A. THE SHAPE OF THE COMPTON LINE FOR HELIUM AND MOLECULAR HYDROGEN

B. BOND FORMATION IN SIMPLE MOLECULES

Thesis

by

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ABSTRACT

By using variation functions which take into consideration the instantaneous interaction of the electrons, momentum distribution functions and intensity distributions in the Compton line are computed for helium and molecular hydrogen, neglecting small relativity and binding corrections. The half-value breadths are expressed in terms of $l/2\lambda^*$ where l is the wave-length displacement from the center of the shifted line and $2\lambda^* = (\lambda_1^2 + \lambda_c^2 - 2\lambda_1\lambda_c \cos\chi)^{1/2}$. λ_1 and λ_c are the primary and scattered wave-lengths and χ the scattering angle. The absolute breadth of the line may therefore be computed for any λ_1 and χ . For helium and molecular hydrogen the values of $l/2\lambda^*$ at half-maximum are 10.8 and 8.5, respectively.

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INTRODUCTION

THERE have been many theoretical investigations of the shape of the Compton line differing from one another both in the treatment of the scattering process itself and in the electronic configuration assumed to exist before scattering has occurred.[1, 2] However, in no

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[1] J. W. M. DuMond, Rev. Mod. Phys. **5**, 1 (1933); Phys. Rev. **33**, 643 (1929).

[2] G. E. M. Jauncey, Phys. Rev. **25**, 314, 723 (1925); P. A. Ross and Paul Kirkpatrick, Phys. Rev. **45**, 223

calculation has the interaction of the electrons found suitable representation, for the Hartree functions or hydrogen-like wave functions with screening constants which have heretofore been used introduce only an average perturbing effect of the electrons upon one another. Since computations of the Compton line shape have been most successful for gases, it is natural when attempting a more rigorous investigation to turn to the simplest elementary gases containing two electrons, namely helium and molecular hydrogen. For these substances it is not necessary to depend upon the Hartree or screening-constant-type wave function since variation functions containing interaction terms explicitly have been developed, the most accurate of which lead to energy values for the ground state which are correct within experimental error. Line shapes for helium and molecular hydrogen are here computed from some of the less accurate of these variation functions which nevertheless approximate the true wave functions much more closely than do the Hartree or the hydrogen-like screening-constant type. By reason of the greater accuracy possible in these calculations as compared to calculations on other gases or solids, the line shapes for these two gases probably offer the best opportunity to compare in a quantitative fashion theory and experiment.[3]

GENERAL METHOD

The variation function chosen to describe the He or H_2 system is here represented by $\phi(r_1, \vartheta_1, r_2, \vartheta_2)$, where r_1, ϑ_1 are polar coordinates of the first electron, r_2, ϑ_2 of the second electron with respect to the same origin. Azimuthal angles do not appear in any of the variation functions used. $A(P_1, \Theta_1; r_2, \vartheta_2)$, the mixed wave function in the polar coordinates of the first electron in momentum space and the position coordinates of the second electron, can be obtained from this ϕ by the following Dirac transformation,

$$A(P_1, \Theta_1, r_2, \vartheta_2) = h^{-\frac{3}{2}} \int_{r_1=0}^{\infty} \int_{\vartheta_1=0}^{\pi} \int_{\varphi_1=0}^{2\pi} \exp\left[-(2\pi i/h)\mathbf{P}_1 \cdot \mathbf{r}_1\right] \cdot \phi(r_1, \vartheta_1, r_2, \vartheta_2) r_1^2 \sin \vartheta_1 dr_1 d\vartheta_1 d\varphi_1 \quad (1)$$

(No azimuthal angle enters in A as none enters in ϕ.) Here, $\mathbf{P}_1$ and $\mathbf{r}_1$ are the vectors whose endpoints lie at (P_1, Θ_1), (r_1, ϑ_1), respectively. All the transformation integrals which must be evaluated may be written down immediately by using the general expression for the momentum wave functions of a hydrogenlike atom, Υ_{nlm}, given by Podolsky and Pauling.[4] Those functions which will be used here are:

$$\begin{aligned} \Upsilon_{100} &= (1+\zeta_1^2)^{-2}, \\ \Upsilon_{200} &= 2(1+\zeta_1^2)^{-2}(\zeta_1^2-1)/(\zeta_1^2+1), \\ \Upsilon_{300} &= (1+\zeta_1^2)^{-2}\left[4\left(\frac{\zeta_1^2-1}{\zeta_1^2+1}\right)-1\right], \quad (2) \\ \Upsilon_{210} &= -4i \cos \theta \frac{\zeta_1}{(1+\zeta_1^2)^3}, \end{aligned}$$

where $\zeta_1 = 2\pi P_1 a_0/Z'h$, Z' = effective nuclear charge and a_0 = radius of first Bohr orbit in hydrogen, the subscripts in Υ_{nlm} referring to the quantum numbers, n, l, m. ζ_1 will be used in place of P_1, in the explicit functions of P_1 developed later for He and H_2. The momentum distribution function $B(P_1, \Theta_1)$ can now be found by integrating the modulus squared of $A(P_1, \Theta_1; r_2, \vartheta_2)$. Thus

$$B(P, \Theta) = 2\pi \int_{r_2=0}^{\infty} \int_{\vartheta_2=0}^{\pi} AA^* r_2^2 \sin \vartheta_2 dr_2 d\vartheta_2. \quad (3)$$

The subscripts have been dropped in $B(P, \Theta)$ for the electrons contribute equally to the momentum.

Since for this case of scattering by field-free gases, all orientations of the molecule are equally probable, the function $B(P, \Theta)$ must be averaged over the angle Θ to obtain the radial momentum distribution function, $C(P)$:

$$C(P) = \int_{\Theta=0}^{\pi} B(P, \Theta) \sin \Theta d\Theta. \quad (4)$$

(1934); F. Bloch, Phys. Rev. **46**, 674 (1934); F. Schnaidt, Ann. d. Physik **21**, 89 (1934); W. Franz, Zeits. f. Physik **90**, 623 (1934); **95**, 652 (1935); G. Burkhardt, Ann. d. Physik **26**, 567 (1936); Kirkpatrick, Ross, and Ritland, Phys. Rev. **50**, 928 (1936).

[3] The complete experimental results of DuMond and Kirkpatrick (Phys. Rev., this issue) on scattering in He demonstrate the feasibility of such a comparison and its importance in determining the position of the shifted line accurately.

[4] Boris Podolsky and Linus Pauling, Phys. Rev. **34**, 109 (1929).

TABLE I. *Variation functions for the normal He atom.*

	Z'	c_2	c_5	$E-$ (UNITS $R_{\text{He}}hc$)	% ERROR
1	1.6875	0	0	5.695	1.93
2	1.850	0	0.112	5.755	0.91
3	1.69	0.142	0	5.754	0.92
4	1.822	0.126	0.089	5.784	0.40

DuMond[1] has shown that the shape of the Compton line can be computed from such a momentum distribution function or *vice versa*, the formula for the intensity y as a function of wave-length displacement l from the center of the shifted line being

$$y=k\int_{l=l}^{\infty} l^{-1}C\left(\frac{l}{2\lambda^*}\right)dl, \tag{5}$$

in which $l=\lambda_2-\lambda_1-(h/mc)(1-\cos\chi)$, $2\lambda^*=(\lambda_c^2+\lambda_1^2-2\lambda_1\lambda_c\cos\chi_1)^{\frac{1}{2}}$, $\lambda_c=\lambda_2$ for $l=0$. λ_1 and λ_2 are initial and scattered wave-lengths and χ is the scattering angle. $C(P)$ has been replaced by $C(l/2\lambda^*)$ where

$$\frac{l}{2\lambda^*}=\beta=\frac{v}{c}=\frac{P}{mc}\qquad \zeta=\frac{l}{2\lambda^*}\cdot\frac{1}{\alpha Z'},$$

α being the fine structure constant. Since the constant of integration k is arbitrary, all constant factors multiplying ϕ, A, B, and C are omitted.

It should be mentioned that DuMond's formula for the intensity distribution in the modified line does not consider the generally small effect due to binding and relativistic corrections. However, for the case of scattering from helium and the hydrogen molecule, binding and relativistic corrections to the shape are less than the error in the calculations due to the use of a variation function as an approximation to the true wave function. The error produced in the half-width itself is negligible since the corrections to the intensity corresponding to a given absolute value of l are nearly equal, though of opposite sign, on either side of the maximum.

Scattering from helium

The variation functions developed by Hylleraas[5] for He are of the form

$$\phi=\sum_{nlm}c_{nlm}e^{-Z's}s^nt^lu^m \tag{6}$$

$$(l \text{ even})$$

in which $s=(r_1+r_2)/a_0$, $t=(r_1-r_2)/a_0$, $a_0u=r_{12}$ = interelectronic distance, a_0 = radius of first Bohr orbit. Since a ϕ which involves the first power of u cannot be transformed in finite terms to the mixed wave function, variation functions which may be represented by

$$\phi=e^{-Z's}(1+c_2t^2+c_5u^2)$$

are used here. In Table I appear the four variation functions of this type together with the energy values to which they lead and the percentage difference from the true value. $E=-78.605$ ev $=-5.8074\ R_{\text{He}}hc$. The first of these is due to Kellner[6] and is a hydrogen-like screening constant type function. The second is due to Hylleraas[7] and the third and fourth have been developed by the author using Hylleraas' formulae.[5] The terms in u^2 were included in an effort to compensate for the missing linear u term which is primarily responsible for the accuracy of Hylleraas' energy calculations. The third function describes the actual electronic system well since it represents a He atom with electrons in two different orbits with effective nuclear charges 2.15 and 1.19 corresponding to almost complete shielding of the outer one and slight negative shielding of the inner one. The second function, in comparison, although it now introduces the interelectronic interaction, represents this interaction as being much stronger than is actually the case. Consequently, of the two functions, the third probably corresponds more closely to the actual state of the system although the energy E calculated from the two functions is about the same. To check the effect of adding further integrable terms, values of E resulting from many different combinations of u^2, u^4, t^2, t^4, s, s^2 were computed. The most accurate value of the energy obtained in this way was only 0.1 percent better than the fourth variation function above. In view of the rapidly increasing complexity of the algebra entering into the evaluation of the integrals, it was not considered that the inclusion of further terms

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[5] Egil A. Hylleraas, Skrifter det Norske Vid.-ak. Oslo, I Nat. Nuturw. Klasse 1932, p. 107.

[6] G. W. Kellner, Zeits. f. Physik **44**, 91 (1927).

[7] Egil A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

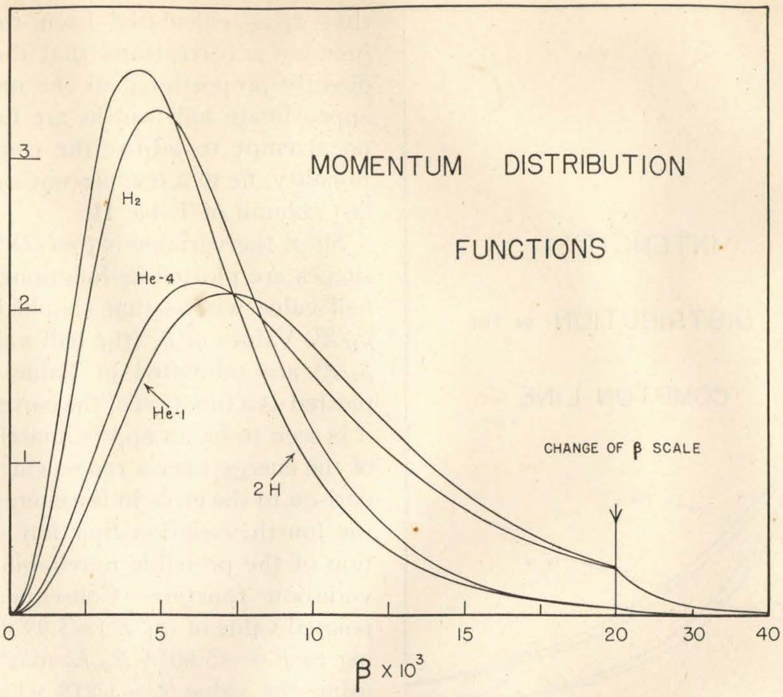

FIG. 1. Momentum distribution functions for helium and molecular hydrogen, normalized to the same area. The ordinates are in arbitrary units, the abscissae, in terms of $\beta = v/c$, the ratio of the velocity of an electron to that of light.

was justified. Furthermore, functions two and four lead to practically identical line shapes so that further terms would probably have little significance.

The necessary restriction of the exponents in the ϕ's to even powers of u and t makes it possible to express these as linear functions of hydrogen-like 1s, 2s, 2p, and 3s wave functions:

$$\phi = a_1\psi_{100}(1Z') + a_2\psi_{200}(2Z') + a_2'\psi_{210}(2Z') + a_3\psi_{300}(3Z'). \quad (7)$$

Here a_1, a_2, a_2', a_3 are quantities involving r_2 which are constants for the first integration and ψ_{nlm} is a hydrogen-like wave function for the first electron around a nucleus with charge $1Z'$, $2Z'$, $\cdots$. From Eqs. (2) the mixed wave function then can be immediately written down as

$$A(\zeta_1, \Theta_1, r_2) = (1+\zeta_1^2)^{-2}\left[a_1 + 2a_2\cdot\frac{\zeta_1^2-1}{\zeta_1^2+1} + a_3\left\{4\left(\frac{\zeta_1^2-1}{\zeta_1^2+1}\right)^2 - 1\right\} - 4i\cos\Theta_1\frac{\zeta_1\cdot a_2'}{1+\zeta_1^2}\right] \quad (8)$$

and it becomes after integration over r_2 and Θ

$$C(\zeta) = (1+\zeta^2)^{-4}\sum_{p=0}^{4} D_p\cdot\left(\frac{\zeta^2-1}{\zeta^2+1}\right)^p, \quad (9)$$

$$y = (1+\zeta^2)^{-3}\sum_{p=0}^{4} E_p(1+\zeta^2)^{-p}. \quad (10)$$

The coefficients D_p and E_p are polynomials in c_2/Z'^2 and c_5/Z'^2. (For the first variation function $y \propto (1+\zeta^2)^{-3}$ so that the polynomial in $(1+\zeta^2)^{-1}$ may be considered to be a correction factor in the other expressions.) Consequently there should be expected a simple relationship between the *half-value breadths*, $\beta_{\frac{1}{2}}$, and the energy values corresponding to the different variation functions. A rough calculation of the line breadths of different many-electron systems may be made from a knowledge of the total energy E of the system alone if this energy has been computed by minimizing with respect to the effective nuclear charge Z' appearing in a hydrogen-like wave function with screening constants. This minimizing insures that the virial theorem hold so that the root mean square momentum and the

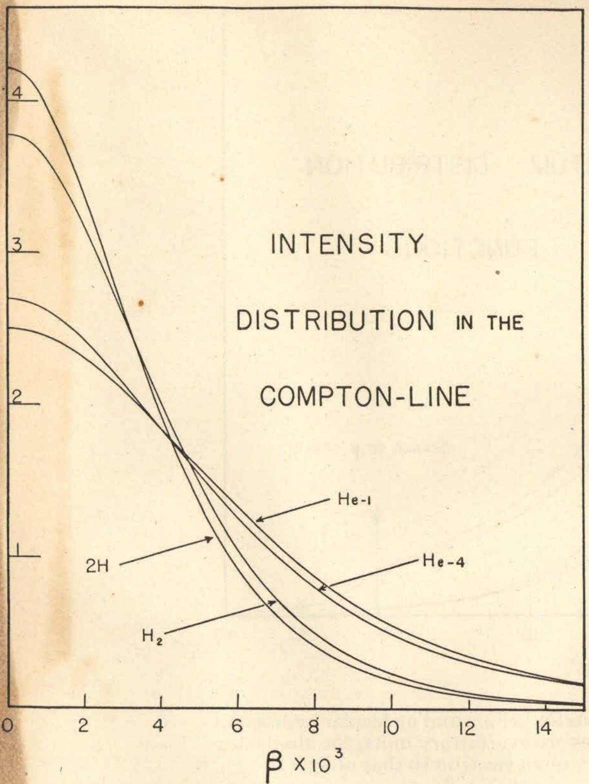

FIG. 2. Intensity distribution of the Compton line as a function of $\beta = l/2\lambda^*$ where l = displacement from the center of the shifted line, $2\lambda^* = (\lambda_1^2 + \lambda_c^2 - 2\lambda_1\lambda_c \cos\chi)^{\frac{1}{2}}$, λ_1 and λ_c being the initial and scattered wave-lengths and $\cos\chi$ the scattering angle. Ordinates are in arbitrary units and the curves are normalized to the same area.

half-value breadth may be taken as proportional to $(-E)^{\frac{1}{2}}$. For systems which may be considered to be hydrogen-like with all electrons in the same shell, this method will be exact since in this case $E \propto Z'^2$ and $\beta_{\frac{1}{2}}$ should be proportional to Z', which is obviously true from a consideration of the simple form which y assumes for the hydrogen-like case.

A more accurate comparison may be made on the basis of the momentum distribution function, Fig. 1, for in general, $\beta_{\frac{1}{2}}$ corresponds closely in value to the most probable β. Thus, assuming that $\beta_{\frac{1}{2}}$ as calculated from the first variation function is correct and that the half widths are directly proportional to the most probable β's, approximate half widths are found which, with no attempt to adjust the constant of proportionality, fit to a few percent as is seen from the last column of Table II.

TABLE II. *Half-value breadths.*

$\beta_{\frac{1}{2}} \times 10^3$	Z'	$10^3 \times \beta_{\frac{1}{2}}/Z'$	$\beta_{\frac{1}{2}}$ calculated from most probable β
12.67	1.69	7.50	12.67
12.08	1.85	6.53	11.91
11.24	1.69	6.65	10.87
11.38	1.82	6.25	11.02

Since the variable is $\zeta = l/2\lambda^* Z'\alpha$ and the line shapes are plotted as functions of $l/2\lambda^* = \beta$, the half-value widths that should be compared are $\beta_{\frac{1}{2}}/Z'$. Values of $\beta_{\frac{1}{2}}$ (the half-value breadth) and $\beta_{\frac{1}{2}}/Z'$ are tabulated in Table II. If $(\beta_{\frac{1}{2}}/Z')$ is plotted as a function of the corresponding energy, it is seen to be an approximately linear function of the energy over a range which is long in comparison to the error in the energy computed from the fourth variation function and in consideration of the probable unreliability of the second variation function. Consequently, the extrapolated value of $(\beta_{\frac{1}{2}}/Z') = 5.99 \times 10^{-3}$ corresponding to $E = -5.8074\ R_{\mathrm{He}}hc$ may be assumed. By using the value $Z' = 1.818$ which occurs in the most accurate of the Hylleraas functions, the value $\beta_{\frac{1}{2}} = 10.8 \times 10^{-3}$ is then found, which is the best value that can be calculated from these variation functions. This method would not be valid if the constants did not enter into the variation function linearly.

