{n\bar{n}}(a,\bar{a})$

9. Tabulate $\phi^{o4}_{n\bar{n}}(a,\bar{a})$

10. Tabulate $\phi^{o5}_{n\bar{n}}(a,\bar{a})$

STOP AT THIS POINT IF $M = 0$.

11. Tabulate $\phi^{10}_{n\bar{n}}(\alpha,\bar{\alpha})$

12. Tabulate $\phi^{11}_{n\bar{n}}(\alpha,\bar{\alpha})$

13. Tabulate $\phi^{12}_{n\bar{n}}(\alpha,\bar{\alpha})$

14. Tabulate $\phi^{13}_{n\bar{n}}(\alpha,\bar{\alpha})$

15. Tabulate $\phi^{14}_{n\bar{n}}(\alpha,\bar{\alpha})$

STOP AT THIS POINT IF $M = 1$

16. Tabulate $\phi^{20}_{n\bar{n}}(\alpha,\bar{\alpha})$

17. Tabulate $\phi^{21}_{n\bar{n}}(\alpha,\bar{\alpha})$

18. Tabulate $\phi^{22}_{n\bar{n}}(\alpha,\bar{\alpha})$

19. Tabulate $\phi^{23}_{n\bar{n}}(\alpha,\bar{\alpha})$.

etc.

Numerical Examples.

Several numerical examples were calculated: they were

$$A(1s_a 2p_{xb} :: 2s_a 2p_{xb})$$

$$A(2p_{za} 2p_{zb} :: 2p_{za} 2p_{zb})$$

$$A(2p_{za} 2p_{xb} :: 2p_{za} 2p_{xb})$$

$$A(2p_{xa} 2p_{xb} :: 2p_{xa} 2p_{xb})\Sigma$$

$$A(2p_{xa} 2p_{xb} :: 2p_{xa} 2p_{xb})\Delta$$

where $k_{1s} = 8{\cdot}97$ $\quad k_{2s} = 2{\cdot}934$ $\quad k_{2p_z} = 2{\cdot}88$ $\quad k_{2p_x} = 2{\cdot}88$.

$R = 2{\cdot}0$ atomic units.

Applying the final A equation on page 97 we can write out the summations for these integrals -

$$A(1s_a 2p_{xb}::2s_a 2p_{xb}) =$$

$$\frac{1}{64\sqrt{3}} R^8 k_a \bar{k}_a k_b \sum_{l=1}^{\infty} \Big[- B_2^{11}(\beta) B_3^{11}(\beta)\, \phi_{00}^{11}(\alpha,\bar{\alpha}) + B_2^{11}(\beta) B_2^{11}(\beta)\, \phi_{01}^{11}(\alpha,\bar{\alpha})$$
$$+ B_2(\beta) B_1(\beta)\, \phi_{02}(\alpha,\bar{\alpha}) - B_2(\beta) B_0(\beta)\, \phi_{03}(\alpha,\bar{\alpha})$$
$$+ B_0(\beta) B_3(\beta)\, \phi_{20}(\alpha,\bar{\alpha}) - B_0(\beta) B_2(\beta)\, \phi_{21}(\alpha,\bar{\alpha})$$
$$- B_0(\beta) B_1(\beta)\, \phi_{22}(\alpha,\bar{\alpha}) + B_0(\beta) B_0(\beta)\, \phi_{23}(\alpha,\bar{\alpha}) \Big]$$

where $k_a = 8{\cdot}97$ $\bar{k}_a = 2{\cdot}934$ $k_b = \bar{k}_b = 2{\cdot}88$

$\beta = 6{\cdot}09$ $\bar{\beta} = 0{\cdot}054$ $\alpha = 11{\cdot}85$ $\bar{\alpha} = 5{\cdot}814$

$$A(2p_{za} 2p_{zb}::2p_{za} 2p_{zb}) =$$

$$\frac{1}{64} R^9 k_a^{10} \sum_{l=0}^{\infty} \Big[B_2^{01}(0) B_2^{01}(0)\, \phi_{00}^{01}(\alpha,\bar{\alpha}) + 2B_2^{01}(0) B_2^{01}(0)\, \phi_{04}^{01}(\alpha,\bar{\alpha})$$
$$- \left\{ 2B_2(0) B_0(0) + 2B_2(0) B_4(0) \right\} \phi_{02}(\alpha,\bar{\alpha})$$
$$+ \left\{ B_0(0) B_0(0) + 2B_0(0) B_4(0) + B_4(0) B_4(0) \right\} \phi_{22}(\alpha,\bar{\alpha})$$
$$- \left\{ 2B_0(0) B_2(0) + 2B_4(0) B_2(0) \right\} \phi_{24}(\alpha,\bar{\alpha})$$
$$+ B_2(0) B_2(0)\, \phi_{44}(\alpha,\bar{\alpha}) \Big]$$

where

$k_a = \bar{k}_a = k_b = \bar{k}_b = 2{\cdot}88$

$\beta = \bar{\beta} = 0$ $\alpha = \bar{\alpha} = 5{\cdot}76$

for the above case and also for the remaining three integrals set out below.

$$A(2p_{za}2p_{xb}::2p_{za}2p_{xb}) =$$

$$\frac{1}{128} R^9 k_a^{10} \sum_{l=1}^{\infty} \Big[B_2^{11}(0)B_2^{11}(0)\, \phi_{00}^{11}(a,\bar{a}) - 2B_2^{11}(0)B_3^{11}(0)\, \phi_{01}^{11}(a,\bar{a})$$

$$- 2B_2(0)B_0(0)\, \phi_{02}(a,\bar{a}) + 2B_2(0)B_1(0)\, \phi_{03}(a,\bar{a})$$

$$+ B_3(0)B_3(0)\, \phi_{11}(a,\bar{a}) + 2B_3(0)B_0(0)\, \phi_{12}(a,\bar{a})$$

$$- 2B_3(0)B_1(0)\, \phi_{13}(a,\bar{a}) + B_0(0)B_0(0)\, \phi_{22}(a,\bar{a})$$

$$- 2B_0(0)B_1(0)\, \phi_{23}(a,\bar{a}) + B_1(0)B_1(0)\, \phi_{33}(a,\bar{a}) \Big]$$

$$A(2p_{xa}2p_{xb}::2p_{xa}2p_{xb}) =$$

$$\frac{1}{256} R^9 k_a^{10} \sum_{l=2}^{\infty} \Big[\Big\{ B_2^{21}(0)B_2^{21}(0) - 2B_2^{21}(0)B_4^{21}(0) + B_4^{21}(0)B_4^{21}(0) \Big\} \phi_{00}^{21}(a,\bar{a})$$

$$+ 2\Big\{ -B_2(0)B_0(0) + B_2(0)B_4(0) + B_4(0)B_0(0) - B_4(0)B_4(0) \Big\} \phi_{02}(a,\bar{a})$$

$$+ 2\Big\{ B_2(0)B_0(0) - B_2(0)B_2(0) - B_4(0)B_0(0) + B_4(0)B_2(0) \Big\} \phi_{04}(a,\bar{a})$$

$$+ \Big\{ B_0(0)B_0(0) - 2B_0(0)B_4(0) + B_4(0)B_4(0) \Big\} \phi_{22}(a,\bar{a})$$

$$+ 2\Big\{ -B_0(0)B_0(0) + B_0(0)B_2(0) + B_4(0)B_0(0) - B_4(0)B_2(0) \Big\} \phi_{24}(a,\bar{a})$$

$$+ \Big\{ B_0(0)B_0(0) - 2B_0(0)B_2(0) + B_2(0)B_2(0) \Big\} \phi_{44}(a,\bar{a}) \Big]$$

$$A(2p_{xa}2p_{xb}::2p_{xa}2p_{xb}) =$$

$$\frac{1}{512} R^9 k_a^{10} \sum_{l=2}^{\infty} \Big[B_2^{21}(0)B_2^{21}(0)\, \phi_{00}^{21}(a,\bar{a}) - 2B_2^{21}(0)B_0^{21}(0)\, \phi_{02}^{21}(a,\bar{a})$$

$$+ B_0^{21}(0)B_0^{21}(0)\, \phi_{22}^{21}(a,\bar{a}) \Big]$$

Starting with the calculation of the B functions; tables were given earlier for the case $\beta = 0$. With the appropriate range equations the following table was compiled for $\beta = 0\cdot054$.

Table of $B^{01}_{j}(0\cdot054)$

l / j	0	1	2	3	4
0	$1\cdot000486\sqrt{2}$	$0\cdot018\sqrt{6}$	$0\cdot0001944\sqrt{10}$	$0\cdot0$	
1	$0\cdot018\sqrt{2}$	$0\cdot333624\sqrt{6}$	$0\cdot0072\sqrt{10}$	$0\cdot0$	
2	$0\cdot333624\sqrt{2}$	$0\cdot0108\sqrt{6}$	$0\cdot1334\sqrt{10}$	$0\cdot003086\sqrt{14}$	$0\cdot000111\sqrt{2}$
3	$0\cdot0108\sqrt{2}$	$0\cdot20021\sqrt{6}$	$0\cdot00617\sqrt{10}$	$0\cdot05723\sqrt{14}$	$0\cdot004114\sqrt{2}$
4	$0\cdot20021\sqrt{2}$	$0\cdot00771\sqrt{6}$	$0\cdot1143\sqrt{10}$	$0\cdot003429\sqrt{14}$	$0\cdot0762\sqrt{2}$

Table of $B^{11}_{j}(0\cdot054)$

l / j	0	1	2	3	4
0	$0\cdot0$	$0\cdot66678\sqrt{3}$	$0\cdot0072\sqrt{15}$	$0\cdot0$	
1	$0\cdot0$	$0\cdot0072\sqrt{3}$	$0\cdot13338\sqrt{15}$	$0\cdot002057\sqrt{42}$	
2	$0\cdot0$	$0\cdot13346\sqrt{3}$	$0\cdot003086\sqrt{15}$	$0\cdot038127\sqrt{42}$	$0\cdot002057\sqrt{10}$
3	$0\cdot0$	$0\cdot00617\sqrt{3}$	$0\cdot05714\sqrt{15}$	$0\cdot001371\sqrt{42}$	$0\cdot03814\sqrt{10}$

The other case directly connected with the problem is $\beta = 6\cdot09$. Two sets of auxiliary functions are involved: the $a_M(l)$ which were tabulated earlier and the $b^{l}_{o}(\beta)$ defined previously. For certain values of l the b's were evaluated directly from the equations while the remaining values were obtained by the appropriate bessel function recurrence relations.

	by direct equations	forward recurrence	backward recurrence
b_o^0	36·239573		
b_o^1	30·289277		30·289241
b_o^2		21·318744	21·318722
b_o^3		12·786204	12·786185
b_o^4	6·6219696	6·6219582	
b_o^5	3·0000232		3·0059132
b_o^6		1·2032086	1·2054851
b_o^7		0·4315982	0.4326282
b_o^8	0·1398980	0·1401589	
b_o^9	0·0413801		
b_o^{10}		0·0107978	

Comparison shows that these recurrence relations soon break down due to differencing effects which are fully described in Barnett and Coulson (1951a). Trouble from such effects was also encountered in the compilation of the B_j^{01} and B_j^{11} tables below.

The time involved in a $\phi(a)$ calculation for a single integral at one value of R is in excess of 30 hours using a desk computing machine. When one considers that there may be many such integrals all to be evaluated at a series of separations R, it is clear that the complete project is impossible on account of the time factor. Not only that, no time has been included for checking the results in the above estimate, and that is extremely important since in handling the complex recurrence formulas

Table of B^{01}_{j} and B^{11}_{j}(6·09)

	B^{01}_{j}				B^{11}_{j}		
ℓ ↓	j → 0	1	2	3	0	1	2
0	51·250489	42·835506	37·182975	32·934257	0	0	0
1	74·193281	64·402806	57·043814	51·301206	17·229086	11·586345	9·2642267
2	67·415717	62·573526	57·772537	53·515901	25·908974	20·715441	15·916752
3	47·841526	48·344374	47·444206	45·930345	27·213121	22·453775	19·423673
4	28·094638	31·180985	33·007710	35·863258	20·631040	19·509780	17·551129
5	14·071356	17·202210	19·807464	21·795396	12·655499	13·394121	13·418148
6	6·1467918	8·2480704	10·380565	12·341095	6·5411763	7·7056492	8·5168630
7	2·3696035	3·4899357	4·7933147	6·1907508	2·9117375	3·8102709	4·6407381
8	0·8157408	1·3148615	1·9704960	2·7631001	1·1565829	1·6450363	2·2052777
9	0·2550843	0·4435339	0·7223786	1·0979334	0·3975633	0·6256765	0·9172834

numerical errors creep in all too easily. Although most of the results quoted have been checked by repetition, a guarantee could not be given on their accuracy without performing the same integration by a different method. This has not yet been possible. As with the B functions, trouble arose due to the differencing effects in the application of the recurrence relations; so much so that some of the values of $\emptyset$, a positive definite function, became negative.

The values of the intermediate functions A, G, and $\emptyset$ are not included: only the final $\emptyset$'s appearing in the integral are tabulated here.

π

$\phi^{00}_{n\bar{n}}$	0	1	2	3	4
0	$0{\cdot}0^{6}366169$	$0{\cdot}0^{6}4181940$	$0{\cdot}0^{6}4855955$	$0{\cdot}0^{6}5746885$	$0{\cdot}0^{6}6970274$
1		$0{\cdot}0^{6}4782876$	$0{\cdot}0^{6}5560516$	$0{\cdot}0^{6}6595011$	$0{\cdot}0^{6}8015002$
2			$0{\cdot}0^{6}6475808$	$0{\cdot}0^{6}7696603$	$0{\cdot}0^{6}9375336$
3				$0{\cdot}0^{6}9168947$	$0{\cdot}0^{5}1119844$
4					$0{\cdot}0^{5}1371857$

$\phi^{01}_{n\bar{n}}$					
0	$0.0^{6}153025$	$0{\cdot}0^{6}1720448$	$0{\cdot}0^{6}1960080$	$0{\cdot}0^{6}2267930$	$0{\cdot}0^{6}2674875$
1		$0{\cdot}0^{6}1938914$	$0{\cdot}0^{6}2215046$	$0{\cdot}0^{6}2570911$	$0{\cdot}0^{6}3043082$
2			$0{\cdot}0^{6}2538538$	$0{\cdot}0^{6}2957116$	$0{\cdot}0^{6}3514822$
3				$0{\cdot}0^{6}3459106$	$0{\cdot}0^{6}4131348$
4					$0{\cdot}0^{6}4962006$

$\phi^{02}_{n\bar{n}}$					
0	$0{\cdot}0^{7}8262098$	$0{\cdot}0^{7}9200137$	$0{\cdot}0^{6}1035186$	$0{\cdot}0^{6}1180624$	$0{\cdot}0^{6}1367169$
1		$0{\cdot}0^{6}1027857$	$0{\cdot}0^{6}1160931$	$0{\cdot}0^{6}1329691$	$0{\cdot}0^{6}1547522$
2			$0{\cdot}0^{6}1316791$	$0{\cdot}0^{6}1515663$	$0{\cdot}0^{6}1773885$
3				$0{\cdot}0^{6}1754851$	$0{\cdot}0^{6}2067433$
4					$0{\cdot}0^{6}2454678$

$\phi^{03}_{n\bar{n}}$					
0	$0{\cdot}0^{7}508963$	$0{\cdot}0^{7}5626948$	$0{\cdot}0^{7}6285386$	$0{\cdot}0^{7}7098009$	$0{\cdot}0^{7}8128453$
1		$0{\cdot}0^{7}6246328$	$0{\cdot}0^{7}7077950$	$0{\cdot}0^{7}7951468$	$0{\cdot}0^{7}9158518$
2			$0{\cdot}0^{7}7909104$	$0{\cdot}0^{7}8024774$	$0{\cdot}0^{6}1046943$
3				$0{\cdot}0^{6}1037210$	$0{\cdot}0^{6}1212918$
4					$0{\cdot}0^{6}8174896$

$\bar{n} \rightarrow$

$\phi^{10}_{n\bar{n}}$	0	1	2	3
0	$0\cdot0^{9}3267627$	$0\cdot0^{9}3830646$	$0\cdot0^{9}4608415$	$0\cdot0^{9}5679165$
1	$0\cdot0^{9}3553289$	$0\cdot0^{9}4175816$	$0\cdot0^{9}5014966$	$0\cdot0^{9}6181103$
2	$0\cdot0^{9}3888285$	$0\cdot0^{9}4571357$	$0\cdot0^{9}5491302$	$0\cdot0^{9}6770510$
$\phi^{11}_{n\bar{n}}$				
0	$0.0^{10}1207612$	$0\cdot0^{10}1411861$	$0\cdot0^{10}1780453$	$0\cdot0^{10}2253648$
1	$0\cdot0^{10}1373529$	$0\cdot0^{10}1655884$	$0\cdot0^{10}2057715$	$0\cdot0^{10}2558228$
2	$0\cdot0^{10}1571039$	$0\cdot0^{10}1901822$	$0\cdot0^{10}2344795$	$0\cdot0^{10}2952698$
$\phi^{12}_{n\bar{n}}$				
0	$0\cdot0^{11}852417$	$0\cdot0^{11}9158800$	$0\cdot0^{10}1199996$	$0\cdot0^{10}1482810$
1	$0\cdot0^{11}957488$	$0\cdot0^{10}1133961$	$0\cdot0^{10}1375625$	$0\cdot0^{10}1695225$
2	$0\cdot0^{10}1089958$	$0\cdot0^{10}1395132$	$0\cdot0^{10}1579122$	$0\cdot0^{10}1952562$
$\phi^{13}_{n\bar{n}}$				
0	$0\cdot0^{11}6215116$	$0\cdot0^{11}6733112$	$0\cdot0^{11}8962601$	$0\cdot0^{10}1119954$
1	$0\cdot0^{11}7126359$	$0\cdot0^{11}8456845$	$0\cdot0^{10}1031664$	$0\cdot0^{10}1286027$
2	$0\cdot0^{11}8144487$	$0\cdot0^{11}9728635$	$0\cdot0^{10}1137351$	$0\cdot0^{10}1488148$
$\phi^{14}_{n\bar{n}}$				
0	$0\cdot0^{11}5900251$	$0\cdot0^{11}6445357$		
1	$0\cdot0^{11}6693026$	$0\cdot0^{11}8401621$		

$\phi^{04}_{n\bar{n}}$	0	1	2	3	4
0	$0{\cdot}0^7 3415246$	$0{\cdot}0^7 3755489$	$0{\cdot}0^7 4165785$	$0{\cdot}0^7 4678450$	$0{\cdot}0^7 5510098$
1		$0{\cdot}0^7 4168469$	$0{\cdot}0^7 4636898$	$0{\cdot}0^7 5235631$	$0{\cdot}0^7 5989620$
2			$0{\cdot}0^7 5202182$	$0{\cdot}0^7 5916995$	$0{\cdot}0^7 6813825$
3				$0{\cdot}0^5 2132$	$0{\cdot}0^5 5822$
4					$0{\cdot}0^4 1195$

From these results $A(1s_a 2p_{zb}::2s_a 2p_{xb}) =$

$$20,102,109/64\ 3\ (\ 0{\cdot}0^9 317366 - 0{\cdot}0^{10} 7498 - 0{\cdot}0^{10} 3417)$$

$$= 0{\cdot}0^4 3552$$

taking the summation only as far as $1 = 3$. To take it further than that would necessitate more than the 8 significant figures which I carried throughout since differencing errors prevent further extension to the present tables. With this in mind it is seen that the Rüdenberg method has a major practical disadvantage.

For the rest of the examples of exchange integrals the summation was carried to $1 = 4$ and even then the differencing effects caused a divergence in $\phi^{04}_{n\bar{n}}$. Quoting the results:

$A(2p_{za} 2p_{zb}::2p_{za} 2p_{zb}) = 0{\cdot}101132$

$A(2p_{za} 2p_{xb}::2p_{za} 2p_{xb}) = 0{\cdot}007984$

$A(2p_{xa} 2p_{zb}::2p_{xa} 2p_{zb}) = 0{\cdot}0007$ approx.

$A(2p_{xa} 2p_{xb}::2p_{xa} 2p_{xb}) = 0{\cdot}24603$

It should be noted that the results are very approximate for although the series was truncated at $1 = 4$ it is not so rapidly convergent. The $1 = 4$ term is still only smaller than the $1 = 0$ term by a factor of 10.

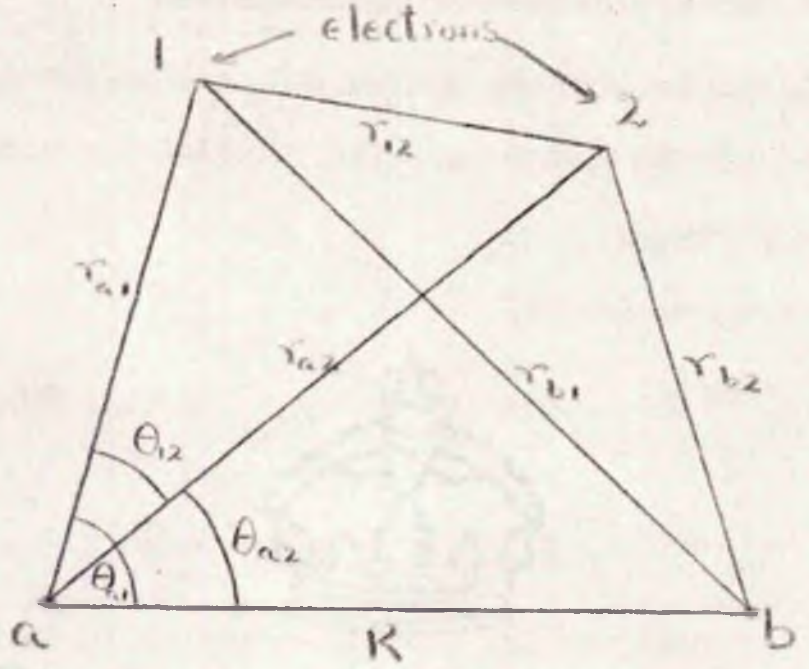

Figure 4·2

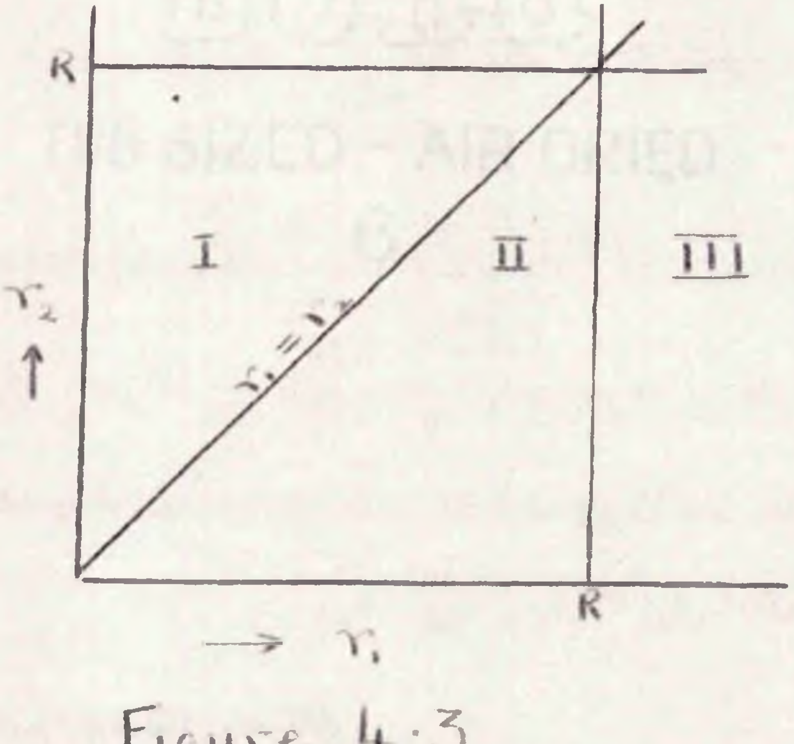

Figure 4·3

4·3 The Method of Barnett and Coulson.

This was outlined in section 3·3 and can be extended straight away to the exchange integrals. For detailed treatment we refer to Barnett and Coulson (1951a,b).

With the expansions

$$r_b^{m-1}\, e^{-kr_b} = \sum_{n\;j=0}^{\infty} (2n+1)/\sqrt{Rr_a}\; \mathcal{J}_{m,n}(k,r_a,R)\; P_n(\cos\Theta_a)$$

and

$$r_{12}^{-1} = \sum_{j=0}^{\infty} \delta_j(r_{a1},r_{a2})\; P_n(\cos\Theta_{12})$$

the radial components of the wave functions can be expanded around a common origin, the nucleus a, Figure 4·2.