In Fig. 2, y as a function of $l/2\lambda^* = \beta = v/c$ is plotted. From such a curve, the line shape for any scattering angle and any incident wave-length can be computed by a proper choice of λ^* (Eq. (5)). [For example, the half-width in He at $\lambda_1 = 710$ X.U., $\chi = 180°$ is 15.8 X.U.] All curves are reduced to the same area since the total number of scattering electrons is constant. The two curves for He correspond to the first and fourth variation functions, and show clearly that

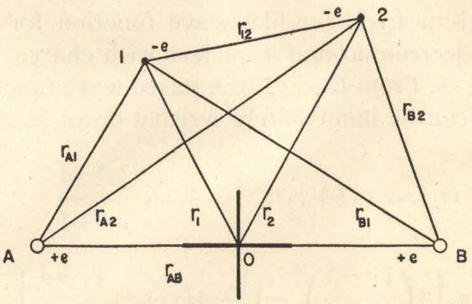

FIG. 3. Coordinates for the hydrogen molecule.

the line whose shape is computed from the more accurate function is narrower than the line derived from the simple hydrogen-like screening constant function.

Scattering from molecular hydrogen

A variation treatment for the hydrogen molecule has been carried out by James and Coolidge[8] using terms in u to introduce the electronic interaction as Hylleraas did for He. However, the exponential of $(r_{A1}+r_{B1}+r_{A2}+r_{B2})/r_{AB}$, occurs in all the variation functions making impossible the evaluation of the transformation integral in finite terms. (See Fig. 3 for coordinates.) Consequently, a function of the ionic-polarization type studied by Weinbaum[9] which permits the direct evaluation of all integrals but that for y has been chosen.

This variation function is

$$\phi=[u_{1sA}(1)+\sigma u_{2pA}(1)][u_{1sB}(2)+\sigma u_{2pB}(2)]+[u_{1sA}(2)+\sigma 2_{pA}(2)][u_{1sB}(1)+\sigma u_{2pB}(1)]$$
$$+c\{[u_{1sA}(1)+\sigma u_{2pA}(1)][u_{1sA}(2)+\sigma u_{2pA}(2)]+[u_{1sB}(1)+\sigma u_{2pB}(1)][u_{1sB}(2)+\sigma u_{2pB}(2)]\}, \quad (11)$$

in which $\sigma=0.07$, $c=0.176$, and u_{1sA} (1) represents a hydrogen-like 1s wave function for electron (1) about nucleus A which carries a charge Z', etc. Thus

$$u_{1sA}(1)=\exp(-Z'r_{A1}/a_0), \quad u_{2pA}(1)=(r_{A1}Z'/a_0)\cos\vartheta_{A1}\cdot\exp(-Z'r_{A1}/a_0),$$
$$\vartheta_{A1}=\text{angle between } r_{AB} \text{ and } r_{A1}, \quad \text{measured from } r_{A1} \text{ to } r_{AB}.$$

The quantity r_{AB}, the internuclear distance, although not occurring in the variation function, enters in the calculation of the transformation integral. The experimental value, 0.7395A, of r_{AB} is taken instead of 0.77 which corresponds to Weinbaum's function. This reduces the dissociation energy by a few percent, but gives a more accurate representation of the actual structure of the molecule. Z' is taken to be 1.19 since most variation functions of this general type lead to this value. ϕ may be rewritten as

$$\phi=a_A[u_{1sA}(1)+u_{2pA}(1)]+a_B[u_{1sB}(1)+\sigma u_{2pB}(1)]$$

in which
$$a_A=u_{1sB}(2)+\sigma u_{2pB}(2)+cu_{1sA}(2)+c\sigma u_{2pA}(2),$$
$$a_B=u_{1sA}(2)+\sigma u_{2pA}(2)+cu_{1sB}(2)+c\sigma u_{2pB}(2),$$

and a_A and a_B are therefore functions of the second electron's position alone. Since the transformation integral, Eq. (1), was expressed in terms of coordinates with but one origin, it is necessary to change its form slightly. Noting that ϕ splits up into two parts containing position variables with A and B as origin, and taking (x_{A1}, y_{A1}, z_{A1}), (x_{B1}, y_{B1}, z_{B1}) to be rectangular Cartesian coordinates of the first electron with respect to A and B, the z-axis lying in the direction of the line AB, then the transformation integral becomes

$$A(P_{x_1}, P_{y_1}, P_{z_1}, x_{A2}, \cdots z_{B2})=h^{-\frac{3}{2}}\Big\{a_A \exp[(\pi i/h)r_{AB}P_{z_1}]\int_{x_{A1}=0}^{\infty}\int_{y_{A1}=0}^{\infty}\int_{z_{A1}=0}^{\infty}$$
$$\times\exp[-(2\pi i/h)\bar{P}_1\cdot\bar{r}_{A1}]\cdot[u_{1sA}(1)+u_{2pA}(1)]dx_{A1}\,dy_{A1}\,dz_{A1}+a_B\exp[-(\pi i/h)r_{AB}P_{z_1}]$$
$$\int_{x_{B1}=0}^{\infty}\int_{y_{B1}=0}^{\infty}\int_{z_{B1}=0}^{\infty}[u_{1sB}(1)+u_{2pB}(1)]\exp[-2\pi i/h)\bar{P}_1\cdot\bar{r}_{B1}]dx_{B1}dy_{B1}dz_{B1}\Big\}.$$

Since these integrals are exactly those for 1s and 2s hydrogen-like atoms, the mixed wave functions can at once be written out in polar coordinates by use of Eq. (2).

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[8] H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933).

[9] S. Weinbaum, J. Chem. Phys. 1, 593 (1933).

$$A(P_1, \Theta_1, r_{A2}, \cdots \vartheta_{B2}) = [a_A \exp[(\pi i/h) r_{AB} P_1 \cos\Theta_1] + a_B \exp[-(\pi i/h) r_{AB} P_1 \cos\Theta_1]][(1+\zeta_1^2)^2 - 4i\sigma\zeta_1\cos\Theta_1]\cdot(1+\zeta_1^2)^{-3}. \quad (12)$$

Here ϑ_{A1} = angle between r_{A2} and r_{AB}, etc., while Θ = polar angle in momentum space of the first electron. Integrating over $r_{A1}\cdots\vartheta_{B2}$ and Θ_1, it follows that $A(P_1\cdots\vartheta_{B2})$ becomes

$$c(\zeta) = (1+\zeta^2)^{-6}\left[(1+\zeta^2)^2\left(1+\frac{\lambda}{f\zeta}\sin(f\zeta)\right) + \frac{16}{3}\sigma^2\zeta^2 + \frac{32\lambda\sigma^2}{f^2}\cos(f\zeta) + \frac{16\lambda^2\sigma^2}{f^3\zeta}(f^2\zeta^2-2)\sin(f\zeta)\right], \quad (13)$$

in which $\zeta = 2\pi P a_0/Z'h$ as before, $f = Z' r_{AB}/a_0 = 1.67$, $\lambda = 2\mu(\mu c + 1 + c^2)/(4c/\mu + 1 + c^2) = 0.857$, where $\mu = 2(e^f/f^2)(1+\sigma^2)$ [polynomial in σ and f].

It is seen that in order to find y it is necessary to evaluate indefinite integrals of the form

$$\int_\zeta^\infty \frac{\sin(f\zeta)}{(1+\zeta^2)^n} d\zeta.$$

As a simplification, all integrals of this type were taken together and integrated graphically with an error of less than 1 percent. For purposes of comparison the resulting y curve was normalized to the same area as for two hydrogen atoms, or for a He atom and plotted with the He curves in Fig. 2.

Many other variation functions which it is possible to integrate have been studied by various investigators, but as each is of essentially different character from every other, and since the difference between any two is not merely a term in a polynomial as in the case of the helium, and the change in λ is consequently of a complicated nature, they would not provide basis for an extrapolation such as was carried out for helium. Accordingly it has not seemed worth while to calculate line shapes for these functions.

Interpolating on the y curve (Fig. 2), the value $8.50\times10^{-3} = \beta_{\frac{1}{2}}$ is found for the half-value breadth of the line in H_2. Since the half-width in atomic hydrogen is only 7.50×10^{-3}, the more accurate calculation leads to a broader line. This is not surprising in view of the change in the electronic configuration which occurs when two hydrogen atoms are brought together to form a molecule. The most important change which affects the momentum distribution is in the effective nuclear charge Z'. Because of the finite separation of the atoms and the interaction of the electrons with each other, Z' does not approach the value 2 as it would for independent electrons but increases to 1.19, according to the variation functions used. This Z' is near to the value 1.13 of the ratio of the two half-widths calculated above and would probably agree more closely if the assumption of the experimental value of r_{AB} had not invalidated the virial theorem in this case. It is interesting to note that the ratio of the most probable β's calculated as in the case of helium is 1.12, checking closely the actual ratio of the half-widths.

The author is indebted to Dr. Linus Pauling for valuable criticisms during the course of this investigation.

B.

BOND FORMATION IN SIMPLE MOLECULES

BOND FORMATION IN SIMPLE MOLECULES

Bruce L. Hicks

ABSTRACT

This thesis is a review of the quantum mechanical methods which have been used to compute the dissociation energies and interatomic distances of homonuclear diatomic molecules in the ground state. In comparing the different methods three qualifications for a successful type of treatment are emphasized. First, it must be of as general applicability as possible. Second, the inherent uncertainty attending its application should either be small or of known order of magnitude. Finally, it should provide a simple and general physical picture of bond formation. These three qualifications are discussed in some detail for H_2^+ up to Li_2.

New calculations for the lithium molecule and for the beryllium molecule-ion, Be_2^{++}, are described. In particular a comparison is made between the permissible types of hybridization treatment for Li_2 and Li_2^+. It is concluded that the complete hybridization of the atomic orbitals in Li_2 is not possible when the K electrons are neglected.

In a section on numerical methods certain improvements in the technique of evaluating some of the two electron integrals are described. The different procedures used in solving secular equations are compared with regard to their accuracy, generality of application, and their amenableness to machine computation. It is shown how the Duncan-Collar-Aitken technique may be extended so that it conforms perfectly to the demands of quantum mechanical calculations.

The problem discussed in this part of the thesis was suggested by Professor Linus Pauling, to whom I am also greatly indebted for advice and guidance during the course of the work. To Dr. Sidney Weinbaum I owe my best thanks for his calculation of the numerical values of most of the integrals.

B. BOND FORMATION IN SIMPLE MOLECULES

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Bond Energies and Interatomic Distances

I. The Diatomic Homonuclear Methods

1. Introduction

In the development of the quantum mechanics during the last fourteen years, mathematically approximate solutions of the fundamental equations have played the all-important roles, particularly in the description of energy characteristic states of atoms and molecules. The primary reason for the use of approximate methods has been one of expedience.

In the first place, no one has exhibited the analytic solution of a Schrodinger amplitude equation which describes the stationary state of motion of more than two particles in a system of atomic dimensions. In fact, the only complete analytic solution of the amplitude equation known is for the hydrogenic atom. The method of solution used in this case has not been generalized to give the analytic solution to the wave equation for many-electron atoms. The only other system for which both the wave function and the energy may be said to have been accurately determined is the hydrogen molecule-ion but again the process of solution, in this case one of analytic approximation by means of series, has not been extended to many-electron molecules.

Considering now, in the second place, a treatment of atomic problems which gives approximate solutions, the Ritz variation method as developed by Hylleraas has supplied a theoretically satisfactory technique of successive approximation through which eigenvalues if not eigenfunctions can be obtained with any desired degree of accuracy. But the application of the method has been attended with such algebraic and numerical complexities that it has been used in the complete treatments only of the simplest, two electron systems, the helium-like atom and the hydrogen molecule. From a practical point of view, it is not surprising then that quantum mechanical calculations for atoms and molecules have been largely of an approximate character as regards finding both wave functions and energy quantities.

Considerations of a more physical nature have provided perhaps the most substantial justification for the use of certain types of approximate treatment. For the most part, these considerations have been based upon new physical concepts which were first introduced in the quantum mechanical theory and, more important here, whose meaning was entirely derived from some particular approximation process applied to the solution of the wave equation. Such a concept is the important quantum mechanical phenomenon of resonance, closely associated with the fundamental principle of superposition of states, for not only has it substantially no classical counterpart, "resonance energy", for example, being unknown in classical mechanics, but also it owed its introduction to a particular type of approximate wave mechanical treatment of an atomic system.

This resonance concept has found its most general and possibly its most important application in the theory of molecular binding where without the use of inexact methods, there would be no theory. The approximate solution depending upon the resonance concept of the problem of the hydrogen molecule given by Heitler and London(31) in 1927 is fundamental to almost all subsequent calculations upon bond formation in molecules. Their treatment provided for the first time a conceptual blue print of the chemical bond which was based upon general physical theory rather than upon hypothesis chosen to fit the empirical chemical data. The considerable extensions of the original Heitler-London theory in the hands of Pauling and Slater, Hund, Mulliken and Huckel serve to exhibit only the more clearly the striking success attending the use of approximate calculations in the field of molecular structure.

In order to illustrate these general remarks and to prepare for the detailed discussion of lithium and beryllium molecules and molecule-ions which is to follow, a survey will be given of those quantum mechanical treatments of homonuclear diatomic molecules and molecule-ions whose purpose it is to determine dissociation energies and interatomic distances. The restriction to diatomic molecules will not be very considerable since calculations upon polyatomic molecules of anything like quantitative accuracy are few in number. Likewise, the theory of heteronuclear molecules is in an unsatisfactory state with regards to accuracy and completeness. Since consideration of these more complicated systems would not aid the understanding of simpler ones, the discussion only of homonuclear diatomic molecules and molecule-ions will be attempted.

2. Fundamental Theory

It is necessary, to insure clarity in the subsequent discussion of various particular molecules, that an outline be given of the quantum mechanical theory useful in bond formation calculations and the general procedure used in applying it to the computation of the dissociation energy and the interatomic distance in an unexcited diatomic molecule.

In quantum mechanical theory, the allowable information concerning a system of atomic particles is contained in the Schrodinger amplitude function or, briefly, wave function, $\psi(\tilde{r}_1, \tilde{r}_2, \cdots \tilde{r}_n)$ for that system, $\tilde{r}_i$ being the position vector for the i-th particle. The quantity $\psi\psi^*$, the modulus squared, is interpreted as a probability density function which is often taken to be proportional to the actual density of electricity. When the wave function is given, the expectation value for any dynamical property of the system may be computed if, as is usually the case, the operator corresponding to that dynamical quantity may be found. In particular, the total energy of a system in an energy-characteristic stationary state is given by

$$W = \frac{\int \psi^* \underset{\sim}{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \tag{1}$$

the integrals being extended throughout position space.

The Hamiltonian operator $\underset{\sim}{H}$ and the dynamical quantity, total energy of the system, W, to which it corresponds also enter into the

Schrodinger amplitude equation,

$$\underset{\sim}{H}\psi = W\psi \tag{2}$$

which is the wave equation for the system in an energy characteristic state. To each of a set of values of W, these being fixed, physically speaking by $\underset{\sim}{H}$, there corresponds a finite number of wave functions. The integral expression for W is here taken to be the fundamental relation rather than the differential equation (2) because in most problems the true solution of the amplitude equation is unknown, so that an approximation function of some kind must be used in its place. In these cases, energy value, W , which is calculated from equation 1 corresponds <u>strictly</u> to the energy of an idealized physical system ~~which~~ whose state is thought to resemble with some fidelity the true physical system that is accurately described by the wave equation (2). Since, for the sake of simplification moreover, the Hamiltonian operator itself is often modified perhaps the following description of the approximation method in general should be adopted as being the least open to criticism:

(i) The wave equation describing <u>completely</u> the physical system of interest is written down.

(ii) A function ψ' and an energy operator $\underset{\sim}{H}'$ are chosen and through the use of 1), the expectation value of the energy corresponding to $\underset{\sim}{H}'$ is computed.

(iii) The true wave function ψ and the approximate one ψ'

as well as $\underset{\sim}{H}$ and $\underset{\sim}{H}'$ are compared and an inference is drawn as to the physical significance of the energy W'.

Unfortunately, this theoretically ideal process cannot be carried out since there is no general procedure through which an estimate may be made of the point to point deviation of an approximate wave function from the true wave function satisfying the wave equation. For this reason, it has been customary to reverse the procedure outlined above and to compare W and W' in order to obtain an estimate of the fidelity of ψ' to ψ.

It is only in special cases that the application of this criterion is strictly justifiable from a mathematical point of view, yet in numerous applications of approximate wave functions to other than energy calculations, use of the criterion has not been shown to introduce serious error. For the purposes of the discussions to follow, the energy criterion will be assumed to possess at least qualitative significance but the point of view assumed in outlining the ideal procedure above will be maintained as far as possible.

The type of approximate wave function ψ_{var} which has proven to be the most useful in molecular calculations is the variation function. It supplies a means of varying the detailed form of a wave function continuously since it is a function of one or more parameters as well as of the positional coordinates of the particles making up the system. Since $W_{var} = \dfrac{\int \psi_{var}^{*} \underset{\sim}{H} \psi_{var} \, d\tau}{\int \psi_{var}^{*} \psi_{var} \, d\tau}$ is a function of the same parameters as ψ_{var} it is possible to vary the parameters and define thereby a minimum value of W'. The fundamental variation principle states that with the variation functions restricted only to be continuous, one-valued and finite, W_{var} is bounded below by W, the true energy. That is, <u>for any "proper"</u> ψ_{var},

$$W_{var} \geqslant W$$

Two characteristics of this method should be emphasized. The first is that, since one can never overshoot the mark, W may be approximated to as closely as is desired given ample "flexibility" in the form of the wave function and patience on the part of the computer. The second characteristic is an illustration of the general principle stated previously: no matter how accurately W is approximated to by W', there is very little assurance that the point to point deviations of ψ_{var} from the true ψ are small. Different types of variation functions will occur frequently in the succeeding detailed discussion of particular molecules.

We will conclude this section with the application of the quantum mechanical methods to the treatment of diatomic molecules. The Hamiltonian operator $\underset{\sim}{H}$ for a molecule is

$$\underset{\sim}{H} = -\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\nabla_i^2 - \sum_{i>j}\frac{Z_i Z_j e^2}{|\tilde{r}_i - \tilde{r}_j|}$$

where m_i, $Z_i e$, $\tilde{r}_i$ are the mass, charge and position vector of the i-th particle and ∇_i^2 the corresponding Laplacian. Born and Oppenheimer(48) showed that as a first approximation, which in most molecules is quite accurate, the electronic and nuclear motions could be separated. The resulting Hamiltonian for the *electronic* wave function in a homonuclear diatomic molecule is

$$(3) \qquad \underset{\sim}{H}_e = -\frac{\hbar^2}{2\mu}\sum_i \nabla_i^2 + \frac{Z^2e^2}{R} - Ze^2\sum_i\left(\frac{1}{a_i}+\frac{1}{b_i}\right) + e^2\sum_{i>j}\frac{1}{r_{ij}}$$

where μ is an electronic reduced mass, R is the fixed internuclear distance, Z is the charge on either nucelus, a_i and b_i are distances of the i-th electron from nuclei A and B respectively, and r_{ij} is the distance between the i-th and j-th electron. The electronic energy levels W_e and the corresponding wave functions ψ_e are then given by

$$\underset{\sim}{H}_e \psi_e = W_e \psi_e$$

Since the electronic energy and wave function is all that is required in the calculation of dissociation energy and interatomic distance, this equation will henceforth be written in the simpler form

$$\underset{\sim}{H}\psi = W\psi$$

it being tacitly understood that $\underset{\sim}{H} = \underset{\sim}{H}_e$, $\psi = \psi_e$ and $W = W_e$, the energy in the ground state.