The δ_j function is not to be confused with the Kronecker delta symbol with which it has no connection:

$$\begin{aligned} \delta_j(r_1,r_2) &= r_1^j / r_2^{j+1} &&\text{for } r_1 \leqslant r_2 \\ &= r_2^j / r_1^{j+1} &&\text{for } r_1 > r_2 \end{aligned}$$

The general exchange integral quoted in the introduction was

$$\int \mathcal{D} \exp(-k_1 r_{a1} - k_2 r_{b1} - k_3 r_{a2} - k_4 r_{b2})\; r_{a1}^{l_1}\, r_{b1}^{l_2}\, r_{a2}^{l_3}\, r_{b2}^{l_4}\; \frac{1}{r_{12}}\, \mathcal{P}\, dt$$

On expanding the integrand in terms of coordinates centred on 'a' we have,

$$\int_0^{\infty}\!\!\int_0^{\infty} \mathcal{D}' \exp(-k_1 r_{a1} - k_3 r_{a2})\; r_{a1}^{l_1+\frac{3}{2}}\; r_{a2}^{l_3+\frac{3}{2}}$$

$$\sum_{i,j,k} \mathcal{P}'_{ijk}\; \mathcal{J}_{l_2+1,i}(k_2,r_{a1},R)\; \delta_j(r_{a1},r_{a2})\, \mathcal{J}_{l_4+1,k}(k_4,r_{a2},R)$$

$$dr_{a1}\, dr_{a2}$$

where ρ'_{ijk} is the integral of all the angular functions. Incidentally the triple summation is not so large as it appears at first sight since the orthogonality of the Legendre functions reduces the number of terms considerably and analytic integration of the angular components is not without the bounds of practicability. Integration over the radial variables r_{a1} and r_{a2} however has to be done by numerical quadrature.

This is complicated by the form of the δ_j function which for j greater than 4 becomes very strongly peaked around the line $r_{a1} = r_{a2}$. In order to obtain reasonable accuracy therefore with a limited number of points Gaussian integration would be necessary. Besides, since the derivative of the integrand is discontinuous along the line $r = R$, the r integration is divided into 3 parts as shown in figure 4·3. In such a situation Gaussian integration is difficult and tedious.

Doubts have been cast on the acceptance of the delta factor and results are available (Dr H.H. Robertson, National Physical Laboratory in a private communication for which I should like to express my gratitude) which show that the delta function method gives rise to a non convergent summation.

4·4 Modification to the Barnett and Coulson Method.

(The work in this section was done under the supervision of Dr M.P. Barnett, by courtesy of I.B.M. Ltd., London.)

The difficulties of the zeta function evaluation of the exchange integrals have been overcome and the method simplified by the introduction of an integral representation for the delta function. This approach was suggested by Dr Cogbetliantz to whom I should like to express my gratitude.

Now
$$r_{a2}^{j}/r_{a1}^{j+1} = \int_0^\infty J_{j+1}(r_{a1}t)\, J_j(r_{a2}t)\, dt \qquad \text{for } r_{a2} < r_{a1}$$
$$= 0 \qquad \text{for } r_{a2} \geqslant r_{a1}$$

$$r_{a1}^{j}/r_{a2}^{j+1} = \int_0^\infty J_{j+1}(r_{a2}t)\, J_j(r_{a2}t)\, dt \qquad \text{for } r_{a1} \leqslant r_{a2}$$
$$= 0 \qquad \text{for } r_{a1} > r_{a2}$$

from page 406, Watson, 1952.

$$\therefore \quad \delta_j(r_{a1}, r_{a2}) = \int_0^\infty \left[J_{j+1}(r_{a1}t)\, J_j(r_{a2}t) + J_{j+1}(r_{a2}t)\, J_j(r_{a1}t) \right] dt$$

The exchange integral now reads

$$\iint_0^\infty \delta' \exp(-k_1 r_{a1} - k_3 r_{a2})\, r_{a1}^{l_1+\frac{1}{2}}\, r_{a2}^{l_3+\frac{3}{2}} \sum_{ijk} \mathcal{P}'_{ijk}\, \zeta_{l_2+1,i}(k_2, r_{a1}, R)\, \zeta_{l_4+1,k}(k_4, r_{a2}, R)$$
$$\int_0^\infty \left[J_{j+1}(r_{a1}t)\, J_j(r_{a2}t) + J_{j+1}(r_{a2}t)\, J_j(r_{a1}t) \right] dt \; dr_{a1} \; dr_{a2} \quad \ldots\ldots(4{\cdot}7)$$

The procedure is then to invert the order of integration after separation of the integrations with respect to r_{a1} and r_{a2}; i.e. to integrate over r_{a1} and r_{a2} first, then over t.

The application is not limited to two centre exchange integrals: in fact it extends to the multicentre integrals as well, thus amplifying the scope and power of the zeta function method in its modified form.

A systematic study of the component bessel transforms of the kind

$$\int_0^\infty\!\!\int e^{-kr}\, r^{1+\frac{1}{2}}\, \mathcal{J}_{m,n}(1,r,R)\; J_j(rt)\; dr\, dt \qquad \ldots\ldots\ldots(4\cdot 8)$$

was carried out and the results follow in the next section. These are just double integrals and it will be shown that a simple Simpson's rule integration is adequate, necessitating only one set of r_1 and one set of r_2 values in contrast to the complications of the Gaussian integration.

4·5 The Study of the Bessel Transforms.

It was hoped that an analytic method could be found to perform the double integration.

1. $J_j(rt)$ was expanded as a power series in t using the basic bessel function expansion

$$J_j(rt) = \sum_{m=0}^{\infty} \frac{(-)^m (\frac{1}{2}rt)^{j+2m}}{m!\;(j+m)!}$$

This was combined with the analytic treatment of the zeta functions - the $\underline{Z}$ method as described in Barnett and Coulson 1951a,b. Taking into account the divergence of the $\underline{Z}$ functions, it was found that the power expansion in t was reasonably convergent only for $t < 0\cdot 5$. For example, taking the first term in the summation over j, viz. $j = 0$ and where $m = n = 0$ in the $\mathcal{J}_{m,n}$ i.e. the $p_0(1,r,R)$ functions

$$\int_0^\infty \left[\int_0^\infty J_0(rt)\, e^{-kr}\, r^{1+\frac{1}{2}}\, p_0(1,r,R)\, dr \right] dt$$

we find with $k = 1 = 1$, $R = 2$ and

$$\underline{P}_{n,l+\frac{1}{2}}(k,R) = \int_0^\infty e^{-kr}\, p_n(l,r,R)\, r^{l+\frac{1}{2}}\, dr$$

by definition that there results

$$\int_0^\infty \left[\underline{P}_{o,\frac{3}{2}} - \frac{t^2}{4}\underline{P}_{o,\frac{7}{2}} + \frac{t^4}{64}\underline{P}_{o,\frac{11}{2}} - \frac{t^6}{2304}\underline{P}_{o,\frac{15}{2}} + \frac{t^8}{147{,}456}\underline{P}_{o,\frac{19}{2}} - \dots \right] dt \quad ..(4{\cdot}9)$$

The $\underline{P}$'s are independent of t and can be evaluated by the $\underline{Z}$ function procedure so that a term by term integration over t is possible.

For $t = 0{\cdot}5$, the first four terms (up to t^6) are

0·20734,   0·061605,   0·00912,   0·00100

showing that for t greater than $0{\cdot}5$ the convergence is no longer reasonably fast.

2. The basic integral equation (4·7) could also be expressed in terms of the hypergeometric function but there are no comprehensive tables of this function to make further investigation of this fact worth-while.

3. Yet another possibility was to express the bessel function in terms of the trigonometric asymptotic expansion (Watson, p.195) and try to fit the zeta functions to a polynomial giving an integral of the form

$$\int e^{-Kr} \begin{matrix}\cos\\ \sin\end{matrix}\, \lambda r \;\; r^m\, dr$$

which could be integrated analytically. Reference is made in this connection to Luke,(1954). The best polynomial approximation is obtained with the Tchebycheff polynomials $T_n(x)$, because they give faster convergence than any other polynomial. It is important to differentiate between the different variations regarding definition of these polynomials. We refer to 'Tables of Chebycheff Polynomials, 1952, and Clenshaw, 1954. The recommended method in the former reference page XVIII was followed, taking not equally spaced points but points corresponding to the zeros of the first neglected $T_n(x)$. This simplifies the orthogonal property of the polynomials and at the same time gives the best fit in the least square sense.

$$f(x) = \tfrac{1}{2}c_0 + c_1 T_1(x) + \ldots\ldots + c_{n-1} T_{n-1}(x) + \tfrac{1}{2}c_n T_n(x)$$

where

$$c_k = \frac{2}{n} \sum_{\alpha=0}^{n} f(x_\alpha) \cos k\alpha\pi/n$$

$$x_\alpha = \cos \alpha\pi/n, \qquad \alpha = 0, 1, \ldots\ldots n$$

The resulting fit was not good and the method was abandoned.

Since no simple general analytic method could be found to integrate equation (4·8), numerical quadrature seemed the only other way out.

The integrand of equation (4·8) is oscillatory and therefore the first operation was to try several simple bessel transforms using Simpson's rule with a varying number of points between the nodes. Transforms with analytically known values were chosen to enable checking between theory and calculations. In the first instance, the transform

$$\int e^{-ar} J_n(rt)\, r^n\, dr = \frac{(2t)^n \Gamma(n+\frac{1}{2})}{(a^2+t^2)^{n+\frac{1}{2}} \sqrt{\pi}} \qquad \ldots\ldots\ldots\ldots(4{\cdot}10)$$

(Watson, page 386) was chosen where $n = 0$, $a = t = 1$

$$\therefore \int e^{-r} J_0(r)\, dr = \Gamma(\tfrac{1}{2})/\sqrt{2\pi} = 1/\sqrt{2} = 0{\cdot}707107.$$

An I.B.M. 602A computer was programmed for a modified Simpson's rule procedure (Appendix II·1) and with an interval of integration

$\Delta r = 0{\cdot}08$, the result was 0·707107

$\Delta r = 0{\cdot}16$, the result was 0·706905.

Taking now $t = 5$, $a = 1$, $n = 0$, the analytic value of equation (4·10) is $1/\sqrt{26} = 0{\cdot}1961$. With only 100 strips and $\Delta r = 0{\cdot}20$ corresponding to three points between nodes, Simpson's Rule gave 0·1957.

In the next case, the zeta function

$$2\sqrt{3}\ r^{\frac{1}{2}} e^{-r} \zeta_{00}(r,3) = r\ e^{-r} \chi_{00}(r,3) = I \qquad \ldots\ldots.(4{\cdot}11)$$

was generated in the machine (Appendix II·2) and punched on cards for $r = 0(0{\cdot}01)10{\cdot}00$. These cards were interleaved with packs of cards bearing selected values of J_0 in such a way that the transform

$$\int_0^\infty r\ e^{-r} \chi_{00}(r,3)\ J_0(rt)\ dr$$

was evaluated for a variety of t values. The results are given in the table below and where an analytic determination was possible it has been added; the details of which are expounded below.