The Hamiltonian operator $\underset{\sim}{H}$ and consequently the energy W computed from Equation 1 or 2 depend upon the interatomic distance R. In fact, when the component atoms of the molecule have been specified, W becomes a function of R alone. For present purposes five types of functional relationship illustrated in Figure 1 may be distinguished. The interaction energy E rather than the total energy W is taken as the energy variable. Taking W_a to be the energy of one isolated atom of the molecule, then E is given by the equation

$$W - 2W_a = E$$

Curves (1) and curve (2) with minima and asymptotic approach to $E=0$ from the negative side are typical of the formation of a strong bond and a weak bond respectively. The measure of bond strength is the dissociation energy D_e which is equal to the minimum value of E with the sign changed. The difference in "stability" of the bonds represented by (1) and (2) is the difference between D_{e_1} and D_{e_2}. The abscissa, R_e of a minimum represents of course the equilibrium separation of the nuclei.

Curves (3) and (5) since they possess no minima and have always negative slopes correspond to repulsion at all distances. Finally, the peculiar binding illustrated by curve (4) represents a molecule which will exhibit predissociation phenomena.

An additional quantity, the true electronic dissociation energy D_0, is sometimes discussed. This is greater, algebraically, than by the zero point vibrational energy $\frac{1}{2}h\nu_0$ for the molecule in the ground state and thus represents the purely electronic contribution to the dissociation energy. Unless the contrary is explicitly stated D_e will be used in all subsequent discussions of the dissociation of diatomic molecules.

Having reviewed the quantum mechanical rules and concepts which are fundamental to molecular structure calculations, we will now turn our attention to those diatomic molecular systems which have already been treated by investigators since the original work of Heitler and London on the hydrogen molecule.

3. The Hydrogen Molecule-Ion

The first molecular system to receive satisfactory treatment by the quantum mechanics was the hydrogen molecule-ion, H_2^+ , discussed by Burrau(1) in 1927. In this one-electron problem, the wave equation

$$\left\{ -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{a} - \frac{e^2}{b} + \frac{e^2}{R} \right\} \psi = W\psi$$

may be separated with the use of elliptic coordinates $\lambda = \frac{a+b}{R}$, $\mu = \frac{a-b}{R}$, $\varphi =$ azimuthal angle ; $\psi = L(\lambda)M(\mu)\Phi(\varphi)$ into three ordinary differential equations. The equations are

$$\frac{d^2\Phi}{d\varphi^2} - m^2\Phi = 0 \quad , \tag{5}$$

$$\frac{d}{d\mu}\left\{ (1-\mu^2)\frac{dM}{d\mu} \right\} + \left\{ \alpha\mu^2 - \frac{m^2}{1-\mu^2} - \beta \right\} M = 0 \tag{6}$$

$$\frac{d}{d\lambda}\left\{ (\lambda^2-1)\frac{dL}{d\lambda} \right\} + \left\{ -\alpha\lambda^2 + 2\rho\lambda - \frac{m^2}{\lambda^2-1} + \beta \right\} L = 0 \tag{7}$$

and

with $\rho = R/a_0$.

The parameters m, α, β must be so chosen that the solutions Φ, L, M will form a physically satisfactory wave function, continuous, one-valued and finite. The parameter α is directly related to the energy W through the equation

$$(8) \qquad \alpha = -\frac{\mu R^2}{2\hbar^2}\left(W - \frac{e^2}{R}\right)$$

The largest possible value of α thus corresponds to the ground state.

The proper values of m are positive and negative integers. In the ground state, $m = 0$ and both α and β must then also be uniquely determined. Since these two parameters enter into both the equation for λ and that for μ, they may not be determined separately. Indeed, to each value of α in the μ equation, there must correspond one and only one value of β for the normal configuration of the molecule. Expressed differently, there must be a functional relationship between α and β in order that the μ equation have a satisfactory solution. In the same way, β must be a certain function of α, ρ and in order that the λ equation possess well-behaved solutions. The essential problem is then to discover these two functional relationships and to find the values of the energy parameter α as a function of ρ which satisfy them both.

Burrau solved the equations by a process of numerical integration which Pauling has described in some detail in his article on H_2 and H_2^+(2). Burrau's computed values of D_e and R_e are given in a part of Table I. More accurate methods of solutions of these equations were found by Hylleraas(6) and Jaffé(8). The former expanded $M(\mu)$

in a finite series of Legendre polynomials $M(\mu) = \sum_\ell P_\ell(\mu) c_\ell$ Upon substituting the series into equation 6 he obtained a set of simultaneous homogeneous linear equations for the c_ℓ . The necessary vanishing of the determinant of the coefficients of the which of course were themselves functions of α and β , provided the desired functional relationship between α and β . A similar, though more complicated treatment of the λ equation produced the second functional relationship, again in the form of a determinantal equation, the dependence of α upon β and ρ which, as discussed above is sufficient to establish the final relation between the energy parameter α and the nuclear separation parameter ρ . Hylleraas' results appear in Table I.

The treatment of Jaffé followed more closely the analytic line of attack than any previous work. Other investigators had made small or even incorrect progress, (cf. Jaffé's paper), toward the solution of the λ equation from an analytic point of view. Jaffé was the first to find an expansion of $L(\lambda)$ which converged for all values of λ . Hylleraas' expansion for example converged only for $\lambda < \left| 1 + \frac{1}{2\sqrt{\alpha}} \right|$

Jaffé first made the substitution

$$(9) \qquad L = e^{-2\sqrt{\alpha}\lambda} (\lambda^2 - 1)^{m/2} y$$

as had Wilson previously$^{(4)}$. Then he introduced the new independent variable $u = \frac{\lambda - 1}{\lambda + 1}$

which made possible the representation of the complete L function throughout the entire range of $1\leq\lambda<\infty$ corresponding to $0\leq u<1$ The substitution $$y=(1-u)^{\sigma}z$$ where $$\sigma = m+1-\frac{\rho}{4\sqrt{\alpha}}$$

led to the infinite series

$$y=\sum_{m=0}^{\infty} a_m u^m$$

and the convergence of this series for $u=1$ could be made to depend upon whether or not a transcendental relationship, in the form of a continued fraction, was satisfied between α and β as a function of ρ . This condition upon α, β and ρ could then be combined with the relation between α and β originating in the μ equation to give as before the desired variation of α with ρ . It is conceivable that Jaffé's continued fraction could be transformed directly into Hylleraas' determinant since the latter is of a specially simple kind and the functional relationship expressed by the two transcendental functions must of course be the same. The great advantage of Jaffé's method was that not only was the continued fraction more amenable to numerical computation than was Hylleraas' determinant but that an explicit analytic expression for the wave function L could be given in terms of an infinite series convergent for all λ .

The close agreement between the results of Hylleraas and Jaffé is misleading for the two investigators used essentially the same approximate relationship between α and β and between α, β and ρ even though the methods used in calculating the latter were different. The error which Sandeman (see below) found in the Jaffé Hylleraas work shows the great advantage of making conservative estimates of computational errors even in a very straightforward calculation of this kind.

An improvement of Hylleraas' technique was made by Svartholm (11) in 1938. He made use of functions in his expansion of $L(\lambda)$ which were the solution of second order differential equation with three regular singularities and was able with rather simple calculations to obtain a value of the energy differing by only 0.01% from the value computed by the "exact" method of Jaffé and Hylleraas.

It is interesting to compare the computed and observed vibrational constants for the hydrogen molecule-ion. Hylleraas made the first calculation of these quantities. Sandeman(10) has increased the accuracy of the Jaffé-Hylleraas type of treatment and has computed perhaps the most accurately known values of the dissociation energy, interatomic distance and vibrational and rotational constants. Not only are Sandeman's primary calculations considerably more accurate than those of Jaffé and Hylleraas but also his computation of the molecular constants is based upon Dunham's analysis(52) of the diatomic rotator-vibrator and hence are based on a more complete and accurate theory. The molecular constants are given in Table I together with the experimental values of Birge and of Richardson. In the case of the hydrogen molecule-ion at least it is safe to conclude that the bond constants are determined with somewhat more accuracy and certainly with greater completeness from the theoretical calculations than from the experimental observations. It is unfortunate that the result of Sandeman's calculation is to increase the small existing disagreement between the theoretical and experimental bond constants as well as between the dissociation energies. (See discussion of James-Coolidge work on H_2, section 4).

It is perhaps unnecessary to point out that the methods described above, though powerful in treating the hydrogen molecule-ion, are not applicable to many-electron systems. The separation of the wave equation is essential to its solution by the numerical or analytic methods known at present and the technique of separating a wave equation for a two-or-more-electron system of any kind into ordinary differential equations has yet to be found.

All of the remaining methods of solution of the hydrogen molecule-ion wave equation depend upon the use of variation functions. These are the simplest type of approximate wave function and yet often lead to quite accurate values of the dissociation energy. Moreover it is ~~only~~ the approximate solution of the wave equation which is capable of physical interpretation and which provides a basis for approximate calculations upon many-electron molecules.

The most flexible form of one-electron variation function is that of James who introduced it in his discussion of Li_2^+,(34).

It is, expressed in the elliptic coordinates of equation (6,7)

$$(10) \qquad \psi = e^{-\delta\lambda}(1+c\mu^2)$$

James found that the optimum values of the parameters were $c = 0.448$ $\delta = 1.35$ corresponding to the dissociation energy $D_e = 2.772$ v.e. which differs by only 0.1% from Sandeman's value. The addition of one or two terms in μ and λ to the polynomial would certainly improve the calculation considerably. Since this is the only one-electron system for which there is known both the true wave function and a variation function which corresponds to an accurate value of the energy, it offers an unparalleled opportunity to discover the fidelity of the "accurate" variation function to the true wave function. Unfortunately, no one has made this valuable comparison which would at least provide a lower bound to the confidence which may be placed in variation functions.

In the preceding discussion of the physical interpretation of the true H_2^+ wave function and of the James function has purposely been omitted for it is only in terms of the Heitler-London type functions to be described next, that a physical picture of the one-electron bond can be satisfactorily given.

In 1928, Pauling gave the first approximation treatment, of the Heitler-London type, to the hydrogen molecule-ion (2). The linear variation function used is constructed with the help of the following argument, the Hamiltonian being the same as in equation 4. For large separation of the nuclei A and B the electron is described accurately by either of the two atomic wave functions A_{1s} or B_{1s}, where A_{1s} is a hydrogen $1s$ wave function for atom A, B_{1s} a similar function for atom B. For smaller nuclear separation, involving perturbation of the atomic orbital by the positively charged proton, a simple variation function of the form

$$\psi = A_{1s} + c\, B_{1s} \tag{11}$$

is assumed. The superposition of the two atomic states described by this wave function corresponds, physically speaking to a concentration of charge in the region between the component atoms in the molecule-ion and gives a finite probability that the electron be on <u>either</u> nucleus A, B. It is found upon carrying through the variation treatment that c must have the value ± 1. The allowed functions ψ_S and ψ_A are symmetric and antisymmetric respectively in the nuclei and correspond to two energy-separation functions $E_S(R)$ and $E_A(R)$ The symmetric function represents a stable bond for the energy curve is of type 1 in Figure 1, while the antisymmetric function, since it leads to a curve of type 5, represents repulsion at all distances. The dissociation energy and equilibrium interatomic distance are of the right order of magnitude, as seen from Table I even as derived from this extremely simple treatment.

If instead of ψ_S, only A_{1s} is used in the treatment, the computed energy distance curve is of the third type (Figure 1) which, having no minimum, cannot correspond to the formation of a stable bond. The fundamental requirement for a one-electron bonding function is thus seen to be that it must represent the superposition of two electronic configurations which possess at least approximately the same energy. When such orbital degeneracy exists, the energy due to resonance between the equivalent states is sufficient to permit the formation of a stable bond. It is clear that a Heitler-London type of treatment such as this gives a valuable physical picture of a chemical bond formation.

The other calculations upon the hydrogen molecule-ion which have been carried out are for the most part essentially refinements of Pauling's treatment. Finkelstein and Horovitz(3) varied the effective nuclear charge Z in the hydrogen-like function A_{1s} and found considerable improvement in the energy value and equilibrium separation for $Z' = 1.23$ instead of $Z = 1$ as in Pauling's $1s$ function. Dickinson(7) used a "polarized" atomic orbital

$$\psi = A_{1s} + \sigma A_{2p} \tag{12}$$

A_{2p} being a hydrogen-like $2p$ wave function. The polarization term contributed 0.5 v.e. to the energy which with the 2.25 v.e. resonance energy gave a value of the dissociation energy differing by only .05 v.e. from the accurate value of Hylleraas, Jaffé, etc. Finally, Guillemin and Zener(5) by introducing the polarization effect through exponential functions, were able to reduce Dickinson's error to 0.01 v.e. All but Pauling's simple treatment give 1.06 A as the equilibrium separation of the nuclei.

The polarization method was designed to take account of the perturbing effect of the neighboring proton upon the $1s$ atomic orbital. James' variation function can be interpreted as a polarization function and, as he points out in his article on the lithium molecule-ion, this variation function expressed in elliptic coordinates is both more accurate and easier to use in computation than that of Guillemin and Zener. Furthermore, in spite of the success of the polarization terms in reducing the error in the calculated energy values, their introduction can be regarded only as a mathematical trick without any considerable physical significance. James function is a better function in this respect also since it is in the same analytic form as the series solution of the hydrogen molecule-ion wave equation given by Hylleraas.

In concluding this long discussion of the hydrogen molecule-ion, it should be emphasized again that it is only the Heitler-London type of treatment which at the same time offers ~~a~~ the physical picture of chemical bonding and admits of generalization to more complicated molecules.

4. The Hydrogen Molecule

No molecular system has been of more fundamental importance in the quantum mechanical theory of bond formation than the hydrogen molecule. It is the only molecule more complicated than H_2^+ for which the theoretical value of the dissociation energy is believed to be comparable in accuracy with the experimental value. Naturally then, the treatment of all polyelectronic molecules follows closely that of the two electron system H_2. This is particularly true when the bond under consideration is covalent for the H - H bond is the prototype of all covalent bonds.

The pioneer work on the hydrogen molecule was that of Heitler and London in 1927 (14).

The wave equation for the system is

$$(13) \quad \left\{ -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + e^2\left(\frac{1}{R} - \frac{1}{a_1} - \frac{1}{a_2} - \frac{1}{b_1} - \frac{1}{b_2} + \frac{1}{r_{12}}\right)\right\}\psi = W\psi$$

in which the r_{12} is the interelectronic and R the internuclear distance, a and b are distances of an electron from nuclei A and B, the subscripts 1 and 2 referring to electrons 1 and 2. Heitler and London considered the approximate wave function

$$(14) \quad \psi = A_{1s}(1)\,B_{1s}(2) + c\,A_{1s}(2)\,B_{1s}(1)$$

in which $A_s(1)$ is a $1s$ hydrogen wave function for the first electron on nucleus A. This linear variation function possesses the property that either the first or second term is an accurate solution of the wave equation for large internuclear separation. This may be easily seen from the form assumed by the wave equation for the hydrogen molecule when $R \rightarrow \infty$ For smaller values of R, the function will, as in the similar case of the hydrogen molecule-ion, correspond to a concentration of charge between the nuclei. It likewise represents a finite probability of finding either electron on either nucleus but, as is proper in a wave function representing an unexcited state, allows but one electron to occupy at any one time the $1s$ orbital of a given nucleus.

Variation of the parameter C leads to two values W_S and W_A of the energy corresponding to the symmetric and antisymmetric functions

$$(15) \qquad \psi_S = A_{1s}(1)\,B_{1s}(2) + B_{1s}(1)\,A_{1s}(2)$$

and

$$(16) \qquad \psi_A = A_{1s}(1)\,B_{1s}(2) - B_{1s}(1)\,A_{1s}(2)\,.$$

The interaction energy curve for W_S is similar to the curve 1 in Figure 1, that for W_A to curve 5 so that, as in the hydrogen molecule-ion, ψ_S represents the stable bonding function, ψ_A corresponds to repulsion at all distances. Furthermore, the function $\psi_N = A_{1s}(1)\,B_{1s}(2)$ leads to a curve of type 2, Figure 1, and yields only a very weak bond. The values computed with ψ_S for D_e and R_e, recorded in Table II are of the right order of magnitude.

Formally at least, the properties of this function for the hydrogen molecule are identical with the properties of Pauling's function for the hydrogen molecule ion. The different functions ψ_S, ψ_N and ψ_A represent respectively a stable bond, a very unstable bond and repulsion at all distances for both of the molecular systems. Also, the bond energy for the single electron bond in H_2^+ is 56% that of the electron-pair bond in H_2 and the interatomic distance is correspondingly greater. These results remain valid for any Heitler-London treatment. If only these computed results are considered then, an electron pair bond might be thought of as two single electron bonds and this is indeed the viewpoint adopted in the "molecular orbital" treatment of Hund, Mulliken and Hückel whose wave function is therefore of the form

$$\psi_{M.O.} = \left[A_{1s}(1) + B_{1s}(1)\right]\left[A_{1s}(2) + B_{1s}(2)\right]$$

Slater(65) has shown that this molecular orbital function and the HLSP function of equation 15 become identical when both are refined through addition of terms representing excited states.

There are two facts which invalidate the concept of the electron-pair bond as being composed of two one-electron bonds. First, on this picture, the three-electron bond should certainly be stronger than the electron-pair bond. From Pauling's calculation on He_2^+ to be discussed later, the opposite is seen to be the case. The three-electron bond actually corresponds both in strength and bond distance to the one-electron bond. In the second place, the Heitler-London type function, particularly when ionic terms are added is capable of describing stable bond formation by two atoms of widely differing electronegativity even though one-electron bonds between such atoms are very weak. Pauling has adopted the view that the electron-pair bond as represented by the function

$$(17) \qquad \psi_s = A_{1s}(1)B_{1s}(2) + B_{1s}(1)A_{1s}(2)$$

is of an essentially different character from either the one or the three-electron bond, and has explained this difference as follows. The function ψ_s called variously a Heitler-London-Slater-Pauling or H-L-S-P function or a valence bond wave function is symmetric to interchange of the two electrons. The two possible configurations of the electrons represented by the two terms in equation 17 correspond to exactly the same energy and this degeneracy between the two states exists whether the component atoms of the molecule are the same or are different. Such degeneracy always results in resonance between the two states and consequent stabilization of the bond, but this type of degeneracy is not found in the other single bonds. This is most clearly brought out by the use of Slater's anti-symmetrized wave functions which include the spin. These functions will be described in Part II. It is interesting, however, for the present discussion that in substantially all cases the spins of the two electrons in a covalent bond must be opposed if the bond is to possess the greatest stability.

The hydrogen molecule and hydrogen fluoride may be taken as good examples of the importance of covalent bonds. For the homopolar molecule H_2, the stabilization amounts to about 4 v.e. which is 80% of the total bond energy. For HF, which cannot form stable one or three electron bonds, the electron-pair stabilization amounts to 50% of the observed bond energy, the remaining energy being ionic. The importance of the electron-pair or covalent bond in chemistry relative to the one or three-electron bond is thus derived not only from its greater strength but also from the possibility of its formation between any and all atoms.