To provide a check on the numerical quadrature, the integration was performed analytically wherever possible, Table of values of the transform $\int_0^\infty r\, e^{-r} \chi_{00}(r,3)\, J_0(rt)\, dr$

Limits and interval of integration	by Simpson's Rule	no of strips	t	analytic integration
0(0·05)10·00	−0·000403	200	10	
0(0·1)10·00	−0·000059	100	5	−0·000061
0(0·02)5·00	−0·002268	250	4	
0(0·02)10·00	−0·007815	500	2	−0·007811
0(0·04)10·00	0·012726	250	1	
0(0·08)10·00	0·185771	125	0·5	0·185807
0(0·1)10·00	0·298721	100	0·0	0·298722

By definition,

$$\chi_{00}(r,R) = e^{-|r-R|} - e^{-(r+R)}$$

and so the transform reads

$$I = \int_0^R (1 - e^{-2r})\, e^{-R}\, r\, J_0(rt)\, dr + \int_R^\infty e^{-2r}(e^{R} - e^{-R})\, r\, J_0(rt)\, dr \qquad (4{\cdot}12)$$

$$= (e^{R} - e^{-R}) \int_0^\infty r\, e^{-2r} J_0(rt)\, dr \quad + \quad e^{-R} \int_0^R r\, J_0(rt)\, dr$$

$$- \quad e^{R} \int_0^R e^{-2r}\, r\, J_0(rt)\, dr$$

Examining this term by term, the first is

$$(e^{R} - e^{-R}) \int_0^\infty r\, e^{-2r} J_0(rt)\, dr = (e^{R} - e^{-R}) \frac{2}{(4+t^2)^{3/2}}$$

Watson, page 386, equation (6)

The second term $e^{-R}\int_0^R r\,J_o(rt)\,dr$

Consider

$$rt\,J_o(rt) = r\frac{d}{dr}J_1(rt) + J_1(rt)$$

Watson, page 45, equation (3),

then $$e^{-R}\int_0^R r\,J_o(rt)\,dr = e^{-R}/t\int_0^R \left[r\frac{d}{dr}J_1(rt) + J_1(rt)\right]dr$$

integrating by parts

$$= R/t\;\;e^{-R}\,J_1(rt)$$

The third term:

Consider $\int_0^R e^{-ar}\;r\;J_o(rt)\;dr$

and put $rt = v$, therefore $r = v/t$

then $$\int_0^R e^{-ar}\,r\,J_o(rt)\,dr = \int_0^{Rt} e^{-av/t}\,.\;u/t^2\,.\,J_o(v)\,dv$$

$$= 1/t^2\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{-a}{t}\right)^n\int_0^{Rt} v^{n+1}\;J_o(v)\,dv$$

on expanding the exponential as a power series,

$$= \sum_{n=0}^{\infty} I_n(a,t)$$

where $$I_n(a,t) = \frac{1}{t^2 n!}\left(\frac{-a}{t}\right)^n\int_0^{Rt} v^{n+1}\,J_o(v)\;dv$$

$$= 1/t^2 n!\left(\frac{-a}{t}\right)^n\;T_{n+1}(Rt)$$

Now $$T_{n+1}(Rt) = -n^2\,T_{n-1}(Rt) + (Rt)^n\left[Rt\,J_1(Rt) + n\,J_o(Rt)\right]$$

Watson, page 133, equation (4)

$$\therefore\;\; I_n = -n/(n-1).a^2/t^2.I_{n-2} + (-aR)^n/t^2 n!\left[Rt\,J_1(Rt) + n\,J_o(Rt)\right]$$

$$I_0 \quad = \quad 1/t^2 \int_0^{Rt} v\, J_0(v)\, dv \quad = \quad R/t \;\; J_1(Rt)$$

(see analysis of second term)

$$I_1 \quad = \quad 1/t^2.(-a/t) \int_0^{Rt} v^2\, J_0(v)\, dv$$

$$\quad = \quad a/t^3 \,.\int_0^{Rt} J_0(v)\, dv \quad - \quad aR/t^2.\left[Rt\; J_1(Rt) \; + \; J_0(Rt) \right]$$

using the recurrence relation for the $T_n(Rt)$ above.

All $J_0(Rt)$, $J_1(Rt)$ and $\int_0^{Rt} J_0(v)\, dv$ can be found immediately from tables. Returning now to our problem, namely the evaluation of the third term in the integral I, we see that

$$e^R \int_0^R e^{-2r}\, r\, J_0(rt)\, dr \quad = \quad \sum_{n=0}^{\infty} I_n(2,t)$$

This analysis is suitable for $t > 2$ and although the series of $I_n(a,t)$ is only slowly convergent (up to 50 terms had to be taken to get four significant figures in the final value of I for $t = 2$), it is subject to very rapid computation on a desk machine.

For $t = 2$, the three terms give

$$1{\cdot}7709268 \quad - \quad 1{\cdot}7580751 \quad - \quad 0{\cdot}0206629 \quad = \quad -0{\cdot}007811(2).$$

For $t = 5$, the three terms give

$$0{\cdot}2565893 \quad + \quad 0{\cdot}0061269 \quad - \quad 0{\cdot}2627774 \quad = \quad -0{\cdot}000061(2)$$

A more general but longer to compute method follows from equation (4·12)

$$
\begin{aligned}
I = {} & e^{-R}\int_0^R r\, J_0(rt)\, dr - e^{-R}\int_0^R e^{-2r}\, r\, J_0(rt)\, dr \\
& + (e^R - e^{-R})\int_0^\infty r\, e^{-2r}\, J_0(rt)\, dr - (e^R - e^{-R})\int_0^R e^{-2r}\, r\, J_0(rt)\, dr \\
= {} & (e^R - e^{-R})\int_0^\infty r\, e^{-2r}\, J_0(rt)\, dr + e^{-R}\int_0^R r\, J_0(rt)\, dr \\
& - e^R\int_0^R e^{-2r}\, r\, J_0(rt)\, dr \quad ..(4\cdot 13)
\end{aligned}
$$

Consider now the third term of the last equation

$$
e^R\int_0^R e^{-2r}\, r\, J_0(rt)\, dr = e^R\int_0^\infty e^{-2r}\, r\, J_0(rt)\, dr - e^R\int_R^\infty e^{-2r}\, r\, J_0(rt)\, dr
$$

and the last term of this can be transformed by change of variable,

$$
r = x + R
$$

thus

$$
\begin{aligned}
e^R\int_R^\infty e^{-2r}\, r\, J_0(rt)\, dr = {} & e^R\int_0^\infty e^{-(2x+2R)}\,(x+R)\, J_0(xt + Rt)\, dx \\
= {} & e^R\int_0^\infty e^{-2x}\, x \sum_{s=-\infty}^{\infty}(-1)^s J_s(xt)\, J_s(Rt)\, dx \\
& + R\, e^{-R}\int_0^\infty e^{-2x} \sum_{s=-\infty}^{\infty}(-1)^s J_s(xt)\, J_s(Rt)\, dx
\end{aligned}
$$

which follows immediately from Watson, page 143, equation (1) and page 15, equation (2).

It is convenient to define the auxiliary integral

$$
I_{nm}(a,t) = \int_0^\infty e^{-ar}\, r^m\, J_n(rt)\, dr
$$

Equation 4·12 now reads

$$
\begin{aligned}
I = {} & (e^R - e^{-R})\, I_{01}(2,t) + e^{-R}\, I_{01}(0,t) - e^R\, I_{01}(2,t) \\
& + e^{-R}\sum_{s=-\infty}^{\infty}(-1)^s I_{s1}(2,t)\, J_s(Rt) + R\, e^{-R}\sum_{s=-\infty}^{\infty}(-1)^s I_{s0}(2,t)\, J_s(Rt)
\end{aligned}
$$

$$= e^{-R}\, I_{01}(0,t) \quad - \quad e^{-R}\, I_{01}(2,t)$$

$$+ \quad e^{-R} \sum_{s=-\infty}^{\infty} (-1)^s \left[I_{s1}(2,t) + R\, I_{s0}(2,t) \right] J_s(Rt)$$

Because of the symmetry of the product $J_s(rt)\, J_s(Rt)$ only positive values of s need be considered in the summation. Finally then,

$$I = e^{-R} \Big[I_{01}(0,t) - I_{01}(2,t) + \left\{ I_{01}(2,t) + R\, I_{00}(2,t) \right\} J_0(Rt)$$

$$+ \quad 2 \sum_{s=1}^{\infty} (-1)^s \left\{ I_{s1}(2,t) + R\, I_{s0}(2,t) \right\} J_s(Rt) \Big]$$

The evaluation of the $I_{nm}(a,t)$ presents little difficulty:

First, $I_{01}(0,t) = \int_0^{\infty} r\, J_0(rt)\, dr$

Now
$$rt\, J_0(rt) = r \frac{d}{dr} J_1(rt) + J_1(rt)$$

Watson, page 45, equation (3)

$$\therefore \int_0^R r\, J_0(rt)\, dr = 1/t \int_0^R \left[r \frac{d}{dr} J_1(rt) + J_1(rt) \right] dr$$

$$= R/t \,.\, J_1(Rt) \qquad \text{by partial integration}$$

$$\therefore I_{01}(0,t) = R/t \,.\, J_1(Rt)$$

$$I_{01}(a,t) = \int_0^{\infty} e^{-ar}\, J_0(rt)\, r\, dr = \frac{2a\, \Gamma(\frac{3}{2})}{(a^2+t^2)^{3/2} \sqrt{\pi}}$$

Watson, page 386, equation (6).

$$I_{nn}(a,t) = \int_0^{\infty} e^{-ar}\, J_n(rt)\, r^n\, dr = \frac{(2t)^n\, \Gamma(n+\frac{1}{2})}{(a^2+t^2)^{n+\frac{1}{2}} \sqrt{\pi}}$$

Watson, page 386, equation (5).

$$I_{n0}(a,t) = \int_0^\infty e^{-ar} J_n(rt)\, dr = \frac{\left(\sqrt{a^2+t^2} - a\right)^n}{t^n \sqrt{a^2+t^2}}$$

Watson, page 386, equation (8).

The only other values required are $I_{n1}(a,t)$

Consider $I_{nm}(a,t) = \int_0^\infty e^{-ar} r^m J_n(rt)\, dr$

where $du = e^{-ar}$ and $v = r^m J_n(rt)$

$$\therefore \quad dv = m\, r^{m-1} J_n + t\, r^m J_n'$$

But $J_n' = J_{n-1} - n/rt \,.\, J_n$

$$\therefore \quad dv = (m-n)\, r^{m-1} J_n + t\, r^m J_{n-1}$$

integrating by parts $\int v\, du = uv - \int u\, dv$

$$I_{nm}(a,t) = (m-n)/a \,.\, I_{n,m-1} + t/a \,.\, I_{n-1,m}$$

$$\therefore I_{n1}(a,t) = t/a \,.\, I_{n-1,1}(a,t) - (n-1)/a \,.\, I_{n0}(a,t)$$

To examine the results of the analytic integration, take first $t = 0$.

1. Using immediately the notation of Barnett and Coulson(1951b), the integral is

$$2\sqrt{3}\int_0^\infty r^{\frac{1}{2}}\, e^{-r}\, \mathcal{J}_{00}(1,r,3)\, dr = 2\sqrt{3}\ \underline{G}_{0,}(1,3)$$
$$= 2\sqrt{3}\ e^{-3}\sqrt{3}$$
$$= 0{\cdot}298722$$

2. Recalling equation 4·13, the integral is

$$e^{-R}\left(R^2/2 - 0{\cdot}25 + (2R+1)/4 \right) = 0{\cdot}298722$$

Simpson's Rule integration using only 100 strips in the interval $r = 0(0{\cdot}1)10{\cdot}00$ gave the value 0·29872, to five significant figures.

At $t = 0{\cdot}5$ the power series expansion of the bessel function was used cf. equation(4·9). In this case the series was taken to the 12th power term in t.

$$I = 2\sqrt{3}\Big[\underline{G}_{0,\frac{3}{2}}(1,3) - \underline{G}_{0,\frac{7}{2}}t^2/4 + \underline{G}_{0,\frac{11}{2}}t^4/64 - \underline{G}_{0,\frac{15}{2}}t^6/2304$$

$$+ \underline{G}_{0,\frac{19}{2}}t^8/147{,}456 - \underline{G}_{0,\frac{23}{2}}t^{10}/14{,}745{,}600 + \underline{G}_{0,\frac{27}{2}}t^{12}/2{,}123{,}366{,}400 - \dots\Big]$$

$$= 0{\cdot}2987224 - 0{\cdot}1530248 + 0{\cdot}0222073 - 0{\cdot}0022654 + 0{\cdot}0001801$$

$$- 0{\cdot}0000128 + 0{\cdot}0^67$$

$= 0{\cdot}165807$ to six significant figures.

4·6 Conclusion.

The zeta function method with the bessel modification is workable and the integration over t is seen to be rapidly although oscillatorily convergent. The results of this investigation have been passed on to a computing group in the United States of America where the method is being applied to high speed electronic computing machines. It is reasonable to expect results for the exchange integrals in the not too distant future.

Chapter 5.

5·1 The investigation of a bound state in Neon.

In the investigation of the stationary state of Neon the argument of J. de Boer (1940) was followed. The Schrödinger equation is

$$-\frac{\hbar^2}{m}\frac{d^2 r\psi_{nl}}{dr^2} + \left[V(r) + \frac{h^2\, l(l+1)}{mr^2}\right] r\psi_{nl} = E_{nl}\, r\psi_{nl} \qquad \ldots.(5\cdot1)$$

where $r\psi$ is the radial wave function, m the mass of the Neon atom, $V(r)$ the interatomic potential, and n and l are respectively the orbital and angular quantum numbers.

From the behaviour of the wave function in the case $l = 0$, $E = 0$ at large values of r, conclusions can be drawn on the existence of discrete energy levels in the molecule. If the wave function $r\psi$ increases as a function of r as r tends to infinity and has no nodes, there is no stationary state (figures 5·1a and 5·1b) : if the wave function cuts the r axis there is a stationary state possible in the attractive potential field for a negative energy (figure 5·2). In the case of the wave function becoming constant (figure 5·3), it could be said that the stationary state occurs exactly at zero energy. Kilpatrick, Keller and Hammel (1955) have used the behaviour of phase shifts to determine the existence of discrete energy levels.