Refinements in the functions of Heitler and London have been numerous. Sugiura(15) using Heitler and London's function discovered the method of evaluating the so called two electron exchange integrals which occur in all Heitler-London type treatments of many-electron systems and was thus able to improve the accuracy of Heitler and London's numerical calculations. Wang(17) varied the effective nuclear charge occurring in the hydrogen-like $1s$ orbitals and decreased the error in the dissociation energy by 13%. It is interesting to compare the similar calculations for the hydrogen molecule-ion. For both H_2^+ and H_2, the fractional error in the value of D_e as calculated with the simplest wave functions is about one third while again, for both systems, the varying of the effective nuclear charge is to decrease the fractional error to about one fifth.

As another refinement, Weinbaum(20) has introduced ionic terms into the wave function. His ionic functions are of the form

$$(18) \qquad \psi = A_{1s}(1)B_{1s}(2) + A_{1s}(2)B_{1s}(1) + c\left\{A_{1s}(1)A_{1s}(2) + B_{1s}(1)B_{1s}(2)\right\}$$

thus allowing for the possibility of the ionic structures H^+H^- and H^-H^+. This function might also be considered as a generalization of the molecular orbital function of equation but, as seen from Table II leads to a far more accurate value of the dissociation energy. Since the optimum value of c is 0.256, the over-emphasis of ionic terms by the molecular treatment is clearly shown.

The remaining approximate treatments are of the polarization type introduced by Rosen(19) and applied by Dickinson to H_2^+. Simple polarization of the $1s$ orbitals leads to a D_e which is but slightly better than for the ionic function. More complicated polarization of the Guillemin and Zener type was performed by Inui(24). There was very slight (0.02 v.e.) improvement in the energy over Rosen's value. It is interesting to note the close agreement between experimental and the average of the theoretical values of ν_e as given by Rosen and Inui. (cf. Table II) Polarization(22) of the non-ionic terms in Weinbaum's ionic wave function, equation (15) improved the value of by only 0.04 v.e. Since more accurate wave functions are available (see James and Coolidge's treatment of H_2 below), it would be illuminating to test both the ionic and the polarization type function in order to discover whether the polarization technique is as artificial as it appears to be. The comparison has been made by James and Coolidge only for Rosen's function.(21).

The dissociation energies, the interatomic distance and the vibrational frequency of the nuclei ν_e as calculated on the basis of the various models are listed in Table II together with the experimental values of Beutler and Sandeman. For the most accurate comparison of experiment and theory, it is necessary to describe the work of James and Coolidge(2).

Hylleraas had demonstrated in his computations on helium the great importance of the interelectronic distance as a variable in a two-electron variation function. Consequently, James and Coolidge in forming a variation function for the electrons in a hydrogen molecule, introduced explicitly the interelectronic distance variable $u = \frac{2r_{12}}{R}$ Their function was of the form

$$(19) \qquad \psi = e^{-\delta(\lambda_1+\lambda_2)} \sum_{mnjkp} c_{mnjkp} \left(\lambda_1^m \lambda_2^n \mu_1^j \mu_2^k u^p + \lambda_1^n \lambda_2^m \mu_1^k \mu_2^j u^p \right)$$

λ and μ being elliptic coordinates. It is difficult to interpret in detail such a function but it certainly takes account of the interchangeability of the two electrons and represents a charge concentration between the nuclei. The best value of the energy which can be obtained with p = 0 is D_e = 4.27 v.e., which is not a large improvement over Weinbaum's ionic treatment value. The remaining 0.45 v.e. or 10% error is of course caused chiefly by incomplete representation of the interelectronic interaction and should give an approximate idea of the magnitude of the smallest error to be expected in the best H-L-S-P treatments of more complicated molecules.

Using thirteen terms in the function of equation 19, James and Coolidge obtained as their most accurate value of dissociation energies D_e = 4.722 ± 0.013 v.e., D_0 = 4.454 ± 0.013 v.e., corresponding to R_e = 0.74 A. The true electronic dissociation energy agrees extremely well therefore with the experimental value of Beutler, 4.454 ± 0.005 v.e. Another comparison of experiment and theory is given by making use of the theoretical dissociation energy $D_0(H_2^+)$ of the hydrogen molecule-ion, the ionization energy of the hydrogen atom $I(H)$ and the extrapolated spectroscopic value of the ionization energy $I(H_2)$ of the hydrogen molecule. These quantities are related to $D_0(H_2)$ through the equation

$$I(H_2) + D_0(H_2^+) = I(H) + D_0(H_2)$$

Taking Sandeman's value of $D_0(H_2^+)$ as the most accurate, $D_0(H_2)$ is calculated to be 4.442 v.e. The principal source of uncertainty in this calculation is certainly the determination of $I(H_2)$.

There is but one more treatment of the hydrogen molecule that must be discussed. This is the application of Hartree method made by Coulson(23). Instead of performing the necessary integrations numerically, Coulson employed explicit analytic wave functions the parameters in which were determined by the application of the self-consistent field criterion. Thus the method is essentially a form of variation treatment in which one-electron or molecular orbitals are used and consequently would be expected to give a value of the energy differing from that of Weinbaum only because Coulson's molecular orbitals, being expressed in elliptic coordinates are more flexible than those of Weinbaum. That this is the case is seen from the figures in Table II. The improvement due to Coulson's calculation over Weinbaum's value being only 0.13 v.e. or 6%. There is certainly no great advantage in the Hartree method for simple molecules. In view of the conclusions of James$\binom{34}{37}$ concerning the importance of exchange interactions between core and valence electrons in molecules, its application to many-electron molecules would involve the Fock-Slater method which is difficult to carry out even for electronic systems consisting of single atoms. Thus without considerable further development Coulson's treatment does not seem very valuable.

To conclude this description of the hydrogen molecule, two illustrations will be given of the considerable difference between the one and the two-electron molecular system. Coulson in his work on the Hartree method(23) used a molecular orbital of the form

$$\psi_{M.O.} = e^{-\delta\lambda}(1 + c\mu^2)$$

in a preliminary calculation. This form of function orbital leads to a quite accurate value of the dissociation energy of the hydrogen molecule-ion in error by but 0.2%. Coulson's molecular orbital wave function for hydrogen

$$\psi_{M.O.}(1)\ \psi_{M.O.}(2)$$

led to the value D_e = 3.096 v.e. which is more in error than the value obtained by the simplest Heitler-London treatment. A similar comparison of the work of Rosen with that of Dickinson, and the work of Guillemin and Zener with that of Inui results in the same conclusion. These examples show clearly that the wave function for the electrons in a many-electron molecule has small resemblance to a superposition of wave functions for single electrons whose interaction is neglected.

The second illustration is taken from Sandeman's work(7).

In his extremely accurate treatment of the hydrogen molecule-ion Sandeman found that the energy-separation function is represented by the following expression:

$$-E/E_H = 0.67058 + \frac{1.1931}{1+\xi} + \frac{0.12406}{(1+\xi)^3} - \frac{0.78264}{1+\xi^2}$$

where

$$\xi = \frac{R-R_e}{R_e} .$$

This simple function represented Sandeman's computed energy values to better than <u>one part in two million</u>. When the variable part was expanded it became

$$E_v = 0.41046 E_H \xi^2 (1 - 1.6978\xi + 2.0933\xi^2 - 2.1865\xi^3 + 1.9775\xi^4 - 1.4663\xi^5 + 0.6528\xi^6 + \dots)$$

He then computed from the bond spectral data the energy functions for the neutral hydrogen molecule in ground states(9) $1s1s\,{}^1\Sigma$ and the final state of the Fulcher bonds(66) $1s2s\,{}^3\Sigma$. These are, omitting the constant term,

$$E_v = 0.74051 E_H \xi^2 (1 - 1.6563\xi + 1.9996\xi^2 - 1.7301\xi^3 + 0.0225\xi^4 + \dots) \text{ for } 1s1s\,{}^1\Sigma \quad \text{and}$$

$$E_v = 0.47924 E_H \xi^2 (1 - 1.6438\xi + 1.9588\xi^2 - 2.0945\xi^3 + 2.2775\xi^4 + \dots) \text{ for } 1s2s\,{}^3\Sigma .$$

It is perhaps best to quote Sandeman's own conclusions. Equation shows that "for the ground state of H_2^+ the ... [energy function] ... for the molecular rotating vibrator could be written in a very simple form involving only the first three inverse powers of $(1+\xi)$ Unfortunately this simplification is not capable of extension to the states of the neutral molecule. The potential expansions for the $1s1s\ {}^1\Sigma$ and $1s2s\ {}^3\Sigma$ states of H_2, while bearing considerable resemblance to the corresponding expansion for the $1s\ {}^2\Sigma$ state of H_2^+, do not appear to be capable of reduction to any simple mathematical form". These data from band spectroscopy present possibly the best evidence for the profound difference in character between the one and two-electron molecular systems.

5. The Helium Molecular-Ions

In the foregoing discussion of the hydrogen molecule and molecular-ion, a rather complete description has been given of the principles of the H-L-S-P method as it is applied to the simpler diatomic molecules in the ground state. The calculations upon H_2^{++} add nothing new to the general picture of covalent bond formation although they do verify in one more instance the assumed characteristics of the electron-pair bond. The treatment of He_2^{++} is important because it supplies the quantitative check on the properties of the three-electron bond. Since it is the other single bonds which are the chief concern of this thesis, the helium molecule-ions will be discussed only insofar as their treatment sheds new light upon the one-electron and electron-pair bond.

It was pointed out by Pauling(49) that degeneracy between the structures $He{:}\cdot He^+$ and $He^+\cdot{:}He$ should lead to resonance and formation of a stable bond about as strong as a one-electron bond. Quantitative investigation of He_2^+ proved this to be the case. Of the three calculations which have been made (28,29,30) the results of only the most accurate one, that of Weinbaum, need be discussed since all treatments are of the same general form. The two structures correspond to two wave functions ψ_I and ψ_{II} which when added together constitute a better approximation to the true wave function than either alone. The two wave functions,

$$\psi_S = \psi_I + \psi_{II}$$

and

$$\psi_A = \psi_I - \psi_{II}$$

lead to energy-separation curves of type 1 and 5, Figure 1, just as in the case of the hydrogen molecule-ion. For the attractive, S^N, state Weinbaum gives $R_e = 1.097$ A, $D_e = 2.22$ v.e. and Pauling computed the fundamental frequency $\nu_e = 1950\ cm^{-1}$. This is to be compared with the experimental values of $R_e = 1.09$ A, $D_e = 2.5$ v.e. $\nu_e = 1650\ cm^{-1}$. The dissociation energy and interatomic distance are seen to correspond closely to the values of the same quantities for the hydrogen molecule-ion and are thus characteristic of a much weaker bond than the electron-pair bond in the hydrogen molecule.

It should be pointed out that in the H-L-S-P treatment of three-electron systems, the sign of the error in the computed value of D_e may not be determined. The computed total energy W for the electronic system is, from the variation principle, a lower bound to the true total energy. For one and two-electron systems, the H-L-S-P function may be made rigorously accurate for large internuclear separation by proper choice of the constituent atomic orbitals and the value of D_e computed from such functions must be a lower bound t to the true value. This is not the case with *any three-electron* system because the electronic configuration as $R \to \infty$ must involve *two* electrons on the same atom, a situation which cannot be described accurately by any known wave function.

Only one treatment of the doubly charged helium molecule ion, He_2^{++} has been given(27). The system is isoelectronic with the hydrogen molecule so that the formal work is the same as for H_2. As shown in section 6 Part II the effect of the increased nuclear charge is primarily by increasing the Coulomb interaction of the nuclei to convert the bonding curve of type 1, Figure 1 into a curve of type 4 without greatly altering the equilibrium value of the internuclear distance. This description applies quite accurately to for the computed interatomic distance is 0.75 A as compared to 0.74 A for H_2. Also the "typical" curve 4 of Figure 1, is actually that computed by Pauling for He_2^{++} using an ionic function similar to that of Weinbaum in his later work on hydrogen. Such an energy-separation function would exhibit predissociation characteristics. It is interesting to note that whereas the hydrogen pair bond was found to possess about 20% ionic character, that in He_2^{++} is about 45% ionic in character, a difference which must be attributed to the increase in nuclear charge.

It should be mentioned for the sake of completeness that the interactions of two neutral helium atoms is found to be a repulsive one characteristic of closed shells. (14, 32)

6. The Lithium Molecule and Molecule-Ion

The object of the rather extended discussion of the hydrogen molecule and molecule-ion which was given in sections 3 and 4 was to exhibit the merits and the defects peculiar to each of the many treatments of H_2 and H_2^+ which have been carried out. Particular emphasis was placed first, on the ability of the Heitler-London method to provide a physical picture of bond formation in these two systems and secondly, on the difficulty of obtaining accurate solutions of the wave equation even for such relatively simple systems. The Heitler-London and kindred methods are even more important, and for the same reasons, in treating many-electron molecules. For example Pauling found that bond types may be characterized not only by their heat of dissociation and interatomic distance but also according to the relative magnitude and mutual orientation of the set of bonds which any one atomic species can form. Though Pauling's conclusions were based upon quantum mechanical considerations, the rules which he formulated may be stated in the language of structural chemistry and applied with great generality without even writing down explicitly a Hamiltonian operator or a wave function. This is perhaps the most striking example of the power of the Heitler-London type treatment in deriving new physical pictures of bond formation. It is perhaps unnecessary to point out again that the Heitler-London theory of many-electron molecules would be important even though its application did not lead to important results for at present it supplies the only practicable method available for treating complicated molecular systems.

All theoretical procedures for calculating bond energies and distances in poly-electronic molecules are based on certain simplifying assumptions which involve approximations not inherent in the Heitler-London treatment itself. The principle approximation concerns the core electrons of the atoms composing a molecule. It is assumed that only the valence electrons enter into bond formation and that the inner electrons remain on their respective atoms screening the nucleus but not taking part in interatomic resonance operations. Thus the core electrons are given representations in neither the wave function nor in the Hamiltonian operator. The formal treatment then corresponds to an idealized molecule in which the charges of the core electrons in each atom have coalesced with the nuclei though their "ghosts" remain in the orbits of the core and prevent the collapse of the valence electron shell. An illustration is the simplest treatment of Li_2^+ in which the Hamiltonian used is identical with that for H_2^+ while the atomic orbital used corresponds to the Li L shell. A secondary approximation involves the assumption that it is only the variation of an atomic orbital with direction which need be considered in discussing its bond forming power(49). It is equivalent to assuming that the radial part of an atomic orbital is a function only of the total quantum number and that, consequently the radial function is the same for all orbitals belonging to the same shell. When the molecular model is simplified with the help of these two approximations so that only one electron shell on each atom is occupied by electrons, and so that these electrons differ from one another only in angular distribution the concept of "bond strengths" and "hybridization of bond orbitals" introduced by Pauling makes possible the semi-quantitative corelation of molecule and crystal properties in terms of the bond types which the constituent atoms are capable of forming.

The assumption of identical radial functions for all electrons in a valence shell is not as arbitrary as it may seem. Since no atomic wave functions for valence electrons are accurately known, this choice of radial functions is certainly the simplest and probably does not introduce any uncertainties of greater magnitude than those inherent in the Heitler-London treatment itself. The neglect of the inner electrons is more serious. James has found for example both the magnitude and the sign of the K-L shell interactions in the lithium molecule to be unpredictable so that no simple rule involving the characteristics of the electrons involved may be set up which would permit gradation of the interactions as to size. Such interactions may be of increased importance for the more diffuse shells of higher total quantum number. However, in the treatments of chemical binding, as well as of other problems, which involve neglect of the core electrons, it is found in many cases that good agreement with experiment is obtained, particularly when the method employed is one of the simpler ones available. In lieu of a theoretical reason for the cancellation of error indicated by these results, the empirical fact of this cancellation must be taken as supplying considerable justification itself for the neglect of the core electrons. As usual, the primary reason for making the two approximations described is that without them the treatment of most molecular systems would become incapable of interpretation and probibitively laborious.

The remainder of this section will be devoted to a consideration of the various calculations which have been made for the lithium molecule and molecule-ion.

James has given an almost complete treatment of the Li_2^+ system$^{(34)}$. His most reliable results were obtained by the variation method, using hydrogenic $1s$ functions for the K electrons and a molecular orbital variation function expressed in elliptic coordinates for the valence electron. The principles governing the formation of an antisymmetric wave function for the molecule from these one-electron functions are the same as will be used in Section ~~IV~~ III for the hybridization treatment of Li_2^+ and hence need not be described here. All calculations of the dissociation energy are for an assumed equilibrium separation of the nuclei R_e = 3.0 A. With an eight term variation function, the value D_e = 1.243 v.e. is obtained from which the limiting value D_e = 1.27 ± 0.02 v.e. is estimated. Making allowance for the polarization of the inner electrons by the outer ones for the inexact form of the molecular wave function, and for error in the assumed value of R_e, the final most probable value is D_e = 1.30 ± 0.05. No experimentally determined values for D_e and R_e have been reported.

The other treatments carried out by James were of the Heitler-London type with and without explicit representation of the core electrons in the wave functions and in the Hamiltonian. With the K electrons included, $D_e = 0.304$ v.e., about one fourth of James' reliable value for the dissociation energy. When the K electrons are not considered, $D_e = 0.720$ v.e., a considerable change but still much in error. It is illuminating to compare these results with the values computed with the incomplete variation functions, $e^{-\delta\lambda}$ and $e^{-\delta\lambda}(1+c\mu^2)$ for the valence electron. The former leads to $D_e = 0.49$ v.e., the latter to $D_e = 1.116$ v.e. The obvious conclusion is that the greater part of the error associated with using the complete Heitler-London function is to be attributed to its limited flexibility in representing one bonding electron. The same conclusion is valid for the second Heitler-London treatment but the contribution of the neglected K electrons cannot be estimated when the most accurate variation function for the valence electron is used. It is believed however that if the function $e^{-\delta\lambda}(1+c\mu^2)$ were used in a one-electron treatment of Li_2^+, a value of the dissociation energy in excess of 1.5 v.e. would be obtained.

James' calculations lacked completeness in that he did not attempt to provide the necessary increase in flexibility of the Heitler-London function. A hybridization of the bond orbitals carried out by Pauling and Sherman supplied this defect(35). (cf. Part II). They considered the system as a one-electron problem. With a hybrid bond orbital composed nearly equally of s and p orbitals, the dissociation energy was calculated to be for $Z_{eff.}=1.0$ D_e = 1.19 v.e. and the equilibrium internuclear distance R_e = 3.02 A. The good agreement with James' variational values seems rather fortuitous in view of the assumptions involved in the neglect of the K-shell electrons. However the equivocal nature of the agreement will be partly dispelled by the general results obtained in Part II for the lithium molecule and molecule-ion.

Although the chemical bond in the neutral lithium molecule has received more attention than the bond in the molecule-ion, its nature is not as well understood due primarily to the lack of a quantitative hybridization treatment. The first calculation for Li_2 was that of Delbrück(36). His principal object was to estimate the contributions made by the various interactions of the electrons to repulsion or attraction of the lithium atoms and he concluded that the K electron interactions could be neglected. However, as pointed out by James(39), he did not consider the most important exchange terms involving the core electrons so that this conclusion cannot be accepted. Since, moreover, his estimate of the bond energy and distance was very rough, it is not considered worthwhile to describe his treatment further.

The second calculation for the lithium molecule was made by Bartlett and Furry(37) using two approximations to simplify their Heitler-London treatment. The first approximation, the neglect of the K electrons, has been discussed at the beginning of this section and seems to some extent justified by the reasonable values for the bond constants which they obtained. The other approximation consists of the use of the "interaction operator" in place of the complete Hamiltonian and is equivalent to assuming that the molecular wave function reduces for $R \rightarrow \infty$ to a combination of accurate atomic functions. The "interaction operator" $\underset{\sim}{H}'$ is defined to be that part of the complete Hamiltonian which corresponds to the mutual potential energy of the nuclei or charged "cores" together with the mutual potential energy of electron 1 and nucleus B and of electron 1 and electron 2. If electron 1 is assumed to remain on nucleus A, the "interaction operator" thus represents the change in the energy of electron 1 when it is brought into the field of electron 2 and nucleus B. The "interaction energy"

$$W' = \frac{\int \psi^* \underset{\sim}{H}' \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

then corresponds exactly to the function E defined in section 2, its minimum value as a function of R being equal in magnitude to the dissociation energy D_e. James(39) discussed in some detail the approximation involved in the use of the "interaction operator" and concluded that in the case of Li_2 in particular the error was small when atomic orbitals were used which led to accurate values for the atomic energies.

Bartlett and Furry used the nodeless $2s$ wave function suggested by Slater(65) which leads to an ionization energy for Li I only 0.08 v.e. lower than the correct value of 5.37 v.e. Their calculation of the bond constants should then be almost correct except for the unknown contribution of the neglected K electrons. Actually they obtained D_e = 1.09 v.e. and R_0 = 2.28 Å as compared to the experimental values D_e = 1.14 v.e. and R_e = 2.67 Å. The computed dissociation energy is rather accurate but their interatomic distance is 15% too low, a somewhat greater error than the neglect of the K electrons would be expected to contribute. A reasonable hypothesis as to the cause of this discrepancy is derived from the hybridization treatment of Li_2 described in section 8-II. Bartlett and Furry found that the addition of ionic terms to their molecular wave function served to increase the binding energy by only five per cent showing the predominant covalent character of the Li-Li bond.

The most complete discussion of the lithium molecule to date is to be found in the paper by James(39). His first method is a complete Heitler-London treatment including the K electrons using the same atomic wave functions as for Li_2^+ and results in a dissociation energy D_e = 0.27 v.e. at 3.18 Å separation. The introduction of ionic terms decreases the binding energy by but 5×10^{-4} v.e. showing even more clearly than did Bartlett and Furry's treatment the unimportance of ionic structures in Li_2. Since neither the variation of the parameter in the atomic orbital nor the use of the "interaction operator" change these values substantially he concludes that the disagreement with Bartlett and Furry's results is entirely due to repulsive interactions involving the K electrons. A detailed consideration of these interactions shows some of their surprising characteristics. For example many of the important repulsive terms involve three out of the four electron shells or interchanges of more than two electrons which is in contradiction with the rule generally applied that multiple exchange operations are of much less importance than simple single or two-electron exchanges. Perhaps somewhat less surprising is the fact that the sign of these repulsive contributions is intimately connected with the state of the L electrons taking part in the exchange transition. The complicated nature of the interactions of the K and L shell electrons certainly makes it difficult to understand how any treatment of the lithium molecule involving neglect of the core electrons could be rigorously justified.

As a second method, James uses a linear variation function the individual terms of which are the determinantal functions of Slater. The Slater functions are built up from hydrogenic $1s$ orbitals for the four K electrons and one-electron molecular orbitals for the two L electrons, the latter functions being of the form, expressed in elliptic coordinates

$$f_{mj} = e^{-\delta\lambda}\lambda^{m}\mu^{j}$$

The best value of the dissociation energy calculated with an eighteen term variation function is D_e = 0.62 v.e. using the binding energy for the lithium atom computed by Wilson with the same type of functions for the atomic problem. Though the variation value of D_e is considerably better than that obtained by the complete Heitler-London technique, there is still a large discrepancy, 0.5 v.e. Presumably this could be reduced considerably by introducing interelectronic distances directly into the variation function but such a procedure is not practicable at the present time. The great difference in accuracy between the variation treatment of Li_2^+ and of Li_2 illustrates once again the fundamental dissimilarity between one and two-electron bonding systems.

The need for a hybridization treatment of Li_2 is more acute than it was for Li_2^+. In the first place no study has been made of the properties which a lithium L shell orbital should possess in order that it lead to satisfactory representation of the electron-pair bond in Li_2^+ by a method involving neglect of the K electrons. The necessary properties of the orbitals for a hybridization treatment are different from those required by a unmodified Heitler-London treatment and restrictions are also introduced by the use of the "interaction operator". The choice of these functions was not discussed by Bartlett and Furry. In the second place, since no accurate and complete treatment of Li_2 including the core electrons is possible at the present time, it is all the more important to discuss fully the characteristics of any less complete treatment which yet leads to reasonably good values of the bond constants, which admits of generalization to more complicated systems and which provides a physical picture of the bond formation. Several such treatments developed from the general point of view of the hybridization method are described in detail in the third section of this thesis. It is believed that the postulates derived from these new treatments should be of considerable value in future work on diatomic molecules more complex than Li_2.

7. Nitrogen, Fluorine and the Alkali Molecules

Most of the important calculations upon homonuclear diatomic molecules in the normal state have now been described. The ones remaining will not be discussed in much detail since they add nothing new to the general picture of bond formation.

Hund(44) in 1932 made the first application of the Fermi-Thomas method to molecular systems. It is much more difficult to apply this statistical method to diatomic molecules than to the most complicated atoms so that Hund was obliged to rely on an approximate treatment. His results for N_2 and F_2 show that to first and second order correction terms the statistically determined charge distribution for the molecule is closely approximated by the sum of spherically symmetrical distributions for each atom, thus lending support to the valence bond orbital as opposed to the molecular orbital picture of binding in diatomic molecules. The Fermi-Thomas field for N_2 has been used by Recknagel(43) to study the characteristics of the electronic levels in nitrogen with regard to designation and relative position. Hund did not estimate the energy of his statistical field and hence could not derive the bond distance especially since his calculation was made for but one internuclear separation.

A general treatment has been given by Rosen and Ikehara(45) of the interaction of two identical atoms each possessing one outer s electron of arbitrary quantum number. They use nodeless atomic wave functions of the form

$$\psi(a) = a^{n-1} e^{-Za/n}$$

in which a is the distance from an electron to the nucleus in units of $a_0 = 0.529$ A, Z is the "effective" nuclear charge for the valence electron and n the total quantum number. Curves are given of Coulomb, exchange and singlet interaction energies for various and n, Z as well as the non-orthogonality function, the equilibrium distance and the fundamental vibration frequency as a function of these same two variables.

The diatomic alkali molecules may be treated by the Rosen method if the core electrons are assumed to play no role in the bond formation and for these R_e, D_e and ν_e the fundamental frequency of vibration has been computed. The dissociation energy and interatomic distance for Li_2 are essentially the same as given by Bartlett. Where experimental values are available as for Li_2, Na_2, and K_2 (40,46) the theoretically determined quantities are only in error by about 10% on the average as may be seen from the following table.

Percentage Error in computed value of	Li_2	Na_2	K_2
D_e	-16	-7	+8
R_e	- 3	+6	+6
ν_e	16	6	-14

Though these errors appear at first to be of a random nature, certain trends may be distinguished. Within an accuracy of a few percent, which is all that is significant, the errors in each of the three quantities vary monotomically with increase in atomic number of the atoms in the molecule. Since the principal source of error in the calculations is the neglect of the K electrons, it is seen that the effect of the K electrons upon the three bond constants must also change in this simple fashion with change in the atomic species. Although the magnitude of the K electron contributions cannot be determined in any one case it is fairly clear that it is the sodium covalent bond which is most accurately described in all respects by the Rosen-Ikehara functions.

A similar treatment of valence bond formation by p electrons was given by Bartlett(47) who computed however only the binding energies and these only for $2p$ electrons. It would certainly seem worthwhile to carry out treatments as general as that of Rosen for *all* the important types of interaction involving combination of s, p and d electrons. With this fundamental material available, a much more thorough study of hybridization could be made and many at present unsolved problems regarding bonds formed in many electron atoms could be treated. As a first step toward this goal all integrals necessary for the treatment of any homonuclear diatomic molecules consisting of first row elements are being calculated by Dr. Weinbaum and the author with the immediate object of studying the bond in the fluorine molecule.

II. A Hybridization Treatment of Li_2 and Be_2^{++}

The Formal Computations

In the first four sections of Part II, the general technique of hybridizing the orbitals for an electron-pair bond will be described. Neither the Hamiltonian nor the atomic wave functions will be given explicitly so that the formulae developed are valid for any two electron molecule which can form only pure s, pure p or hybrid sp bonds. For this reason the calculations may be termed "formal" since they possess no numerical and little algebraic content.

1. The Concept of Hybridization

The greater number of molecular wave functions used in the calculation of equilibrium energy and internuclear separation for diatomic molecules are linear variation functions of the Heitler-London type. When $1s$ orbitals enter into the linear combinations as the ground state orbitals of the atoms of which the molecule is composed, it is found useful to add to the $1s$ orbitals other orbitals corresponding to excited atomic states. In particular, if $2p$ orbitals are combined linearly with the $1s$ orbitals, the "polarization" treatment of Rosen is obtained. The principal reason for introducing the 2p polarization terms into the Heitler-London treatment of H_2 is to try to account for the concentration of charge which exists between the nuclei and which is not adequately represented by a combination of $1s$ functions alone. Although hybridization serves the same purpose for the L shell orbitals it is essentially different in character and purpose from polarization.

It should be possible to increase the flexibility of molecular wave functions consisting of one-electron wave functions for the atomic ground states by adding orbitals corresponding to any excited atomic states. As before these refer to the different atoms in the molecule.

If only those excited atomic states are used which lie near the ground state then the process of linear combination is spoken of as hybridization. This definition is purposely loose since the maximum allowable difference in energy between the ground state and the excited state which permits hybridization of a bonding function varies considerably with the atom in question. For the simpler atoms it is sufficient to restrict the total quantum number for the excited state wave function to be the same as the total quantum number for the ground state. Thus for the first row elements only s and p wave functions may be used in constructing hybrid bond orbitals. (See however Furry(38).) For the first transition group on the other hand the d as well as the and s, p wave functions must be included in the hybridization treatment. By making use of approximations described in Part I, Section 6, Pauling was able through the hybridization method to predict the relative magnitude and orientation of the bonds which any one atom could form. The most recent complete account of this subject is to be found in Chapter III of the "Nature of the Chemical Bond" (55).

In the following discussion, hybridized bond orbitals will be considered primarily to be merely a particular type of linear variation function.

2. The Hybridization of Lithium-like Wave Functions

For the simple sp hybridization which occurs in the L shell Pauling's theory(49) predicts that the bond energy D_e and bond strength S are related by the formula $S = k\,D_e$ The bond strength is defined as

$$S = \frac{1 + \sqrt{3}\,c}{\sqrt{1+c^2}}$$

in which c is the relative amount of p and s character in the bond. These formulae were derived from the postulate that the bond forming power of an atomic orbital is proportional to the magnitude of the normalized angular part of that orbital. The maximum value of S is 2 which occurs when $c = \sqrt{5}$ corresponding to a tetrahedral hybrid bond. We may also consider the quantity to be the variation parameter in the one-electron molecular wave function

$$\sqrt{2}\;\Phi_1 = A_s + B_s + c(A_p + B_p)$$

formed from the hybrid atomic orbital $(A_s + A_p)$.

The energy corresponding to this one electron wave function has been calculated by Bauling and Sherman(33) with the assumption of sp degeneracy. It is found that the relation between S and D is most accurately represented by the formula

$D_e \propto S^2$ rather than by a linear proportionality. The deviations from this quadratic formula being less than 10% of the bond energy over the whole range of values of R . The optimum value of C is also found to differ from $\sqrt{3}$ by less than 20% for a considerable range of internuclear separations. The simple picture of binding energy provided by the use of bond strengths does not apply when the energy separation of the Li $2s$ and $2p$ levels is taken into account and in fact the optimum value of c in this case was found to $.9$ instead of $\sqrt{3}$.

The hybridization of the bond orbitals for the neutral lithium molecule is not the straightforward matter it is in the molecule-ion so that the definition and interpretation of a "bond strength" function will be postponed until the numerical results are described in section 8. For the present we will content ourselves with constructing the most general formalism applicable to the sp hybridization of an electron-pair bond.

A direct analogue to the treatment for Li_2^+ would be to build up a Heitler-London molecular wave function using as atomic orbitals $A_s(1)+cA_p(1)$, $A_s(2)+cA_p(2)$ etc. in place of $A_s(1), A_s(2)$. A_s refers to a~~n~~ $2s$ type atomic orbital for nucleus A, A_p to a $2p$ type orbital for nucleus A. The electrons are numbered 1 or 2. Thus the linear variation function of the non-ionic Heitler-London type would be

$$(A_{s_1} + cA_{p_1})(B_{s_2} + cB_{p_2}) + (B_{s_1} + cB_{p_1})(A_{s_2} + cA_{p_2}) \; ,$$

From Bartlett's calculation, we know that the N^S molecular function corresponds as usual to the attractive state. This may be rewritten as

$$(A_s + cA_p)(B_s + cB_p) + (B_s + cB_p)(A_s + cA_p)$$

using the convention from now on that the functions of electron 1 occur first in each product. We must use the same c in every term since we cannot differentiate between the electrons nor between the nuclei.

If we open the parentheses and collect the coefficients of 1, c, and c^2 we find

$$\Phi_2' = \Psi_1 + 2c\Psi_2 + c^2\Psi_3$$

in which

$$\sqrt{2}\,\Psi_1 = A_sB_s + B_sA_s \quad , \quad \sqrt{2}\,\Psi_3 = A_pB_p + B_pA_p \tag{19'}$$

$$2\sqrt{2}\,\Psi_2 = A_sB_p + B_pA_s + A_pB_s + B_sA_p$$

Formally, the computation involved in minimizing with respect to c the energy corresponding to Φ_2' we see is identical with a "polarization" treatment and hence involves the solution of a cubic equation in c and substitution of the appropriate root into Φ_2', in order to compute the molecular energy. We may generalize this form of Φ, however, in a simple way by removing the functional relationship between the coefficients of Ψ_2 and of Ψ_3. Thus we write the linear variation function

$$\sqrt{2}\,\Phi_2 = \Psi_1 + k_1\Psi_2 + k_2\Psi_3 \quad . \tag{19''}$$

which reduces to the first case for $k_1^2 = 4k_2$. As is well known in the case of a variation function such as Φ_2 we may find the corresponding energy value directly by solving a determinantal equation.

A different attack involves the use of Slater's antisymmetric spin-orbital wave functions(5d). We define the equivalent orbitals, sp degeneracy being assumed, A_σ and $B_{\sigma'}$, where σ and σ' may refer to s or p ( ), and the spin functions γ, γ' are either α or β. From these we may construct a wave function, antisymmetric in the electrons in agreement with Pauli's rule, of the determinantal form

$$\frac{1}{\sqrt{2}} \begin{vmatrix} A_\sigma(1)\ \gamma(1), & B_{\sigma'}(1)\,\gamma'(1) \\ A_\sigma(2)\ \gamma(2), & B_{\sigma'}(2)\ \gamma'(2) \end{vmatrix}$$

A linear combination

$$\Phi = \sum_{\sigma,\sigma',\gamma,\gamma'} \mathcal{D}(\sigma,\sigma';\gamma,\gamma')\, c_{\sigma\sigma'\gamma\gamma'} \tag{20}$$

of such functions, also antisymmetric, we may assume to be the non-ionic wave function for the electrons in the molecule if the $\mathcal{D}$'s are independent. We proceed to find which determinantal functions must be included in a linear variation function and try to discover as many relations as possible between the coefficients $c_{\sigma\sigma'\gamma\gamma'}$ making use of orthogonality and symmetry relations. Ionic terms are not included since they were shown in Part I to be unimportant.

Let us consider the sums over γ and γ' first. We may make four distinct permutations of (γ,γ'). These are (i) $\alpha\alpha$ (ii) $\beta\beta$

(iii) $\alpha\beta$ (iv) $\beta\alpha$. However, we may equally well choose any four mutually orthogonal spin functions and we will find it useful to use the three symmetrical functions $\delta_1 = \alpha\alpha$, $\delta_2 = \beta\beta$, $\delta_3 = \alpha\beta + \beta\alpha$ and the antisymmetrical one $\delta_4 = \alpha\beta - \beta\alpha$. In order to express our variation function in terms of these spin functions, let us expand two of the determinants and take the sum and difference as new functions, $F^{\pm}(\sigma, \sigma'; \gamma, \gamma') =$

$$\frac{1}{\sqrt{2}} \{ \mathcal{D}(\sigma, \sigma'; \gamma, \gamma') \pm \mathcal{D}(\sigma, \sigma'; \gamma', \gamma) = \frac{1}{\sqrt{2}} (A_\sigma B_{\sigma'} \mp B_{\sigma'} A_\sigma)(\gamma\gamma' \pm \gamma'\gamma)$$

The $F^{\pm}$ functions are independent and contain explicitly the spin functions that we have chosen as may be seen by giving the ± sign and γ, γ' their various possible values. We notice also that for each choice of (σ, σ') there are but two possible orbital functions entering into $F^{\pm}$, namely

$$f^{\pm}(\sigma, \sigma') = A_\sigma B_{\sigma'} \pm B_{\sigma'} A_\sigma$$

Combining these pieces of information we find it possible to express Φ as follows :

$$(21) \qquad \Phi = (\delta_1 c_1 + \delta_2 c_2 + \delta_3 c_3)\Big(\sum_{\sigma\sigma'} c^-_{\sigma\sigma'} f^-(\sigma, \sigma')\Big) + \delta_4 c_4 \sum_{\sigma\sigma'} c^+_{\sigma\sigma'} f^+(\sigma, \sigma')$$

The δ_i are mutually orthogonal so that the general variation function, eq. 20 may be decomposed into four independent functions which represent four non-combining states. The triplet state, with symmetric spin functions is seen to correspond to the orbital wave functions $f^-(\sigma, \sigma')$ which are anti-symmetric in the electrons while the singlet state, with antisymmetric spin function corresponds to the symmetric orbital wave functions $f^{+}(\sigma\sigma')$ This situation is one which exists generally since Φ as a whole must be antisymmetric in the electron coordinates and, in addition, symmetric and antisymmetric functions are always orthogonal to one another. We will not include the spin in our functions from now on since the spin does not affect the energy in our treatment. Also, since we are primarily interested in the ground state of the molecule we will consider only $\sum f^{+}(\sigma,\sigma')c(\sigma,\sigma')$ the antisymmetric spin function having been shown to give the attractive state in a closely similar system, the hydrogen molecule. The computations for the $\sum f^{-}(\sigma,\sigma')c(\sigma,\sigma')$ function may be obtained formally from the calculations for $\sum f^{+}c$ by changing signs systematically.

We may now begin to write down the $f^{+}(\sigma,\sigma')$ explicitly. The four choices of (σ,σ') are ss, pp, sp and ps . We can transform $f^{+}(s,p)$ into $f^{+}(p,s)$ by interchanging the nuclei and since the energy computed is unaffected by such an exchange (the Hamiltonian is symmetric in A and B coordinates) $f^{+}(s,p)$ and $f^{+}(p,s)$ must enter with coefficients of the same absolute value. Since, moreover, the remainder of the variation function is symmetric in the nuclei, the coefficients of $f^{+}(s,p)$ and $f^{+}(p,s)$ must have the *same sign* in order for two functions *together* to "combine" with $f^{+}(s,s)$ and $f^{+}(p,p)$. This may be seen in more detail by treating the four functions separately, and factoring the secular equation etc. We may now lump the sp functions together into $2f^{+}(\overline{s,p}) = f^{+}(s,p) + f^{+}(p,s)$.