Applying the de Boer conditions the Schrödinger equation reads

$$-\frac{\hbar^2}{m}\frac{d^2 r\psi_0}{dr^2} + \left[V(r)\right] r\psi_0 = 0 \qquad \ldots\ldots.(5\cdot2)$$

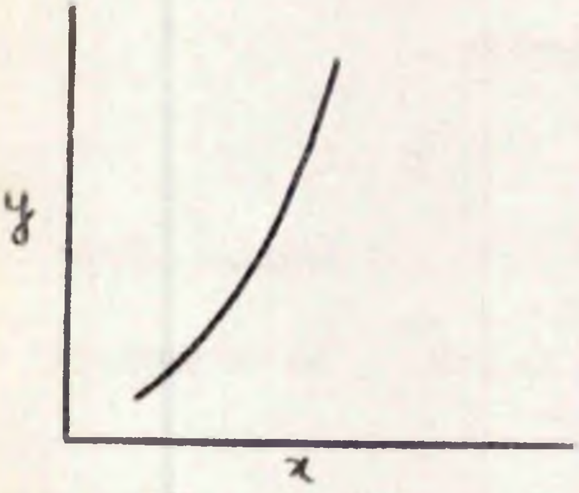

Figure 5·1a

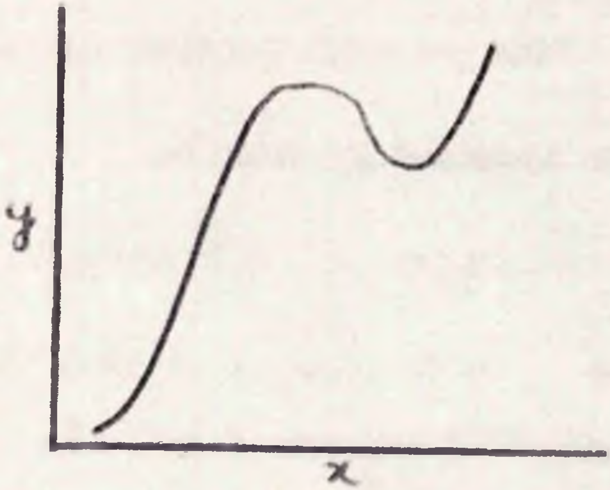

Figure 5·1b

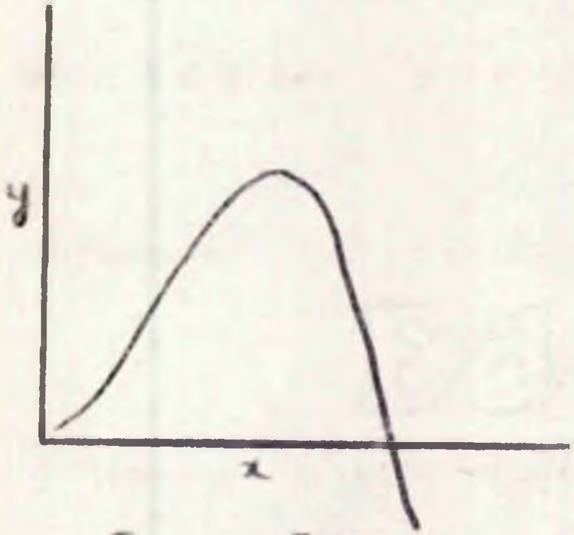

Figure 5·2

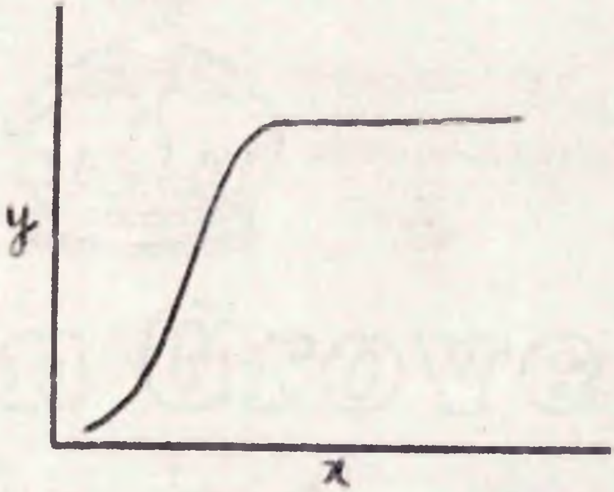

Figure 5·3

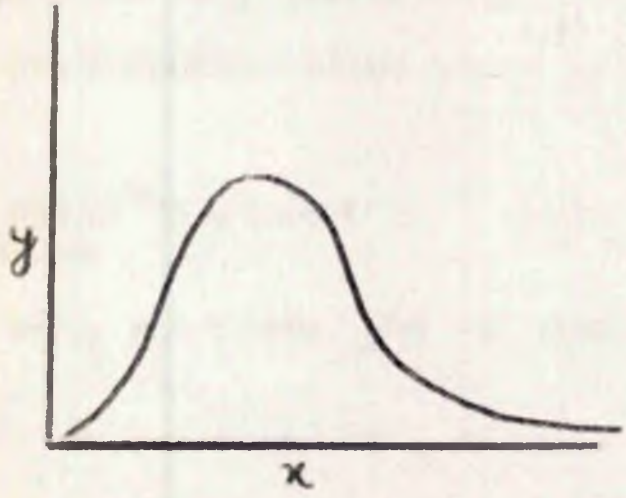

Figure 5·4

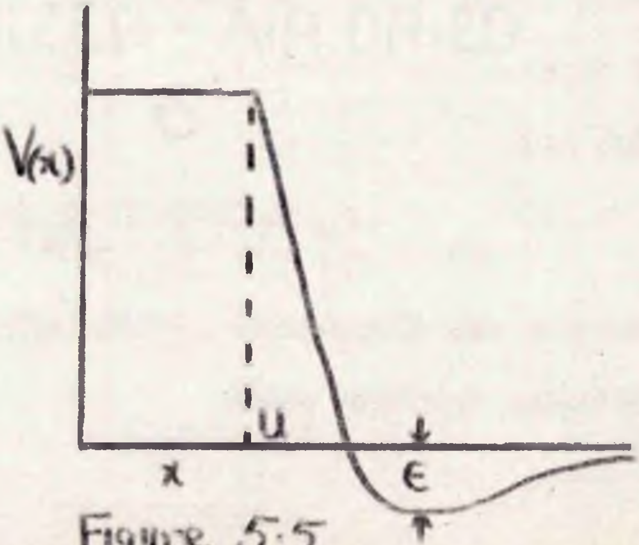

Figure 5·5

Two potential functions were investigated:

I The Lennard-Jones Function.

$$V_L(r) = 4\sigma\epsilon\left[1/r^{12} - 1/r^{6}\right] \qquad ....(5\cdot3)$$

where σ is the value of r when $V(r) = 0$, and ϵ is the depth of the potential well cf. figure 5·5.

The values of the parameters were those listed by J. Corner (1948)

$\epsilon = 1\cdot150 \times 10^{-4}$ atomic units

$\sigma = 5\cdot33$ atomic units

In non-dimensional atomic units with $x = r/\sigma$ and $y = x\psi_0$, the differential equation is

$$\frac{d^2y}{dx^2} - 476\cdot433\left[1/x^{12} - 1/x^{6}\right]y = 0 \qquad ......(5\cdot4)$$

II The modified Buckingham exp-6 function.

$$V_B(r) = \epsilon/(\alpha - 6)\left[6\exp\alpha(1 - r/r_m) - \alpha(r_m/r)^6\right] ......(5\cdot5)$$

where ϵ is the depth of the potential well, r_m its position, and α is a dimensionless numerical parameter. Mason and Rice (1954) give values of these derived experimentally from viscosity, second virial coefficient and crystal data.

$\alpha = 14\cdot5$, $r_m = 5\cdot9456$ atomic units, $\epsilon = 1\cdot2032 \times 10^{-4}$ atomic units.

Introducing non-dimensional atomic units with $x = r/r_m$ and $y = x\psi_0$, the differential equation reads

$$d^2y/dx^2 - \left[109{\cdot}5597 \exp 14{\cdot}5(1-x) - 264{\cdot}7694/x^6\right] y = 0 \quad ..(5{\cdot}6)$$

The boundary conditions are $y = y' = 0$ at $x = 0$. The equations (5·4) and (5·6) are not capable of analytic solution and therefore a numerical step by step method must be sought.

5·2 The choice of numerical method.

Two methods were compared in a test run with judiciously chosed $V(r)$. Actually they were $V_L(r)$ and $V_B(r)$ scaled down by the ratio of the mass of the Neon atom to the mass of the electron to give a less steep solution especially near the origin.

a) In the first place the differentiation formulae (Bickley, 1941) were employed

$$y'_0 = \frac{1}{6h}\left(-2y_{-3} + 9y_{-2} - 18y_{-1} + 11y_0\right)$$

$$y''_{-3} = \frac{1}{h^2}\left(2y_{-3} - 5y_{-2} + 4y_{-1} - y_0\right)$$

$$y''_{-2} = \frac{1}{h^2}\left(y_{-3} - 2y_{-2} + y_{-1}\right)$$

The scheme was to choose $x = y = 1$ arbitrarily (since it is a homogeneous second order differential equation), guess a value of y' at that point and by recurring backwards with equation (5·7) find that y' which will give $y = 0$ at $x = 0$.

$$y_{-4} = \frac{5y_{-3} - 4y_{-2} + y_{-1}}{2 - h^2 V(x)_{-4}} \quad ....(5{\cdot}7)$$

Recursion forward from $x = 1$ with equation (5·8) would then decide the existence or non-existence of a stationary state.

$$y_0 = y_{-3}\left[2 - h^2 V(x)_{-3}\right] - 5y_{-2} + 4y_{-1} \qquad \ldots\ldots(5\cdot 8)$$

In practice it was impossible to reach $x = 0$ due to $V(x)$ tending to $\pm \infty$ as x tended to 0, and therefore two bounding solutions were found between which the true one should lie. The interval of integration was $h = 0\cdot01$. In the forward recursion from $x = 1\cdot00$ it was $h = 0\cdot05$ in the first instance, and with both potential functions the two bounding solutions were of the type shown in figure 5·2, but when h was reduced to 0·01 the bounding solutions diverged from each other thus deciding nothing: consequently another method was investigated.

b) The method of Fox and Goodwin (1949).

For the numerical solution of the second order differential equation

$$y'' = f(x)\, y$$

Fox and Goodwin present

$$\left[1 - \frac{1}{12}h^2 f_0(x)\right] y_0 = \left[2 + \frac{5}{6} h^2 f_{-1}(x)\right] y_{-1} - \left[1 - \frac{1}{12} h^2 f_{-2}(x)\right] y_{-2} + \Delta \qquad .(5\cdot 9$$

where
$$\Delta = \left(-\frac{1}{240}\,\delta^6 + \frac{13}{15120}\,\delta^8 + \ldots.\right) y_{-1}$$

in which δ^6 and δ^8 are the sixth and eighth differences respectively.

The two potential functions were modified (figure 5·5) so that the Lennard-Jones potential was

$$V_L(r) = V_L(0{\cdot}40) \quad \text{for} \quad 0 < r < 0{\cdot}40$$

and as defined in equation (5·3) for $r > 0{\cdot}40$;

while the Buckingham potential was

$$V_B(r) = V_B(0{\cdot}18) \quad \text{for} \quad 0 < r < 0{\cdot}18$$

and as defined in equation (5·5) for $r > 0{\cdot}18$.

Analytic integration was possible to $x = 0{\cdot}40$ and $0{\cdot}18$ respectively while the y_1 viz. at $x = 0{\cdot}41$ and $0{\cdot}19$ were found from a Taylor series expansion. Therefrom step by step integration was effected using equation (5·9) in which $h = 0{\cdot}01$ and continued until the gradient became virtually constant. In both cases the solutions were typified by figure 5·1a. With starting values from the previous iteration, the integration was repeated from $x = 1$ with $h = 0{\cdot}05$. The solutions for both potentials agreed with the $h = 0{\cdot}01$ values to within $0{\cdot}1\%$ thus verifying the consistency of the method. It is seen that this method is to be preferred to the first one, being more accurate in that it neglects only the sixth and higher differences which are small here. Method a) on the other hand assumes the derivatives of order higher than three to be zero which with the function in question is certainly not so.

5·3 The Solution.