Corresponding to $(\alpha\beta-\beta\alpha)$ we then have three possible orbital wave functions

$$\sqrt{2}\ \Psi_1 = A_s B_s + B_s A_s \quad , \quad \sqrt{2}\ \Psi_3 = A_p B_p + B_p A_p$$

$$2\sqrt{2}\ \Psi_2 = A_s B_p + B_p A_s + A_p B_s + B_s A_p$$

and $$\Phi_2 = \Psi_1 + k_1 \Psi_2 + k_2 \Psi_3$$

The functions have also been worked out for the nuclear anti-symmetric state and for all ionic states but as no corresponding numerical results have been obtained, they are omitted. The orbitals for the attractive N^s state are seen to be identical with those obtained by the first method. However our choice of variation function has now been justified by a more general theory so that the two parameters k_1 and k_2 can be thought of as <u>entirely</u> independent. This will prove to be of considerable value for our later development.

3. The Secular Equation

Having chosen a linear variation function of the form $\Phi = \sum_i c_i \Psi_i$ we may calculate the corresponding energy W in terms of the matrix elements

$$W = \frac{\sum c_i c_j H_{ij}}{\sum c_i c_j d_{ij}}$$

where $$d_{ij}' H_{ij} = \frac{\int \Psi_i \underline{H} \Psi_j \, d\tau}{\int \Psi_i \Psi_j \, d\tau}$$

and $$d_{ij} = \int \Psi_i \Psi_j \, d\tau$$

It is well known that W may be minimized with respect to each of the C_i and that the coefficients C_i may be calculated after the secular equation

$$\left| \overline{H}_{ij} - d_{ij} W \right| = 0$$

has been solved for W. We have here placed $2\overline{H}_{ij} = H_{ij} + H_{ji}$. The secular equation is symmetrical as it must be if its roots are to possess physical interpretation in a quantum mechanical problem of this type.

We may make a few remarks upon the significance of the *three* real roots of the secular equation. If we make a linear transformation to orthogonal, normal functions $\chi_i = \eta_{ij} \Psi_j$ for which

$$\int \chi_\lambda \underset{\sim}{H} \chi_s \, d\tau = \mathcal{H}_{\lambda s} \quad , \quad \int \chi_\lambda \chi_s \, d\tau = \delta_{\lambda s}$$

then the secular equation becomes $\left| \mathcal{H}_{\lambda s} - \delta_{\lambda s} W \right| = 0$

although the roots remain the same since a linear transformation corresponds merely to adding rows and columns. From the characteristic matrix of this determinant we may construct the quadratic form,

$$\mathcal{K} = \sum_{\lambda, s} c_\lambda c_s \mathcal{H}_{\lambda s}$$

which has the following properties. The minimum of $\mathcal{K}$ subject to the condition $\sum c_\lambda^{(1)} c_s^{(1)} = 1$

is the lowest root (eigenvalue) of the secular equation, and refers to the eigenfunction $\sum c_n^{(1)} \chi_n = \psi_{(1)}$

The next lowest root (eigenvalue) is the minimum value of K subject to the additional condition on the c_n's that

$$\sum c_n^{(2)} c_n^{(1)} = 0$$

and refers to the eigenfunction

$$\sum c_n^{(2)} \chi_n = \psi_{(2)}$$

The normalized eigenfunction $\psi_{(3)}$ corresponding to the third root is orthogonal to both $\psi_{(2)}$ and $\psi_{(1)}$. Although the transformation to a set of orthonormal functions is not unique we see that the three roots of the original secular equation

$$| H_{ij} - d_{ij} W | = 0$$

can correspond to but one of a number of sets of three orthogonal states.

The roots of the secular equation will of course be dependent upon an interatomic distance parameter ρ since this quantity enters into the Hamiltonian $\underset{\sim}{H}$, as well as implicitly in the wave function. Our procedure will be, then, to find the H_{ij} and d_{ij} for each value of ρ and solve the resulting secular equation, for the energy $W(\rho)$. Then the minimum value $W(\rho)_{\text{min}}$ of W as a function of ρ will give the energy and internuclear separation for the most equilibrium configuration of the molecule. In the next section we begin the process of evaluating the quantities H_{ij} and d_{ij}.

4. The First Reduction of the Energy and Non-Orthogonality Matrix Elements.

The Ψ_i have been seen to be symmetric with respect to interchange either of the two nuclei A, B or of the two electrons 1, 2. This symmetry may be expressed by writing

$$\Psi = \frac{1}{\sqrt{2}} (a+E)(\epsilon+E)\Upsilon_i \tag{22}$$

where Υ_i is a product of two atomic orbitals one for each nucleus and a, ϵ, E are exchange operators with the following properties.

$a \cdot A_\sigma(1) B_{\sigma'}(2) = B_\sigma(1) A_{\sigma'}(2)$	exchange of nuclei
$\epsilon \cdot A_\sigma(1) B_{\sigma'}(2) = A_\sigma(2) B_{\sigma'}(1)$	exchange of electrons
$E \cdot A_\sigma(1) B_{\sigma'}(2) = A_\sigma(1) B_{\sigma'}(2)$	identity operator
$a \cdot \underset{\sim}{H} = \epsilon \cdot \underset{\sim}{H} = \underset{\sim}{H}$	the Hamiltonian is symmetric in nuclei and electrons
$a^2 = \epsilon^2 = E$	

The three operators are assumed to be associative, commutative and distributive.

With these rules which are of quite general application, the expression given in eq. 22 for Ψ_i is equivalent to our former definition, eq. 19′ Applying to the evaluation of the integral we find

$$H_{ij} = \frac{1}{8}\int\{(a+E)(\epsilon+E)\Upsilon_i\}\underset{\sim}{H}\{(a+E)(\epsilon+E)\Upsilon_j\}\,d\tau =$$

$$\frac{1}{2}\int\Upsilon_i\,\underset{\sim}{H}\,\{(a+E)(\epsilon+E)\Upsilon_j\}\,d\tau$$

because

$$\int\Upsilon_i\underset{\sim}{H}\Upsilon_j\,d\tau = \int\{a\Upsilon_i\}\underset{\sim}{H}\{a\Upsilon_j\}\,d\tau = \int\{\epsilon\Upsilon_i\}\underset{\sim}{H}\{\epsilon\Upsilon_j\}\,d\tau$$

$$= \int\{a\epsilon\Upsilon_i\}\underset{\sim}{H}\{a\epsilon\Upsilon_j\}\,d\tau$$

If $\Upsilon_j = A_sA_s,\ B_sB_s,\ A_pA_p$ or B_pB_p then $\epsilon\Upsilon_j = \Upsilon_j$ while if $\Upsilon_j = A_sB_s,\ B_sA_s,\ A_pB_p$ or B_pA_p then $a\epsilon\Upsilon_j = \Upsilon_j$ In either case H_{ij} may be reduced still further to

$$\int\Upsilon_i\underset{\sim}{H}\{(E+a)\Upsilon_j\}\,d\tau$$

Finally the <u>general</u> expression for $\bar{H}_{ij} = \frac{1}{2}(H_{ij}+H_{ji})$ which is what occurs in the secular equation is

$$\bar{H}_{ij} = \frac{1}{4}\int\left\{\Upsilon_i\,\underset{\sim}{H}[(\epsilon+E)(a+E)\Upsilon_j] + \Upsilon_j\,\underset{\sim}{H}[(\epsilon+E)(a+E)\Upsilon_i]\right\}d\tau$$

Taking $\Upsilon_1 = A_sB_s,\ \Upsilon_2 = A_sB_p,\ \Upsilon_3 = A_pB_p$ we find

$$\bar{H}_{11} = \overline{(A_sB_s|\underset{\sim}{H}|A_sB_s)} + \overline{(A_sB_s|\underset{\sim}{H}|B_sA_s)}$$
$$\bar{H}_{12} = \overline{(A_sB_s|\underset{\sim}{H}|A_sB_p)} + \overline{(A_sB_s|\underset{\sim}{H}|B_sA_p)}$$
$$\bar{H}_{13} = \overline{(A_sB_s|\underset{\sim}{H}|A_pB_p)} + \overline{(A_sB_s|\underset{\sim}{H}|B_pA_p)}$$
$$\bar{H}_{22} = \frac{1}{2}\left\{\overline{(A_sB_p|\underset{\sim}{H}|A_sB_p)} + \overline{(A_sB_p|\underset{\sim}{H}|B_sA_p)} + \overline{(A_sB_p|\underset{\sim}{H}|B_pA_s)} + \overline{(A_sB_p|\underset{\sim}{H}|A_pB_s)}\right\}$$
$$\bar{H}_{23} = \overline{(A_sB_p|\underset{\sim}{H}|A_pB_p)} + \overline{(A_sB_p|\underset{\sim}{H}|B_pA_p)}\quad,\quad \bar{H}_{33} = \overline{(A_pB_p|\underset{\sim}{H}|A_pB_p)} + \overline{(A_pB_p|\underset{\sim}{H}|B_pA_p)}$$

The customary symbol $(A_sB_s|\underset{\sim}{H}|A_sB_p)$ has been used for the function

$$\int A_sB_s\,\underset{\sim}{H}\,A_sB_p\,d\tau$$

with similar symbols for the other integrals.

The two functions $(A_s B_s | \underset{\sim}{H} | A_s B_p)$ and $(A_s B_p | \underset{\sim}{H} | A_s B_s)$ must be distinguished from one another since $B_p \underset{\sim}{H} A_s \neq A_s \underset{\sim}{H} B_p$ The "barred" function, equal to the arithmetic average, is introduced to unify the nomenclature. The bar is of course superfluous where γ_i and γ_j contain the same number of S functions, that is, for H_{11}, H_{22}, H_{33}

The d_{ij} may be easily obtained, formally, by putting $H = 1$.

Algebraic and Numerical Computation

We have now developed the formal apparatus for treating a hybrid sp electron-pair bond in a perfectly general manner. In order to give numerical content to our equations we must now introduce explicitly our atomic wave functions and Hamiltonian operators.

5. The Choice of Atomic Wave Functions

It is of considerable importance, in practice, to choose atomic wave functions properly. The very rapid increase in the algebraic complications attending the evaluation of the integrals with an apparently very simple change in the atomic orbital function, directed towards increasing their accuracy, forces the computer to choose relatively simple functions. On the other hand, too great simplification prevents obtaining results which are quantitative enough to make the computation worth while in view of the many qualitative discussions of bond formation which have appeared. In addition, atomic wave functions of the analytical character suitable for this type of calculation have not been developed in a coherent fashion for all the first row elements and for each of the two L orbitals. This latter limitation makes it necessary to use atomic wave functions at least as simple as hydrogen-like ones. Here, we shall use so-called "nodeless" wave functions of Slater(65).

The $2S$ functions are of the form

$$A_s = e^{-\alpha a}(\alpha a)\frac{\alpha^{3/2}}{\sqrt{3\pi}} \quad , \ a = \text{radius vector from nucleus A,}$$

which is seen to be a normalized function proportional to the radial part of a hydrogenic $2p$ wave function. The $2p$ nodeless wave function is of the form

$$A_p = e^{-\alpha a}(\alpha a)\cos\theta_A \frac{\alpha^{3/2}}{\sqrt{\pi}} \quad , \ \theta_A \text{ measured from the axis of the molecule, cf. Figure 1a.}$$

thus being normalized and depending in the same way as the $2S$ function upon the parameter α. There is actually no difference between this function and a hydrogenic $2p$ wave function with $Z' = 2\alpha$. The introduction of the "nodeless" functions having the <u>same</u> radial part for both $2p$ and $2S$ orbitals simplifies the evaluation of the integrals considerably and makes it possible to study the dependence of bond formation upon the angular part of the atomic orbitals in a less ambiguous fashion. As will be seen, however, these functions represent the atomic orbitals quite well, if a proper choice of α is made, in <u>the range of</u>

r greater than the most probable value as given by the distribution function. Since it is in this region that the orbitals for the two different atoms "overlap", a fit here is most important.

We may compare these nodeless wave functions with those computed by the variation method or the method of the self-consistent field. For the Li atom two calculations are available—that of Wilson (63) in which the system is treated as a variation problem, and that of Fock and Petrashen (64) who use the Hartree's method including exchange terms. The 2s wave functions as derived in the two different ways agree without appreciable error. Fock and Petrashen also give the radial part of the $2p$ wave functions. Since the wave functions for the atoms, in our treatment often involve linear combinations of $2s$ and $2p$ wave functions and since, further, the radial parts of the wave functions for these two orbitals are taken to be the same, some average of Fock and Petrashen's $2s$ and $2p$ functions should be used for comparison with the nodeless functions. In a physical sense, the "overlapping" of the atomic orbitals is most real if the electron distribution functions overlap. For this reason the arithmetical mean of Fock's $2s$ and $2p$ distribution functions is plotted as well as the $2s$ and $2p$ functions themselves. The arithmetic mean is suggested by the fact that in Li_2^+, Pauling and Sherman found the bond to have 50% character. This average distribution function is fitted most closely by a nodeless function with $\alpha = .588$. So good is the agreement that we may consider that for Li the only sources of error in these L shell atomic wave functions lies in the assumption of identical radial parts for the $2s$ and $2p$ wave functions, and equal importance of the $2s$ and $2p$ functions in comparing with Fock-Petrashen values. It will be found in section 9 that using $\alpha = .588$ it is not necessary to hybridize the angular part of the none function. Consequently we also make calculations with $\alpha = .5$ corresponding to the $2s$ orbital in order to be able to use a hybridization treatment which may be compared with that of Pauling and Sherman for Li_2*.

For convenience in determining α, a table of values of the function

$$\frac{4}{3}\alpha^5 r^4 e^{-2\alpha r}$$

was made up for $\alpha = 1.5$ and thirty-five values between zero and ten of r. By merely changing the ordinate and abscissa scales it is then possible to find the values of this distribution function for any value of other than 1.5. This table may be applied to any nodeless radial wave function for the L shell.

The choice of α for use in the BeII orbitals is made quite simple by a procedure which probably does not introduce as much uncertainty as the method of treatment itself. We assume that the K electrons screen the nucleus to the same extent in both beryllium and lithium so that the effective nuclear charge Z' for the beryllium L shell is greater by one than for the lithium L shell. Since Z' for lithium is 1.176

we take Z' for beryllium to be 2.176. It will be shown in the next section that with the proper definition of energy and length units, the quantity α for an L electron in any system is given by

$$\alpha = \frac{Z'}{2Z}$$

, where Z is the nuclear charge less two.

Thus for BeII α =0.544. This value will be used in the non-hybridization treatment while as in Li_2 α =o.5 will be used in the hybridization treatment. It is interesting to note that our value of α chosen essentially to fit an average sp wave function for BeII agrees quite closely with the value chosen by Slater $\alpha = 0.545$ for BeII using an energy criterion. This is not the case for LiI where Slater's value is 0.63.

6. Modifications of the Hamiltonian Operator

We treat Li_2 and Be_2^{++} as two-electron systems containing two attracting centers each with charge +Ze. If we choose a coordinate system as shown in Figure 1a, the Hamiltonian operator H is

$$\underset{\sim}{H} = \left\{ -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{Z^2e^2}{R} + \frac{e^2}{r} - \frac{Ze^2}{a_1} - \frac{Ze^2}{a_2} - \frac{Ze^2}{b_1} - \frac{Ze^2}{b_2} \right\}$$

We define a set of "atomic units," which we designate by $a.u.$, .

Unit of length, a_0 (radius of first Bohr orbit) $\frac{\hbar}{me^2}$ = 0.5285A

Unit of energy, $\frac{e^2}{a_0}$ = 2x energy of a hydrogen atom in ground state = 27.06 v.e.

It might be mentioned for the sake of completeness that if the electronic rest mass is taken as the mass unit then the unit of time is the part of the period of an electron in the first Bohr orbit of hydrogen. An extensive list of various physical quantities expressed in these atomic units is to be found in Condon and Shortley.(67) We should point out that for the purpose of reducing the Schiodinger equation to atomic units it is necessary to define only the energy and length units. In $a.u._Z$ the Hamiltonian becomes

$$\bar{\underset{\sim}{H}} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{Z^2}{R} + \frac{1}{r} - \frac{2}{a_1} - \frac{2}{a_2} - \frac{2}{b_1} - \frac{2}{b_2}$$

We introduce now a change of scale such that the units of length and energy become $a_0' = a_0/Z$ and $\frac{Z^2e^2}{a_0} = \frac{e'^2}{a_0'}$ with $e' = \sqrt{Z}e$

The Hamiltonian is then reduced to the form

$$\underset{\sim}{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{Z}{R} + \frac{1}{rZ} - \frac{1}{a_1} - \frac{1}{b_1} - \frac{1}{a_2} - \frac{1}{b_2}$$

For convenience in computation we will divide the Hamiltonian into parts which are functions respectively of only electron 1, only electron 2, or of both electrons.

$$\underset{\sim}{H_1} = -\frac{1}{a_1} - \frac{1}{b_1} - \frac{1}{2}\nabla_1^2 \, , \quad \tilde{\underset{\sim}{H}} = -\frac{1}{a_2} - \frac{1}{b_2} - \frac{1}{2}\nabla_2^2$$

and write

$$\underset{\sim}{H} = H_1 + H_2 + \frac{Z}{R} + \frac{1}{Zr}$$

Using H_1 alone with $\rho = b_1 = \infty$ it is possible to compute the energy of an L shell electron in a Li atom as it is described by our A_s or A_p functions for comparison with the experimental values.

The 2s and 2p energies are given by

$$W_s = \int A_s\left(-\tfrac{1}{2}\nabla^2 - \tfrac{1}{a}\right)A_s\,d\tau \quad \text{and} \quad W_p = \int A_p\left(-\tfrac{1}{2}\nabla^2 - \tfrac{1}{a}\right)A_p\,d\tau$$

respectively. We may find $-\frac{1}{2}\nabla^2 A_p$ directly since A_p is a hydrogenic wave function and is therefore a solution of the wave equation

$$\left(-\frac{1}{2}\nabla^2 - \frac{2\alpha}{a}\right)A_p = W_p A_p$$

The effective nuclear charge here is 2α so that, since the total quantum number n = 2,

$$W_p = -\frac{(Z')^2}{2n^2} = -\frac{\alpha^2}{2} \quad \text{and} \quad -\frac{1}{2}\nabla^2 A_p = \left(\frac{2\alpha}{a} - \frac{\alpha^2}{2}\right)A_p$$

The function A_s is not hydrogenic so that $\left(-\frac{1}{2}\nabla^2 A_s\right)$ must be computed directly. We find

$$-\frac{1}{2}\nabla^2 A_s = \left(\frac{2\alpha}{a} - \frac{\alpha^2}{2} - \frac{1}{a^2}\right)A_s$$

The extra last term is cancelled by the $\frac{1}{a^2\sin\theta_A}\frac{\partial}{\partial\theta_A}\left(\sin\theta_A\frac{\partial}{\partial\theta_A}\right)$ term of the

Laplacian in the case of the A_p function. We see upon substitution into the expressions for W_s and W_p that the 2s- 2p separation is

$$-W_s + W_p = \frac{1}{3}\alpha^2 = \int \frac{A_s^2}{a^2}\, d\tau > 0$$

In order to achieve 2s 2p degeneracy necessary for a simple hybridization treatment we will modify the operator $\left(-\frac{1}{2}\nabla^2\right)$ when it is followed by the function A_s by adding to it the term $\frac{1}{a^2}$. This includes all cases since we always compute ∇^2 in the same coordinates as the orbital upon which it operates is expressed. Then for either A_s or A_p we will have

$$-\frac{1}{2}\nabla^2 A_{s \text{ or } p} = \left(\frac{2\alpha}{a} - \frac{\alpha^2}{2}\right) A_{s \text{ or } p}$$

This expression will be used in evaluating all of the integrals of the type $(A_s B_s | \underset{\sim}{H} | A_s B_p)$, $(A_s B_s | H | A_s B_s)$ etc.