In the solution of the Schrödinger equation we shall use equation (5. If as in this case the sixth and higher order differences are very small, we can justifiably put $\Delta = 0$: arranging equation (5·9) to make it suitable for the automatic machine

$$\left[1 - \frac{1}{12}h^2 f_n(x)\right] y_n = \left[\frac{2 + \frac{5}{6}h^2 f_{n-1}(x)}{1 - \frac{1}{12}h^2 f_{n-1}(x)}\right]\left[1 - \frac{1}{12}h^2 f_{n-1}(x)\right] y_{n-1}$$

$$- \left[1 - \frac{1}{12}h^2 f_{n-2}(x)\right] y_{n-2} \qquad \ldots(5\cdot10)$$

The three auxiliary functions are defined thus

$$w_n = -\frac{1}{12}h^2 f_n(x) \qquad \ldots\ldots\ldots(5\cdot11)$$

$$R_n = y_n(1 + w_n) \qquad \ldots\ldots\ldots(5\cdot12)$$

$$a_n = (2 - 10w_n) / (1 + w_n) \qquad \ldots\ldots\ldots(5\cdot13)$$

The recurrence relation (5·14) follows immediately from equation (5·10)

$$R_n = a_{n-1} R_{n-1} - R_{n-2} \qquad \ldots\ldots\ldots(5\cdot14)$$

Finally,

$$y_n = R_n / (1 + w_n).$$

As was cursorily mentioned in the previous section, the form of the potential, $V(r = 0) = \pm\infty$, makes it impossible to integrate step by step wise from $x = 0$. Thereupon as in the test case it was assumed constan but very large for all x less than a specific value U according to the potential form used. In this constant region the solution is

$$y = A\exp(\sqrt{V}\,x) + A'\exp(-\sqrt{V}\,x) \qquad \ldots\ldots\ldots(5\cdot15)$$

But $y = 0$ at $x = 0$, therefore $A = -A'$.

The constant potential was chosen so large that the negative exponential was small enough to be neglected compared with the positive exponential. Since the Schrödinger equation is homogeneous the value of A merely determines the scale of the solution and it shall be chosen here for numerical convenience. Having found y_o from equation (5·15), y_1 was obtained by using a Taylor expansion and equation (5·15), neglecting the second term.

$$y_1 = y_o + h\, y_o' + h^2/2!\; y_o'' + h^3/3!\; y_o''' + \ldots.$$

$$= \sum_{n=0}^{\infty} (\sqrt{V}\, h)^n\, y_o/n! = y_o \exp(h\sqrt{V}) \qquad \ldots\ldots.(5{\cdot}16)$$

The preparation of the auxiliary functions and the programming details will be found in Appendix II·4.

In the first instance equations (5·4) and (5·6) were solved on the machine. Several restrictions prevented starting the solution at very small x. The programme was not able to handle negative values of $(2 - 10w_n$ and $(1 + w_n)$ and this meant that the least x was 0·52 for the Buckingham and 0·62 for the Lennard-Jones potential. The restricted counter capacity of the machine enabled the calculations to be done throughout to only eight figures. Commencing respectively at $x = 0{\cdot}52$ and 0·62 the gradient of the solution was so steep that although y_o was chosen to be unity in the lowest digital position the subsequent y_n very quickly overflowed the counter. The starting value of x was gradually increased until the y_n could just be contained in the counter. Even this was not wholly satisfactory for the smaller y_0 the less accurate was y_1. A compromise is suggested in which the y_0 is not too small and the x_0 is not too large. Several y_0 and x_0 were taken for both potentials.

a) Lennard-Jones potential:

With $x_0 = 0{\cdot}70$ it was found that the counter overflowed; but starting at $x_0 = 0{\cdot}75$ and $x_0 = 0{\cdot}80$ the solution remained within the counter capacity. The initial values were respectively

$y_0 = 0{\cdot}0000100$	$y_0 = 0{\cdot}0010000$
$y_1 = 0{\cdot}0000304$	$y_1 = 0{\cdot}0020442$
$a_1 = 3.1333836$	$a_1 = 2{\cdot}4443532$
$R_0 = 0{\cdot}0000090$	$R_0 = 0{\cdot}0009574$
$R_1 = 0{\cdot}0000278$	$R_1 = 0{\cdot}0019712$

In both cases the solutions were of the type as shown in figure 5·2 with the maximum around $x = 1{\cdot}12$ and the intersection of the x axis between $x = 1{\cdot}26$ and $x = 1{\cdot}27$. The conditions for a stationary state were therefore fulfilled.

b) Buckingham potential:

With $x_0 = 0{\cdot}60$ the counter overflowed but from $x_0 = 0{\cdot}6$ and $x_0 = 0{\cdot}70$ the solutions did not exceed the capacity of the counter. The starting values were respectively

$y_0 = 0{\cdot}0000100$

$y_1 = 0{\cdot}0000327$

$a_1 = 3{\cdot}3291950$

$R_0 = 0{\cdot}0000088$

$R_1 = 0{\cdot}0000294$

$y_0 = 0{\cdot}0010000$

$y_1 = 0{\cdot}0022030$

$a_1 = 2{\cdot}5518492$

$R_0 = 0{\cdot}0009480$

$R_1 = 0{\cdot}0021061$

In both cases the solutions were of the form shown in figure 5·2 with the maximum around $x = 1{\cdot}01$ and the intersection of the x axis between $x = 1{\cdot}12$ and $1{\cdot}13$. The conditions for a stationary state were therefore fulfilled.

The Energy of the Stationary or Bound State.

The method of estimating the energy of the bound state was one of trial and error, but this proved to be quite sufficient for the nonce.

Equation(5·1) now reads

$$-\frac{\hbar^2}{m}\frac{d^2 r\psi_0}{dr^2} + \left[V(r) - E\right] r\psi_0 = 0 \qquad \ldots\ldots(5{\cdot}17)$$

which in non-dimensional atomic units is

$$d^2y/dx^2 - L\left[V_L(x) - E\right]y = 0 \qquad \ldots\ldots(5{\cdot}18)$$

where $L = 1{\cdot}034458 \times 10^6$ atomic units (Lennard-Jones case)

and

$$d^2y/dx^2 - B\left[V_B(x) - E\right]y = 0 \qquad \ldots\ldots(5{\cdot}19)$$

where $B = 1{\cdot}238279 \times 10^6$ atomic units (Buckingham case)

The actual function of E as read into the machine however was

$h^2 L\,E/12$ or $h^2 B\,E/12$ and the absolute values of these were increased if the previous trial resulted in the form of figure 5·2 and decreased if it was similar to figures 5·1a or 5·1b. It was found that the nearer the true value one approached the more pronounced became the form of figure 5·1b. The ultimate aim of course was to get a solution like figure 5·4.

Commencing at $x = 0{\cdot}75$ the result was $h^2 L\,E/12 = 0{\cdot}0003992$ to four significant figures, while starting at $x = 0{\cdot}80$ to three significant figures $h^2 L\,E/12 = 0{\cdot}000393$. The difference between the results shows that the energ is dependent on where the iteration is started and suggests that the assumption of potential constancy up to $x = U$ in figure 5·4 is too crude. The above figures lead to an attractive energy of approximately $0{\cdot}46 \,.\, 10^{-4}$ atomic units.

For the Buckingham potential the agreement was not good between the results by starting at $x = 0{\cdot}70$ and $x = 0{\cdot}65$: for the former $h^2 B\,E/12 = 0{\cdot}00069$ and for the latter $h^2 B\,E/12 = 0{\cdot}000764$. The approximate attractive energy is then $E = 0{\cdot}65 \times 10^{-4}$ atomic units.

The differences between the two results in either set was not apparent in the $E = 0$ solution because the gradient at the intersection of the x axis was very steep.

It is concluded then that on the assumption of the rather artificial potential form (figure 5·5), a bound state does exist at a depth of approximately $0{\cdot}5 \times 10^{-4}$ atomic units (0·0015electron volts) with both potentials.

Discussion.

When we embarked on the project of finding the interatomic potential of Neon we did not anticipate the vast amount of numerical work which it has subsequently incurred.

The quantum mechanical approach is indeed one of no little magnitude and the leading question is: do the initial crude approximations make it worthwhile carrying through the calculations to the exacting limits demanded by the various methods and particularly their constituent recurrence formulae.

Three main topics are worthy of consideration:

1. The wave function approximation
2. The number of integrals
3. The computation project

1. The wave function approximation was fully discussed in chapter 2. Theoretically it should be possible to obtain a very accurate representation of the wave function by a sum of Slater type nodeless wave functions provided a sufficient number of terms are taken. However the more terms, the greater the task of determining the coefficients and with an eye to the integral project, the fantastically great number of integrals to be computed.

2. The number of integrals: even although the wave functions are of a very simple form the enormous number of integrals and the just as vast field of permutations to be accounted for immediately suggests the question of simplifying assumptions. These have been considered and have been

rejected, cf. the overlap integral paradox in chapter 5. In some cases of the more difficult integrals a selection from the total number was calculated but no attempt was made to find the residual overlap integral permutations (chapter 2)

$$\int xa \; xb \quad P \quad xa \; xb \; dt$$

which consisted of hundreds of terms.

5. The computation project: It is clearly seen that to evaluate the integrals a major computation project is inevitable. In order to obtain a sufficient number of values of the atomic potential for a graph the project is not only major but well nigh prohibitive. Consider finally that all this results from a mere zero order solution of the Schrödinger equation.

Reasonably accurate experimentally determined potentials being simple of formulation and easy of access, I consider it inadvisable to press this mammoth theoretical project further. As it is we are not even able to exploit fully the accuracy of the available computational results.

o-o-o-o-o-o-o-o-o

Appendix I.

Units.

As far as possible a unified system of units has been maintained throughout the thesis. It is the system of atomic units (Hartree, 1927).

The unit of length a_H the radius of the first Bohr orbit of Hydrogen
$= h^2/4\pi^2me^2 =$ 0·5293 Angstrom units.
The unit of charge e the electron charge $= 4{\cdot}80.10^{-10}$ E.S.U.
The unit of mass m the electron mass $= 9{\cdot}11.10^{-28}$ gm.
The unit of action $h/2\pi = 1{\cdot}054.10^{-27}$ erg secs.
The unit of energy $e^2/a_H = 2hcR$ twice the ionisation potential of the hydrogen atom.
$=$ 27·206 electron volts
$= 4{\cdot}3584 . 10^{-11}$ ergs.
(R is here the Rydberg constant)
The unit of time $1/4\pi cR$.

Appendix II.

The programming of Computing Machines.

In the course of the evaluation of the integrals and in solving the Schrödinger equation, I.B.M. calculating machines types 602A and 626 were employed. The handbooks of these machines, published by I.B.M. Ltd, contain full details of their capabilities and modes of operation but an independent summary will follow below.

The type 602A is a purely mechanical relay decimal calculating punch while in the type 626 the storage units are read into mechanically yet the actual calculating is effected electronically.. Both machines do all the arithmetic operations of addition, subtraction, multiplication and division. Numerical information is fed in on punched cards to either the storage units (holding about 100 digits) or to the counting devices which are known technically as accumulators holding in all 40 digits. The operation of the machines is actuated by appropriate wiring of the control panel. This is a matrix of impulse exits and entries which emit and receive respectively at particular times during the machine cycle. Selectors are incorporated which allow alternative paths for instructional impulses. These paths are determined by the state of the selector which is either "transferred" when it has been "picked up" or "normal" when it has been "dropped out". Coselectors which appear in batteries of five function similarly to the selectors and are used primarily for filtering digits.

On being fed into the machine a card is read by the reading brushes whence it is moved to the punch bed where it remains until the required sequence of programme steps has been carried out, then it is ejected, punching of information from the storage units having been effected if required. Four main programmes will be explained:

1. Simpson's Integration Rule.
2. The modified Zeta Functions.
3. The polynomial Function.
4. The Stationary State.

Programmes 1, 2 and 3 were compiled for the 602A while 1 and 4 were prepared for the type 626.

II·1 Simpson's Integration Rule with multiplication.

a) for the 602A machine:

The purpose of the programme was to multiply one factor on primary cards with another on secondary cards and to integrate the product by the simple Simpson's Integration Rule. The actual order of computation was multiplication of the primary factors by the Simpson's Rule coefficients viz. 1 - 4 - 2 - 4 - 2 etc., and multiplying the product by the secondary factors, the total products being accumulated in a counter unit. There was provision for the possibility of secondary factors being negative when an X punched on such a card actuated a selector so that the second product was subtracted from instead of added to the product accumulator. The descriptio of the actual programming is best done in tabular form, Table II·1. The primary and secondary cards were interleaved and the pack headed by a master card containing 0 and X punched in column 1. (The cards have 80 columns each with 12 punching locations - 0 to 9, X and 12).

Table II·1 Simpson's Rule Product

Card	Program step	Operation	Storage 1 (multiplier)	counters 1-2-3-4 (coupled)
M C	R C	select P 12	R I	
	P 12			R S
primary card	R C	select P 1,2	R I 1 or4 or 2	
	P 1	multiply		
	P 2			
secondary card	R C	select P 3,4	R I secondary factor	
	P 3	multiply		plus or minus
	P 4			R O

Table II·2 Simpson's Rule Product

Card	Program step	Operation	Multiplier	counters 1-2-3-4 (coupled)
M C	R C	pick up P 4		
	P 4			
primary card	R C	pick up P 1,6		R O to (1)
	P 1	multiply 8 figures	from (2)	
	P 6			
secondary card	R C	pick up P 3,4		
	P 3	multiply 8 figures	from (2)	plus from [5]
	P 4			
trailing card	R C	pick up P 5		R O to (1)
	P 5	punch, storage read in		R S

for machine type 602A

counters 7-8 (coupled)	Storage 2	Storage 5	Storage 7
R S	R I		
plus R O	R I primary factor R O	R I from [7-8]	
R S	R I	R O	R I

for machine type 626

counters 5-6 (coupled)	Storage 1	Storage 2
	R I S U	R I S U
plus 1 or 4 or 2	↓ from [1]	↓ primary factor R O to multiplier R I S U
R O R S to [1]	R I S U	↓ secondary factor R O to multiplier R I S U
	↓ from [1]	

The code number zero in column 1 of the secondary cards picked up a selector which determined whether the Simpson's Rule coefficients or the secondary factor reached the multiplier. The coefficients 4 and 2 were alternated by another selector which was normal and transferred for alternat cards. The initial 1 was taken through the final selector picked up from the X on the master card. The alternating selector also arranged which programme steps were to be performed. It must be noted that it was assumed that the integrand was negligible at the upper end of the range of integrati The programmes are tabulated in a code which is explained hereunder:

(x) denotes storage unit x   [x] denotes counter unit x
P - programme step   R I - read in
R O - read out   R S - reset
M C - master card   R C - read cycle
D C - detail card   cos - coselector
R I S U - read in set up (626 only)

After the read cycle the 602A automatically runs through all of it 12 programme steps in order, unless it has been instructed to omit any or all of them, and continues to the read cycle of the next card. The 626 on the other hand will perform after the read cycle in numerical order only those of the 14 programme steps which have been picked up, before proceeding to the read cycle of the next card. One can add to (plus), subtract from (minus), read out of (R O), or reset to zero (R S) the counters which can be used singly or coupled in sequence. Reading out of and into storage units on the 602A can be effected on any cycle, the read in (R I) impulse resetting the unit and inserting the required information. It is not so simple with the type 626 since reading into storage units can only be done on mechanical or long cycles. The unit must be R I S U'd on a previous electronic cycle. This instruction resets it to zero and prespar it to accept the required data on the next mechanical cycle. It is however possible to read out of the units on any cycle. With the electronic machin too, the multiplying and dividing hub chosen depends on the number of digit in the multiplier or divisor. The physical size of the machine limits the number of operations which can be performed on any cycle and it is often necessary on larger programmes to choose the sequence of operations judiciously that they may dovetail most efficiently and in the least number of steps.

b) for the 626 machine:

The purpose of the programme was identical with that for the 602A and the scheme is shown in table II·2. The code punchings were slightly different and provision was made to punch the accumulated total on a trailing card.

To obtain the actual result of the integration it remains to multipl the accumulated total by h/3 where h is the interval of integration.

II·2 The Modified Zeta Function.

$$
\begin{aligned}
I &= r\ e^{-r}\chi_{oo}(r,3) && \text{equation } (4{\cdot}11)\\
&= r\ e^{-2r}(e^{R} - e^{-R}) && \text{for } R \leqslant r\\
&= r\ e^{-R}(1 - e^{-2r}) && \text{for } R > r
\end{aligned}
$$

The programme was arranged to cope with both ranges of r by subtracting R for each card from the running argument $n\Delta r$ and using the negative balance when it existed to select the appropriate quantities. It was necessary to add R again since the argument $n\Delta r$ was required later in the programme.

e^{-R}, $e^{-2\Delta r}$, $e^{R} - e^{-R}$, and unity were read into the respective storage units as shown in table II·3 from the master card for which only programme steps 11 and 12 were performed. That had the effect of clearin the counters and inserting unity into the coupled counters 5,6 and 7. The computation fell into several sections: steps 1 to 4 were concerned wit the generation of the exponential by multiplying in two stages the previous value by the initial $e^{-2\Delta r}$. Since the calculations were carried through in this case to 12 figures and the multiplier capacity is only 8 digits, two stage multiplication was necessary. According as there was a negative balance or not, steps 5 to 9 by a two stage multiplication gave either

$$e^{-R}(1 - e^{-2r}) \qquad \text{or} \qquad e^{-2r}(e^{R} - e^{-R}).$$

A final single multiplication using $n\Delta r$ as multiplier sufficed to reach the required function. The final steps 11 and 12 were preparatory operations for the next card. It is clear that for the first detail card the first two programme steps should be omitted since the first value of th exponential would be there already and would therefore merely be multiplied by unity. Counters 1,2,3 and 4 were coupled to form a 20 digit accumulator in which the significant figures of the 12 by 12 products were developed. The leading 12 digits were taken and rounded off by an

Table II·3 The Modified Zeta Function

card	program step	operation	storage 1 (multiplier)	counters 1-2-3-4 (coupled)	counters 5-6-7 (coupled)
M C	R C	select P 11,12			
	P 11			R O R S to (6)	R S
	P 12				plus 1
D C	R C	all steps but omit P 1,2 for first D C.	R I from (5) R		
	P 1	multiply		plus	
	P 2		R I from (5) L		
	P 3	multiply		plus	
	P 4			R O R S to [5] and (5)	minus 1 giving 1 - exp(-2m r)
	P 5		R I from (5)R or $[5]_t$		R O terminal digits to (1)
	P 6	multiply		plus (2) or (4) to give Y_t	
	P 7		R I from (5)L or $[5]_i$		R O initial digits to (1)
	P 8	multiply		plus (2) or (4) to give Y_{total}	
	P 9		R I $n\Delta r$ from [8]	R O R S to (7)	
	P 10	multiply		plus (7) to give I	
	P11			R O R S to (6)	R S
	P12				plus 1

counter 8	storage 2	storage 3	storage 4	storage 5		storage6	storage 7
				left	right		
R S	R I e^{-R}	R I $e^{-2\Delta r}$	RI $e^{R} - e^{-R}$		R I 1	R I 0	
plus r					R 0 to (1)		
minus R		R 0 to $[1]_{term}$ R 0 to $[1]_{init}$		R 0 to (1) R I e^{-2n} r from [1]			
plus R	R 0 to [1]		R 0 to [1]	R 0 to (1)	R 0 to (1)		
R 0 to(1)						R I I from [1]	R I Y from [1] R 0 Y to [1]

impulse which, before the multiplication, reset the counter to zero and added a 5 to the 13th digit position.

Care had to be exercised over the possibility of back circuiting in the counter and storage entries and exits which required that coselectors be used to block certain paths at the troublesome programme steps. In this case there was little difficulty with that, cf. sections II·3 and II·4, but coselectors were used to read in the multiplicand to the different counter positions as required in the two stage multiplication.

II·3 The Polynomial Function.

It was required to compute the general polynomial function

$$e^{\pm kr}(a_0 \mp a_1 r + a_2 r^2 \mp a_3 r^3 + a_4 r^4 \mp a_5 r^5 + a_6 r^6 \mp a_7 r^7)$$

This programme exploited the 602A to the full: so much so that the division steps had to be withdrawn ultimately to allow the other steps to be spread out, otherwise the machine omitted instructions and performed multiplication wrongly at random intervals. The coefficients a_i were limited to homogeneous 3 digit figures and all 8 were read into the storage units 2 and 4 with $e^{\pm k\Delta r}$, Δt, and unity into storages 5, 6 and 7 respectively from the master card which was followed by no programme ste

On the subsequent detail cards the calculation fell into five parts.

1. Programme steps 3,4,5,6.

The exponential was formed by multiplying in two stages the previou value from storage 7 by the incremental value from storage 5; the counter entry positions for the two stages were determined by coselectors which were first transferred and then normal for stage 2.

2. Programme steps 7,8,9.

The running argument $n\Delta r$ was built up by addition of Δr for each card. The former was stored in the right hand component of storage 6 (6R), while the latter was in the left hand section (6L). $n\Delta r$ was read out to the coupled counters 5,6,7,8 and to this was added Δr which was also read into another part of the same counter through a coselector. Both were then transferred to their respective sections of storage unit 6.

3. Programme steps 10,11.

Theoretically these steps could have been used for the production of the factor $1/r$ when it was necessary but as explained earlier this was not practical.

4. Programme steps 12,1,2.

The generation of the polynomial was effected by cycling these three steps eight times, adding in a different coefficient a_i each time and multiplying by r. The cycling was controlled by three selectors operating in series such that the first was alternately normal and transferred; the second was normal for two cycles and transferred for two cycles etc; while the third was normal for four cycles and transferred for the other four. These selectors picked up corresponding coselectors which instructed the appropriate storage unit to be read out, (2) or (4), and selected the contents to allow only one a_i to reach the accumulator at a time. Provision was made for both the positive and the alternating positive-negative types

Table II·4 The Polynomial Function.

card	program step	operation	storage 1 (multiplier)	counters 1-2-3-4 (coupled)	counters 5-6-7-8 (coupled)
M C	R C	omit all steps using cos 9			
D C	R C	start at P 3, punch		R O to (8)	
	P 3		R I from (7L)	R S	R O R S to (3)
	P 4	multiply		plus (3) thro' cos 10,11 T	
	P 5		R I from (7R)		
	P 6	multiply		plus (3) thro' cos 10,11 N	
	P 7			R O R S to (7)	plus from (6R)
	P 8			plus 1 thro' selector	plus from (6L)
	P 9		RI r from [5]		R O R S to (1),(6) cos 8,12 T
	P10	divide	R O to [1]	minus from (1)	plus (quotient)
	P11		R I 1/r from [5]		R O R S to (1) cos 8,12 T
	P12			R S	plus a_1 from (2) or (4)
	P 1	R I 1 on last cycle	R I 1 on last cycle	plus/minus* from [5]	R O R S to (3) and [1]
	P 2	multiply		R O to [5] thro' cos 5,6,7 T	plus for + poly -/+* for - poly
	P 3		R I from (7L)	R S	R O R S to (3)
	P 4	multiply		plus (3) thro' cos 10,11 T	
	P 5		R I from (7R)		
	P 6	multiply		plus (3) thro' cos 10,11 N	

* by a selector if there is a negative balance.

storage2	storage3	storage4	storage5	storage 6 left	storage 6 right	storage 7 left	storage 7 right	storage8
R I a_4 to a_7		R I a_0 to a_3	R I $e^{-k\Delta r}$	R I Δr	punch $n\Delta r$	R I 1 punch $e^{-n\Delta r}$		punch poly. fn.
	R I from [5]		R 0 to [1] R 0 to [1]			R 0 to (1)	R 0 to (1)	
				RO to [5] cos1 T R I Δr	R 0 to [5] from [5] $n\Delta r$	R I from [1]		
RO to [5] cos 2,3	R I from [5]	RO to [5] cos 2,3						
	R I from [5] R 0 to [1] R 0 to [1]					R 0 to (1)	R 0 to (1)	

of polynomial and even, using the negative balance impulse, for the possibility of the function going negative since in its complementary form erroneous multiplication would result. When a counter goes negative an impulse is available at the negative balance (NB) hubs. On the addition of the last coefficient a_o the polynomial is complete and therefore the final multiplication on step 2 is by unity and not by r. This was taken account of in the programme.

5. Programme steps 3,4,5,6.

These steps are repeated for the final multiplication of the polynomial just generated - and stored in (3) - and the exponential produced in the previous actuation of these steps - and stored in (7).

Figure II·1 shows the wiring arrangement of the storage and counter exit and entry hubs, and indicates how the coselectors isolate the various circuit blocks when required. The exits are laid out, as always, on the left hand side while the entries are opposite on the right.

II·4 The Stationary State.