If we are interested in arranging for the <u>correct</u> sp separation $\varepsilon_{sp} = 1.839\text{ v.e.} = .06795\text{ a.u.}$, for Li I rather then in making the levels degenerate, we modify the Hamiltonian $\underset{\sim}{H_1}$ by adding to it the constant $\varepsilon_{sp} = \underset{\sim}{H_1}$ whenever $\underset{\sim}{H_1}$ is followed by the function A_s. Thus for example,

$$(A_s A_s | \underset{\sim}{H_1'} | B_s B_p) = (A_s | B_s)(A_s | B_p)\, \varepsilon_{sp}$$

, while $(A_s A_s | \underset{\sim}{H_1'} | B_p B_s) = 0$

This alteration gives for the added one-electron energy corresponding to the bond orbital $(A_s + B_s)\frac{1}{\sqrt{2}}$,

$$W_1' = \frac{(A_s | \underset{\sim}{H_1'} | B_s) + (A_s | \underset{\sim}{H_1'} | A_s)}{(A_s | A_s) + (B_s | A_s)} = \varepsilon_{sp}$$

and upon letting $R \longrightarrow \infty$, we find that W_s has also been changed by the proper amount, ε_{sp}.

The atomic L shell energies calculated for two values of α and for the various choices of operators are tabulated in Table $\overline{III}$ together with the experimental $2S$ and $2p$ energies for LiI and BeII.

7. The Second Reduction of the Matrix Elements

We have expressed H_{ij} in terms of functions of the type $\overline{(A_s A_p | H | B_s B_p)}$ which we may now reduce to the numbered integrals $I_1 \cdots I_{54}$ and S_1, S_2, S_3 given in Tables $\overline{V}, \overline{VI}$. We proceed to evaluate the general integral

$$\int \overline{A_1 B_2 \underset{\sim}{H} C_1 D_2}\, d\tau = \overline{(A B | H | C D)}$$

in which A, B, C or D may represent A_s, A_p, B_s or B_p. Writing $\frac{1}{R} = \frac{\alpha}{\rho}$ and using the modified Laplacian $(-\frac{1}{2}\nabla_s^2)$ but not the modified Hamiltonian $(\underset{\sim}{H_1} + \underset{\sim}{H_1'})$, we find

$$(AB | \underset{\sim}{H} | CD) = \frac{\alpha}{\rho}(A_1|C_1)(B_2|D_2) + \int \frac{ACBD}{r}\, d\tau_1\, d\tau_2$$
$$+ \frac{1}{2}\left\{ (A_1|C_1) \int B_2 D_2 \left(-\frac{\alpha^2}{2} + \frac{2\alpha - 1}{d} - \frac{1}{d'}\right) d\tau + (B_2|D_2) \int A_1 C_1 \left(-\frac{\alpha^2}{2} + \frac{2\alpha - 1}{c_1} - \frac{1}{c_1'}\right) d\tau_1\right.$$

$$+(C_1|A_1)\int D_2 B_2\left(-\frac{\alpha^2}{2}+\frac{2\alpha-1}{b_2}-\frac{1}{b_2'}\right)d\tau_2+(D_2|B_2)\int(C_1|A_1)\left(-\frac{\alpha^2}{2}+\frac{2\alpha-1}{a_1}-\frac{1}{a_1'}\right)d\tau_1\Bigg\}$$

$$=\quad(AC|BD)\left\{\frac{\alpha}{\rho}-\alpha^2\right\}+\int\frac{A_1C_1B_2D_2}{r}\,d\tau_1 d\tau_2$$

$$+\ (A|C)\int\frac{1}{2}\left\{(2\alpha-1)\left(\frac{1}{b_1}+\frac{1}{d_1}\right)-\frac{1}{b_1'}-\frac{1}{d_1'}\right\}B_1D_1\,d\tau_1$$

$$+\ (B|D)\int\frac{1}{2}\left\{(2\alpha-1)\left(\frac{1}{a_1}+\frac{1}{c_1}\right)-\frac{1}{a_1'}-\frac{1}{c_1'}\right\}A_1C_1\,d\tau_1$$

The symbols $a_1 \ldots\ldots b_2$ correspond to the arguments of the functions A_2, B_1, B_2 and not <u>necessarily</u> to the two nuclei. The <u>primed</u> and <u>unprimed</u> letters $a, a'; b, b'$ etc. always correspond to two <u>different</u> nuclei. We have two cases to consider; when $b \equiv d$ and when $b \equiv d'$. Since we are only interested in non-ionic terms, $b \equiv d$ implies that $a \equiv c$ while $b \equiv d'$ implies that $a \equiv c'$. The two types of integrals are usually called "Coulomb" and "exchange" integrals. They become

$$\int A_1 B_2 \underset{\sim}{H} C_1 D_2\,d\tau = (A|C)(B|D)\left(\frac{\alpha}{\rho}-\alpha^2\right)+\int\frac{A_1C_1B_2D_2}{r}\,d\tau_1 d\tau_2$$

$$+\left\{\begin{array}{l} (A|C)\int\left(\frac{2\alpha-1}{b_1}-\frac{1}{b_1'}\right)B_1D_1\,d\tau_1+(B|D)\int\left(\frac{2\alpha-1}{c_1}-\frac{1}{c_1'}\right)A_1C_1\,d\tau_1 \\ \underline{\text{Coulomb}} \\ (A|C)\int(k-1)\left(\frac{1}{b_1}+\frac{1}{d_1}\right)BD\,d\tau+(B|D)\int(\alpha-1)\left(\frac{1}{a_1}+\frac{1}{c_1}\right)d\tau_1 \\ \underline{\text{Exchange}} \end{array}\right.$$

Our procedure in evaluating the functions $(A, B_2|H|.017)$ is then as follows. We first determine the form of the $1/r_{12}$ integral by rearranging $A - - - D$ into the order given in Table VI . i.e. $A_1 C_1 B_2 D_2$. A knowledge of this ordered product of four atomic orbitals is then sufficient to determine the coefficients of the remaining integrals and the form of the integrals themselves in equation. We give as an example the calculation of

$$(A_s B_s|H|A_s B_s) \longrightarrow \int A_{s_1}^2\left(\frac{1}{r}\right)B_s^2(2)\,d\tau_1\,d\tau_2$$

which is of Coulomb type $\longrightarrow (A_s|A_s)(B_s|B_s)\cdot\left(\frac{\alpha}{\rho}-\alpha^2\right)$

$$+\int\frac{A_s^2(2)\,B_s(1)^2}{r_{12}}\,d\tau_1\,d\tau_2+(A_s|A_s)\int\left(\frac{2\alpha-1}{b_1}-\frac{1}{a_1}\right)B_s\,d\tau+(B_s|B_s)\int\left(\frac{2\alpha-1}{a_1}-\frac{1}{b_1}\right)A_s^2\,d\tau$$

$$=\alpha\left\{\left(\frac{1}{\rho}-\alpha\right)+F_{14}+2(2\alpha-1)F_1-2F_2\right\}$$

Since α is always a factor of the I_i and of $\frac{\alpha}{\rho}-\alpha^2$ we can use $F_i=\frac{1}{\alpha}I_i$ in preparing ~~the following~~ a table ~~of~~ $\overline{H}_{ji}$ using Table X to give $\overline{H}_{ij}$ in terms of the $(A_1 B_2|H|C_1 D_2)$ functions. Without sp separation correction the d_{ij} may be computed formally by placing $\underset{\sim}{H} = 1$ in the expressions for H_{ij} on page 58.

The foregoing calculations show us what the sp separation corrections must be for the H_{ij}, namely $\mathcal{E}_{sp} d_{ij} N_{ij}$. The quantity gives one-fourth the number of times an function occurs in We may tabulate these correction coefficients:

	11	12	13	22	23	33
separation correction coefficient	2	3/2	1	1	1/2	0

The numberical evaluation of the H_{ij}, d_{ij} and individual integrals and methods of solving the secular equation are given in Part IV.

Bond Energies and Interatomic Distances

8. Results of the Different Treatments

In carrying out the arithmetical work which is necessary to translate our formulae for the $\overline{H_{ij}}$ into their numerical values, it is convenient to separate that portion of an $\overline{H_{ij}}$ which is dependent upon α alone from the remainder dependent on α and Z. To do this we rewrite $\overline{H_{ij}}$ in the form

$$H_{ij} = \alpha \left\{ \mathcal{H}_{ij} + \frac{1}{Z} \mathcal{R}_{ij} + d_{ij} \left(-\alpha + \frac{Z}{\zeta} \right) \right\} = \alpha \left\{ \Lambda_{ij} - d_{ij} \left(\alpha + \frac{Z}{\zeta} \right) \right\}$$

For given choice of ζ and $\mathcal{E}$ (= 0 or an ε_{sp}) $\mathcal{H}_{ij}$ is a linear function of α, as we see from Table **X**, so that the computation of the $\mathcal{H}_{ij}$ and Λ_{ij} is a simple matter once the values of $\mathcal{H}_{ij}$ for two choices of α have been determined. In the above expression $\mathcal{R}_{ij}$ is the two-electron integral (average)

$$\frac{1}{\alpha} \int \overline{\Psi_i \left(\frac{1}{r_{12}} \right) \Psi_j \, d\tau}$$

which is a function of ζ alone. Consequently we may, alternatively, compute $\left(\mathcal{H}_{ij} + \frac{1}{Z} \mathcal{R}_{ij} \right) = \Lambda_{ij}$ directly for two values of α, and given Z, ϵ from these obtain the values of Λ_{ij} for other α.

A second useful device involves the introduction of the quantity λ, $\lambda = \frac{W}{\alpha} + \alpha - \frac{Z}{\zeta}$ The secular equation then becomes

$$\left| \Lambda_{ij} - d_{ij} \lambda \right| = 0$$

instead of

$$|\overline{H}_{ij} - d_{ij}W| = 0$$

Though formally there is no difference between these two expressions, the use of the former effects a great saving of computational labor by making it unnecessary to calculate $d_{ij}\left(-\alpha + \frac{Z}{\rho}\right)$ for each α, ρ, Z, d_{ij}. Indeed, once λ has been found the dissociation energy D is calculated at once from the formula

$$D = \left(\lambda - 2\alpha + 1 + \frac{Z}{\rho}\right)\alpha + \mathcal{E}$$

The first calculation made for the lithium molecule was for the complete hybridization treatment described above. With $\mathcal{E} = 0$, $\alpha = .588$, corresponding to sp degeneracy and the correct geometrical distribution for the atomic orbitals, the values of D computed are of the order of 4.5 v.e. as compared to the experimental $D_e = 1.14$ v.e. The equilibrium internuclear separation is found to be about 2 Å, although the experimental value is 2.67 Å. Since similar though smaller discrepancies exist in Pauling and Sherman's calculations on Li_2^+ when there is assumed to be zero sp separation, the degeneracy was removed, in the manner described previously, for the Li_2 hybridization treatment as well. The calculated bond constants change to $D_e \sim 3$ v.e. and $R_e \sim 2.2$ Å, in the right direction but not enough. A parallel computation with $\mathcal{E} = 0$, $\alpha = .500$ likewise lead to energy and separation values considerably different from the experimental ones.

In an effort to discover the source of these discrepancies k_1 and k_2 are given the constant value unity. The total energy and the dissociation energy corresponding to such a choice of parameter values are always smaller in absolute value than the energies computed by a complete variation (our hybridization) treatment and consequently constitute lower boundsto these quantities for the whole class of linear variation functions. Distortion of the energy curves is likely to occur in this treatment since the values of k_1 and k_2 obtained by variation change considerably with interatomic distance. When the calculations for $k_1 = k_2 = 1$ are carried out, the distortion of the curves is the only significant change over the variation results, this being the case for $\mathcal{E} = \varepsilon_{sp}$ or 0 and $\alpha = .500$ or .588. However, this simple treatment makes it possible to study the effect of the individual terms, $\overline{H}_{ij}$ and d_{ij}. Since by this method

$$W = \frac{\sum \overline{H}_{ij}}{\sum d_{ij}}$$

the size of the quantities $\gamma_{ij} = \left(\frac{\overline{H}_{ij}}{d_{ij}} \right)$ governs to a large extent the value of the enrgy W and consequently also of D. The value of γ_{ij} is abnormally large for (ij) = (12) and (13) which results in their making considerable contributions to the energies. In order to obtain more accurate results, it seems reasonable to adopt a policy of omitting those terms Hij in the energy matrix which correspond to the greatest excitation of the lithium atoms, thus removing the p^2p^2, p^2sp etc. terms first.

In accord with this policy we shall place $k_2 = 0$, thus maintaining the linear variational form for our molecular wave function. The computed energies D for $\mathcal{E} = \mathcal{E}_{sp}$, $\alpha = .5$ are listed in Table IV in both atomic units and electron-volts. From Figure 2 we estimate the equilibrium internuclear distance to be 2.54 Å with a D_e of 1.14 v.e. The agreement with experiment is thus quite close. It is unnecessary to make a similar computation for α = .588 or $\mathcal{E} = 0$ or both since we know that only greater disagreement with experiment can result.

In order to round out these calculations on Li_2, the dissociation energies are also computed for H_{11} and H_{33} alone with α = .5 or .588, the values being recorded in a part of Table IV. The p^2p^2 (H_{33}) bound energy is seen to be too large for either value of α giving additional weight to our plan of omitting the H_{33} term in the variation ($k_2 = 0$) treatment. It is to be noticed also that with α = .588 excellent agreement for both D_e and R_e is obtained in the s^2s^2 (H_{11}) calculation (see Figure 2). This is to be contrasted with the similar ss treatment of Li_2^+ in which case no reasonable value of α led to a large enough dissociation energy.

The corresponding calculations for Be_2^{++} are not as complete as for Li_2. This is due primarily to the fact that the numerical evaluation of the integrals has been completed only for $\rho \leqslant 5$. However the s^2s^2 and p^2p^2 calculations have been made with the two values of α as well as the variation treatment with $\epsilon = \epsilon_{sp}$, $\alpha = .5$. Since no experimental or theoretical data is available, the results recorded in Table IV must be regarded as tentative only. There is definite indication of an energy minimum near $R \approx 2$ Å with a value of $D \simeq 2$ v.e.

We have included in Table IV the values of the parameter k_1 corresponding to the various values of ρ for both Li_2 and Be_2^{++}. Since a hybridization treatment based on Pauling's simple theory would give $k_1 = 2\sqrt{3} = 3.46$ (compare Part I section 6) we see that there is no simple correlation between the "best" value of k_1 in the bariational sense for the electron-pair bond and the hybridization value obtained from the consideration of one-electron systems. The fundamental difference between Li_2^+ and Li_2 is also indicated by a comparison of the hybridization calculations for the two systems. A simple extension of Pauling and Sherman's hybridization calculations for Li_2^+ to $\alpha = .588$ leads to the value 1.54 v.e. at 2.51 Å in but poor agreement with experiment as compared to the calculation with $\alpha = .500$ (see section 6 Part I). The calculation for Li_2 which at least from our original ingenuous point of view corresponds most closely to this hybridization treatment of Li_2^+ has been seen to lead to a much larger disagreement with experiment for <u>any</u> value of α.

9. Conclusions

The considerable arbitrariness in the choice of α and indeed of the type of treatment itself can be traced directly to the neglect of the K shell electrons. We have no complete variational principle to guide us when only part of a system is included in the treatment as in our discussion of Li_2 and Li_2^+. Consequently we adopt the experimental values of R_e and D_e as standards and estimate the worth of a theoretical calculation by the quality of the agreement or disagreement between the computed and observed bond constants.

We may summarize the calculations on Li_2^+, Li_2 and Be_2^{++} from this point of view.

(i) The orbital in Li_2^+ must be hybridized in order to account for the large observed dissociation energy. In order to balance properly the K-L shell interactions, however, it is necessary to choose an effective nuclear charge for the L electron which corresponds to maximum screening of the nucleus by the K electrons.

(ii) The electron-pair bond in Li_2 may be represented by either a pure s orbital of a "semi-hybridized" orbital. As in the case of the molecule-ion an effective nuclear charge of one must be used in the hybridization treatment. But with the s orbital the appropriate value of the effective nuclear charge is one which corresponds to an average 2s-2p distribution function. The "semi-hybridized" bond, which includes only the terms s^2s^2, s^2sp, and spsp might be visualized as representing a two-electron, two-center configuration in which one of the electrons is allowed to occupy an sp hybrid orbital.

(iii) The introduction of p^2 terms in the bond orbital for Li_2 is not possible due probably to the fact that although the bond formed by the electron in the L shells is stronger for the p^2 terms than for the s^2, the <u>repulsive</u> K-L shell interactions are also correspondingly stronger for the p^2 functions, the increased bond strength and repulsive force both being due to greater "overlapping."

Numerical Methods

1. Coulomb Integrals

There is no difficulty in computing the "simple" (i.e. one-electron) integrals listed in Table V . The simplest, I_1 and I_4, can be calculated by integrating in spherical coordinates although this is unnecessary since the two integrals are well known in the theory of hydrogenic atoms. For the evaluation of the remaining one-electron integrals, we use spheriodal coordinates

$\lambda = \frac{a+b}{R}$, $\mu = \frac{a-b}{R}$ and φ the azimuthal angle, with the volume element $d\tau = (\lambda^2-\mu^2)\, d\lambda\, d\mu\, d\tau$. In all cases our integrations reduce to elementary integrals of the type

$$\int_{\lambda=1}^{\infty}\int_{\mu=-1}^{+1} \lambda^m \mu^n e^{-a_1\lambda - a_2\mu} \cdot d\lambda\, d\mu$$

which may be expressed in terms of the $A_n(\beta\rho)$ functions of Rosen or as polynomials in ρ multiplying exponential factors. The latter form is given in Table VII and the numerical values in a part of Table IX.

Both types of two electron integrals, Coulomb and exchange, are evaluated by expanding $\frac{1}{r}$ in infinite series in appropriate coordinates of electrons 1 and 2, thus making possible the separation of the integrand into functions each dependent upon but one coordinate. With our choice of atomic wave functions, $2s$ and $2p$, whose nuclear charge parameter is the same, only a finite number of terms from the infinite series survive after the integrations have been performed. The Coulomb integrals are of the form

$$\int A_{\sigma_1}(1)\, A_{\sigma_1'}(1)\, \frac{1}{r}\, B_{\sigma_2}(2)\, B_{\sigma_2'}(2)\, d\tau_1\, d\tau_2$$

in which each of $\sigma_1', \sigma_1, \sigma_2, \sigma_2'$ may be either s or p. If the coordinates of one electron enter in the integrand only in s functions, say A_s^2, then we may evaluate the integral directly by considering the function A_s^2 to be a spherically symmetrical charge density and by applying the Newtonian laws of potential theory for such distributions.