The initial computational problem was the production of the $V_L(x)$ and $V_B(x)$ leading to the $f_L(x)$ and $f_B(x)$

$$f_L(x) = 476\cdot 344\, V_L(x) - L\,E = F_L(x) - L\,E$$

$$= 476\cdot 344\,(1/x^{12} - 1/x^{6}) - L\,E \qquad \text{from equation } (5\cdot 4)$$

$$f_B(x) = 109\cdot 5597 \exp 14\cdot 5(1-x) - 264\cdot 769/x^{6} - B\,E \qquad \text{equation } (5\cdot 6)$$

$$= F_B(x) - B\,E$$

Counter - Storage Exit - Entry diagram

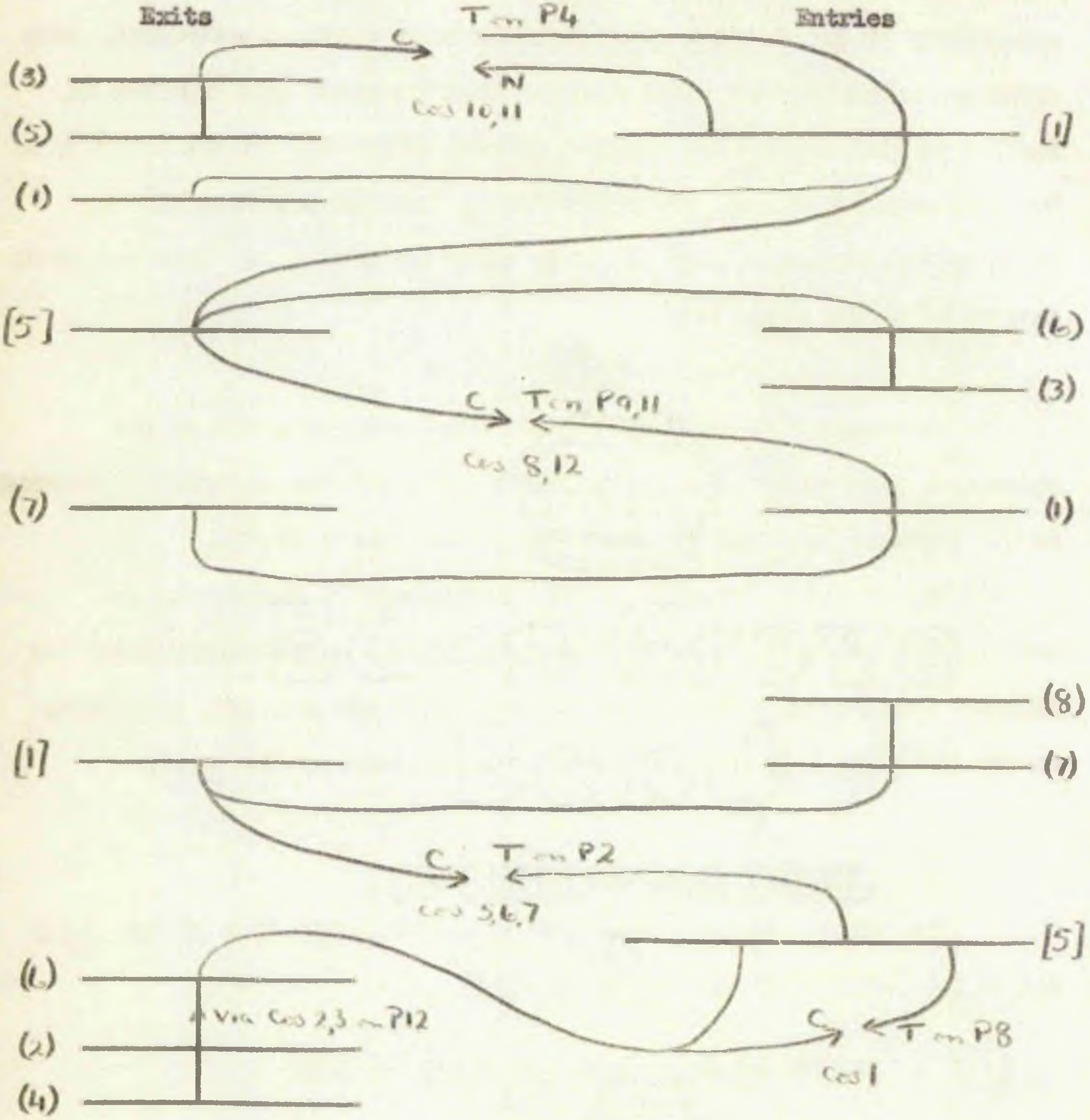

Figure II·1

where L and B are constants corresponding to the Lennard-Jones and Buckingham potentials respectively.

x^6 and x^{12} were calculated in the range $0{\cdot}20 < x < 3{\cdot}00$ and by a simple operation $476{\cdot}344(x^6 - 1)/x^{12}$ was formed and punched out on cards at intervals of $x = 0{\cdot}01$. $F_B(x)$ presented no greater difficulty. The type 626 machine used had a limited counter capacity and because of this it was necessary to compute from the $F(x)$ the corresponding $W(x)$ and punch on the cards $2 - 10W(x)$ and $1 + W(x)$. These detail cards were typified by an x punch in column 1, while a 12 in the same column denoted a negative $W(x)$.

When a suitable value of x had been chosen at which to start the solution (i.e. from y_o) R_o, R_1, a_1, $h^2L\,E/12$ or $h^2B\,E/12$ and y_1 were read into the machine from the master card and first detail card, see table II·5. On the detail cards' read cycles the y_{n-1} from the previous calculation and $1 + W_n$, $2 - 10W_n$ were read into storage units. Programm steps 1 to 4 were concerned with the formation of

$$R_n = a_{n-1}\,R_{n-1} - R_{n-2}$$

in the coupled counters 1,2 and 3 while R_{n-1} was held in counters 4,5,6 also coupled. The 'R' storage units could then be cleared and the new pair of values R_n and R_{n-1} were returned to the storages. By combining the W_n with either L E or B E in steps 5,6,7 the functions $2 - 10w$ and $1 + w_n$ were prepared for the next stage in the programme. Since w_n was negative in the lower and positive in the upper range of $V(x)$ a

Counter- Storage Exit - Entry diagram.

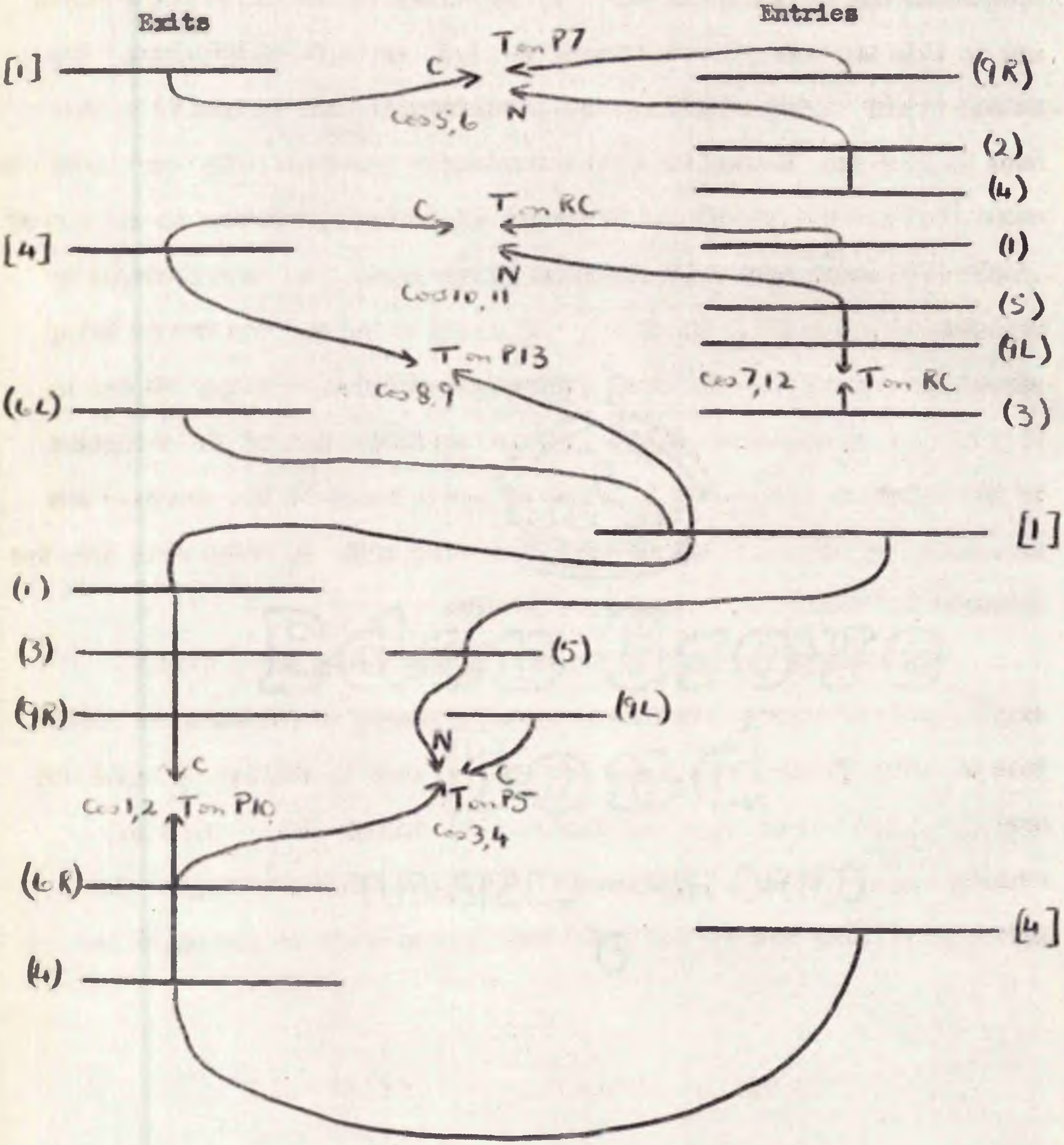

Figure II·2

coselector was picked up by the 12 in column 1 of the negative cards and in this way added or subtracted the L E or B E as required. The rather tricky wiring of storage and counter units made it easier in this case to read the E product into two separate storages (6L) and (6R) in order that the factor 10 be accounted for without reverting to the use of coselectors which were fully occupied in any case. a_n was produced by division of $2 - 10w_n$ by $1 + w_n$ in steps 8 and 9, the result being stored for use on the next card. A further division on steps 10 and 11 yielded y_n in counters 4,5,6. To give an indication of the curvature of the solution $(y_{n-1} - y_n)$ which is proportional to the gradient was calculated on steps 12 and 13 and this along with y_n were read into two storages for visual inspection on each card.

The counter capacity being limited the wiring was a trifle complicated and necessitated a considerable amount of selecting to avoid back cicuits, figure II·2. For instance on step 1, storage 3 exit and counter 1,2,3 entry must be isolated from storage 4,5,6 exit and counter 4,5,6 entry by coselectors 1,2,3,4,8 and 9 otherwise the information being transferred would have become mixed up and quite useless.

Table II·5 The solution of the second order equation.

card	program step	operation	multiplier	counters 1-2-3 (coupled)	counters 4-5-6 (coupled)
M C_1	R C	pickup P14			
	P14				
M C_2	R C	pickup P15			
	P15			minus	R O
D C	R C	P. U. P1to15		R O R S to (2)	R O R S to (1)
	P 1			minus R_o from (3)	plus R_1 from (4)
	P 2	multiply 8 figures	R_1 from (4)	plus a_n from (5) to give R_2	
	P 3				
	P 4	storage read in		R O R S to (4)	R O R S to (3)
	P 5			plus 2-10w'	plus 1+w'
	P 6			plus/minus* E from (6L)	minus/plus* E from (6R)
	P 7	storage read in		R O R S to (9R)	R O R S to (9L)
	P 8			plus 2-10w	
	P 9	divide 8 figures		minus 1+w from (9L) R S	plus quotient to give a
	P10	storage read in		plus R_2 from (4)	R O R S a to (5)
	P11	divide 8 figures		minus 1+w from (9L) R S	plus quotient to give y_2
	P12			plus y_1 from (1)	
	P13			minus y_2 to give y_1-y_2	R O y_2 to [1]
D C	R C	pick up P 1 to 15		R O R S to (2)	R O R S to (1)

* by a selector from a 12 on negative cards.

storage1	storage2	storage3	storage 4	storage5	storage 6	storage 9	
						left	right
		RISU	RISU	RISU	RISU		
		R_o	R_1	a_1	$h^2LE/12$		
RISU	RISU					RISU	
y_1						1+w'	2-10w'
		R O R_o to [1]	R O R_1 to [4]				
			R O R_1 to mult.	R O a_n to [1]			
		RISU	RISU				
		R_1 from [4]	R_2 from [1]				
						R O to [4]	R O to [1]
					R O L to [1] and R to [4]	RISU	
						1+w	2-10w
				RISU			R O to [1]
						R O to [1]	
			R O R_2 to [1]	a_2			
						R O to [1]	
R O y_1 to [1]							
RISU	RISU					RISU	
y_2	$y_1 - y_2$					1+w'	2-10w'

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