In general for the Coulomb integrals, however, we make use of the expansion

$$\frac{1}{r} = \frac{1}{a_{1,2}} \sum_{n=0}^{\infty} \left(\frac{a_{2,1}}{a_{1,2}} \right)^n \sum_{m=\bar{n}}^{n} P_n^m(\cos\theta_{a_1})\, P_n^m(\cos\theta_{a_2}) (-)^m \frac{(n-m)!}{(n+m)!} \cos m(\varphi_1-\varphi_2)$$

for $a_1 > a_2 \quad , \quad a_1 < a_2$

The definitions of the angles and distances are those of page This series may be derived directly from the generating function of the Legendre polynomial $(1+2h\cos\vartheta+h^2)^{-1/2}$ and the addition theorem

$$P_n(\cos(\theta_{a_1}-\theta_{a_2})) = P_n(\cos\theta_{a_1})\, P_n(\cos\theta_{a_2}) + 2\sum_{m=1}^{m} (-)^m \frac{(n-m)!}{(n+m)!}\, P_n^m(\cos\theta_{a_1})\, P_n^m(\cos\theta_{a_2}) \cos m(\varphi_1-\varphi_2)$$

We see at once that only those terms with $m=0$ and $n \leq 2$ will survive after integrating over θ_{a_1} and φ_1. For none of the wave functions contain φ and the highest power of $\cos\theta_{a_1}$ that can enter is $\cos^2\theta_{a_1} = \frac{1}{3}\left[2P_2(\cos\theta_{a_1})-1\right]$ so that terms in the expansion with $m>0$ or $n>2$ will vanish due to the orthogonality properties of the trigonometrical and the Legendre functions. The integration over a_1 involves only elementary integrals of the type $\int e^{-\alpha a_1} a_1^n \, da_1$ with limits $0, a_2$ or ∞ The result of the first triple integration over the coordinates of electron 1 is thus a function of a_2, θ_{a_2} there being only two cases to consider, namely when the orbitals of the first electron entering into the original integrand were a_s, a_{p_1} or $a_{p_1}^2$. Since the remaining integrand is a function of b_2, θ_{b_2} for our non-ionic type integrals, it is convenient to introduce spheroidal coordinates $\lambda_2, \mu_2, \varphi_2$, as previously defined, in place of $a_2, b_2, \cos\theta_{a_2}, \cos\theta_{b_2}$. The type of integrals which result from this transformation are

$$\int_1^\infty\int_{-1}^1 e^{-\delta_1\lambda_1-\delta_2\mu_1}\lambda^m\mu^m \, d\lambda \, d\mu$$

already discussed and

$$\int_1^\infty\int_{-1}^1 \frac{\lambda^n e^{-\delta_1\lambda-\delta_2\mu}}{(\lambda+\mu)^p} \, d\lambda \, d\mu .$$

In the latter integral the integration over μ may be performed with the aid of the formulae given in Table where the exponential integral $Ei(-x)$ is defined by the equation

$$-Ei(-x) = \int_x^\infty \frac{e^{t}}{t} \, dt$$

The remaining integration over λ is then possible in terms of the functions

$$\Phi_n = \int_1^\infty \left\{Ei\left[\rho(\lambda+1)\right)-Ei\left[\rho(\lambda-1)\right]\right\} e^{-2\rho\lambda}\lambda^n \, d\lambda$$

$$\mathcal{F}_m = \int_1^\infty \lambda^m \log \frac{\lambda+1}{\lambda-1} e^{-2\rho\lambda} d\lambda$$

together with simpler integrals of the incomplete Gamma Function type which we have already used. To evaluate $\mathcal{I}_m$ we make use of recurrence relations derived by partial integration. Taking

$$\mathcal{I}_m' = \int_1^\infty Ei[\rho(\lambda+1)] e^{-2\rho\lambda} \lambda^m d\lambda$$

and $\quad \mathcal{I}_m'' = \int_1^\infty Ei[\rho(\lambda-1) e^{-2\rho\lambda} \lambda^m d\lambda \quad$ we have

We may build up the $\mathcal{I}_m'$ and $\mathcal{I}_m''$ by successive applications of the recursion formulae *omitting all Ei terms since these always cancel corresponding terms from* $\mathcal{F}_m$. No general reason has been found for this cancellation. It is interesting to note that $\mathcal{I}_m''$ may also be evaluated in a much simpler manner. Making the change of variable $x = \lambda - 1$ we find for $\mathcal{I}_m''$ a series of terms like $R_m^{(m)}(\rho)$,

$$R_m^{(m)}(\rho) = \int_0^\infty e^{-2\rho x} x^m Ei(\rho x) dx$$

From a partial integration

$$\left[(m+1) R_m + \frac{m!}{\rho^{m+1}}\right] \frac{1}{2\rho} = R_{m+1}$$

from which it may be shown that

$$R_{m+1}^{(m)} = \frac{(m+1)!}{\rho(2\rho)^{m+1}} \sum_{j=0}^{m} \frac{2^j}{j+1} .$$

Thus $\mathcal{I}_m'' = e^{-2\rho} \sum_{i=0}^{m} \binom{m}{i} R_i = e^{-2\rho} \sum_{i=0}^{m} \binom{m}{i} \rho^{-(i+1)} q_i^{(m)}$ where $q_i^{(m)}$ is defined by

$$q_i^{(m)} = \frac{i!}{2^i} \sum_{j=0}^{m-1} \frac{2^j}{j+1}$$

and satisfies the relation

$$g_{i+1}^{(n)} = \frac{i!}{2} + \frac{n+1}{2} g_i^{(n)}$$

The $g_i^{(n)}$ may be quite easily calculated and from them the functions $\mathcal{I}_n''$

The polynomial part of $\mathcal{I}_n$ was tabulated. ~~in Table~~ We observe that only polynomials and exponentials enter into the final algebraic expression for Coulomb integrals, Table VIII. The numerical values are listed for ρ = 2, 2.5, 3, 4, 5 in Table IX.

Expansions in Bessel functions rather than Legendre functions may prove to be the most useful in future work particularly in the evaluation of three center integrals. Some of these expansions have the advantage that they are valid for all relative values of and so that the range of integration need not be split up. (Compare Coulson(23) and Smith(69)).

2. Exchange Integrals

The functions of one electron in the integrand here involve coordinates defined with respect to both nuclei, A and B. We therefore change to spheriodal coordinates and use the Neumann expansion of $\frac{1}{r}$ (15)

$$\frac{1}{r} = \frac{4}{R}\sum_{\tau=0}^{\infty}\sum_{\nu=0}^{\tau} \frac{2\tau+1}{2} P_\tau^\nu\binom{\lambda_1}{\lambda_2} Q_\tau^\nu\binom{\lambda_2}{\lambda_1} P_\tau^\nu(\mu_1) P_\tau^\nu(\mu_2)(-)^\nu \epsilon_\nu \left[\frac{(\tau-\nu)!}{(\tau+\nu)!}\right]^2 \cos\nu(\varphi_1-\varphi_2), \quad \begin{matrix}\epsilon_0 = 1\\ \epsilon_1 = \epsilon_2 = \cdots 2\end{matrix}$$

the upper variables being taken for $\lambda_1 < \lambda_2$ and the lower for $\lambda_1 > \lambda_2$. As in the case of the Coulomb expansion integration over φ_1, φ_2 reduces the sum over m or ν to the single term $\nu = 0$. Also the polynomials in

μ_1, μ_2 which come from the four wave functions and the volume elements are of not higher than the fourth degree in μ_1 or in μ_2 As a consequence of the well known property of the Legendre polynomials

$$\int_{-1}^{1} P_m(x)\, x^n\, dx = 0 \qquad \text{for } n > m$$

the sum over n then never contains terms beyond $P_4(\lambda_1)\, Q_4(\lambda_2)$ etc. Our final expression for an exchange integral will then be of the following form in which $a_{u,v}$ are readily calculable constants,

$$\Theta_m = \sum_{u,v} a_{u,v} \left\{ \int_{\lambda_1=1}^{\infty} \left[\int_{\lambda_2=1}^{\lambda_1} \lambda_1^{u} \lambda_2^{v} P_m(\lambda_2)\, Q_m(\lambda_1)\, e^{-\rho(\lambda_1+\lambda_2)}\, d\lambda_2 \right.\right.$$

$$\left.\left. + \int_{\lambda_2=\lambda_1}^{\infty} \lambda_1^{u} \lambda_2^{v} P_m(\lambda_1)\, Q_m(\lambda_2)\, e^{-\rho(\lambda_1+\lambda_2)}\, d\lambda_2 \right] d\lambda_1 \right\}$$

Putting $P_m(x) = \sum p_i^{(m)} x^i$ and $Q_m(x) = Q_0(x) \sum p_{j-1}^{(m)} x^j + \sum_{k} -r_k^{(m)} x^k$, Θ_m becomes

$$\sum_{u,v} a_{u,v} \left\{ \int_{\lambda_1=1}^{\infty} e^{-\rho\lambda_1} d\lambda_1 \sum p_i^{(m)} \lambda_1^{i+u} Q_0(\lambda_1) \int_{\lambda_2=1}^{\lambda_1} e^{-\rho\lambda_2} \sum p_j^{(m)} \lambda_2^{j+v} d\lambda_2 \right.$$

$$+ \int_{\lambda_1=1}^{\infty} e^{-\rho\lambda_1} d\lambda_1 \sum p_i^{(m)} \lambda_1^{i+u} \int_{\lambda_2=\lambda_1}^{\infty} Q_0(\lambda_2) \sum p_j^{(m)} \lambda_2^{j+v} e^{-\rho\lambda_2} d\lambda_2 + \int_{\lambda_1=1}^{\infty} e^{-\rho\lambda_1} d\lambda_1 \sum r_k^{(m)} \lambda_1^{k+u} \int_{\lambda_2=1}^{\infty} e^{-\rho\lambda_2} \sum p_j^{(m)} \lambda_2^{j+v} d\lambda_2$$

$$\left. + \int_{\lambda_1=1}^{\infty} e^{-\rho\lambda_1} d\lambda_1 \sum p_j^{(m)} \lambda_1^{j+u} \int_{\lambda_2=\lambda_1}^{\infty} e^{-\rho\lambda_2} \sum r_k^{(m)} \lambda_2^{k+v} d\lambda_2 \right\}$$

which may be written in terms of the H and S functions of Guillemin and Zener(56)

$$\Theta_m = \sum_{u,v} a_{u,v} \left[\sum_{i,j} p_i^{(m)} p_j^{(m)} H_{i+u,\, j+v} + \sum_{j,k}^{m,\, m-1} r_k^{(m)} p_j^{(m)} \left(S_{k+u,\, j+v} + S_{k+v,\, j+u} \right) \right]$$

where $$H_{m,n}(\rho) = \int_{\lambda_1}^{\infty} \lambda_1^m e^{-\rho\lambda} Q_0(\lambda_1)\, d\lambda_1 \int_1^{\lambda_1} \lambda_2^n e^{-\rho\lambda_2} d\lambda_2 + \int_1^{\infty} \lambda_1^n e^{-\rho\lambda_1} Q_0(\lambda_1)\, d\lambda_1 \int_1^{\lambda_1} \lambda_2^m e^{-\rho\lambda_2} d\lambda_2$$

$$S_{m,n}(\rho) = \int_1^{\infty} \lambda_1^m e^{-\rho\lambda_1} d\lambda_1 \int_1^{\lambda_1} \lambda_2^n e^{-\rho\lambda_2} d\lambda_2 = \int_1^{\infty} \lambda_1^n e^{-\rho\lambda_1} d\lambda_1 \int_{\lambda_1}^{\infty} \lambda_2^m e^{-\rho\lambda_2} d\lambda_2$$

Tables of the values of $p_i^{(m)} p_j^{(n)}$ and $\lambda_k^{(m)} p_j^{(n)}$ are easily constructed (cf. Table) so that $\textcircled{M}_m$ may be written out quite rapidly in terms of H, S functions with little chance of error since the process is so systematized as to become almost automatic.

All of the exchange integrals are thus expressed in terms of the H and S functions as in Table VIII, the numerical values for ρ = 2, 2.5, 3, 4, 5, appearing in Table IX. The methods of computing the H and S functions have been discussed in the literature (56-59,68).

3. The Direct Solution of Secular Equations

Our problem is to determine the lowest root of the secular equation $|H_{ij} - d_{ij}\lambda| = 0$ in which the H_{ij} and the d_{ij} are known numbers in general different from zero. The direct method consists of the following steps.

(i) We compute the two determinants $D(\lambda_1)$ and $D(\lambda_2)$ where we estimate λ_1 and λ_2 to be close to the lowest root $\lambda = W_1$ and such that $D(\lambda_1)$ and $D(\lambda_2)$ are of different sign.

(ii) By linear interpolation (or extrapolation) based upon $D(\lambda_1)$ and $D(\lambda_2)$ we find

$$\lambda_3 = \frac{\lambda_1 D(\lambda_2) - \lambda_2 D(\lambda_1)}{D(\lambda_2) - D(\lambda_1)}$$

If $D(\lambda)$ approximates closely to a linear function of λ for $\lambda \lessgtr^{\lambda_2}_{\lambda_1}$ then we would expect $D(\lambda_3)$ to be nearly zero.

(iii) We actually compute $D(\lambda_3)$, interpolate again and continue the process until λ_n approximates λ_{n+1} to the accuracy desired. The quantity λ_n found in this manner will then be an approximation to one of the roots of the secular equation.

The usefulness of this treatment obviously depends on the ease with which determinants may be evaluated, particularly those of order higher than the third. One of the most satisfactory methods(21) for reducing symmetrical determinants is based upon the use of the recursion relation

$$U_{rs} = u_{rs} - \sum_{i=1}^{r-1} \frac{U_{ir} U_{is}}{U_{ii}} , \qquad U_{1r} = u_{1r}$$

U_{rs} and u_{rs} referring to elements occurring in the rth row and the sth column of the transformed and of the original determinants, respectively. The valuable property of the transformation $|u_{rs}| \longrightarrow |U_{rs}|$ is that $U_{rs} = 0$ for $r > s$ so that the value of the determinant is given by $\prod_{r=1}^{n} U_{rr}$. When λ_k has been chosen so that $D(\lambda_k) = 0$ then UU_{nn} will also vanish. This method is quite general, a slight modification only being necessary when U_{rr} vanishes for $r < n$. All of the manipulations involved in this method may be performed in a rapid and systematic manner on the computing machine.

The advantages of the direct method for finding roots are its simplicity, its applicability to any secular equation and the rapid convergence once an approximate value of the root has been obtained. Its chief disadvantage lies in the fact that we have no assurqnce that a root obtained by this means is the lowest root of the secular equation and this uncertainty increases with the order of the equation.

4. The Matrix Solution of Secular Equations

One of the most elegant methods of solving secular equations is to find the polynomial function $R(\lambda)$ equivalent to the determinantal function $D(\lambda)$ and then to determine the zeros of $R(\lambda)$ by the very powerful and general matrix method described below. The direct algebraic computation of the coefficients in the polynomial $R(\lambda)$ is a complicated matter for determinants of higher than the third order and the corresponding numerical work is not suited to the calculating machine. An alternative device for producing the coefficients in the polynomial is sometimes useful. Let us substitute $\lambda_1, \lambda_2, --- \lambda_{m-1}$ in succession in the determinant, find its corresponding values $D(\lambda_1), D(\lambda_2), --- D(\lambda_m)$. The coefficient of the highest power and of the constant term are given by $D_\infty = |d_{ij}|$ and $D_0 = |H_{ij}|$, respectively, while the remaining coefficients $p_1, p_2 --- p_{m-1}$ may be determined from the simultaneous set of equations

$$\eta = 1, 2, \cdots m-1, \quad D(\lambda_\eta) = R(\lambda_\eta) = D_\infty \lambda_\eta^m + p_1 \lambda_\eta^{m-1} + --- + p_{m-1}\lambda_\eta + D_0$$

The method in this form has not seemed to be particularly useful except for m = 3 or 4.

However by using finite difference technique the labor in computing the coefficients p_m is considerably shortened. Let us as before compute D_∞ and $D(\lambda_\eta)$ $\eta = 1, 2, 3 \cdots m$. One of the values of λ_n is generally taken to be zero since $D(0)$ is easier to calculate than $D(\lambda), \lambda \neq 0$. The remaining λ_n are chosen so that they satisfy a relation of the form

$$\lambda_n = \lambda_0 + nh \qquad n = 1, 2 \cdots m$$

If we then define the function

$$R'(\lambda) = D(\lambda) - D_\infty \lambda^m = \sum_{n=1}^{m} p_n \lambda^{m-n}$$

and tabulate its m numerical values corresponding to the m values of λ_n given by equation above, we may immediately calculate the first m differences $\Delta R'(\lambda_0), \Delta^2 R'(\lambda_0) \cdots \Delta^m R'(\lambda_0)$ of the function $R'(\lambda)$. The knowledge of these m differences will, as is well known, suffice to determine completely the behavior of the function $R'(\lambda)$ which is a polynomial of degree $m-1$.

A convenient method for computing the coefficients p_n in terms of the differences $\Delta^s R'(\lambda_0)$ is the following. We may write Newton's interpolation formula

$$R'(\lambda_0 + mh) = R'(\lambda) = R'(\lambda_0) + \sum_{s=1}^{m} \frac{(\alpha^m_s)}{s!} h^s \cdot \Delta^s R'(\lambda_0)$$

in which $(\alpha^m_s) = n!/(m-s)!$

It is necessary to express (α^m_s) as a polynomial in m,

$$(\alpha^m_s) = \sum_{i=1}^{s} a_i(m,s)\, m^i$$

The coefficients $a_i(n,s)$ are related by the simple~~r~~ recursion formulae

$$a_i(m, s+1) = a_{i-1}(m,s) - s\, a_i(m,s) \qquad , \quad a_0(m,s) = a_{s+1}(m,s) = 0$$

which allows a table of their values for various m, s to be computed quite easily. The function $R'(\lambda)$ becomes, using these $a_i(m,s)$

$$R'(\lambda_0+mh) = \sum_{i=1} (\lambda-\lambda_0)^i b_i^m = \sum h^i m^i b_i^m \quad \text{with} \quad b_k^m h^k = \sum_s \frac{\Delta^s R'(\lambda_0)}{s!} h^s a_k(m,s)$$

It is easy to build up the b_n^m from the tabulated values of $a_i(m,s)$ and $\Delta^s R'(\lambda_0)$. The computation of the coefficients p_i then reduces to transforming the polynomial in $(\lambda-\lambda_0)$ to one in λ by a rapid process using synthetic division. In many cases this transformation is not necessary, however, as with proper choice of λ_0 the matrix method of solution (see below) is considerably speeded up.

This "polynomial" technique which we have just described for finding the roots of a secular equation possesses all of the advantages of the general matrix technique and some advantages of the direct method. The evaluation of the determinants $D(\lambda_\nu)$ may be broken off at any point if it so happens that a λ_ν is used for which $D(\lambda_\nu) \sim 0$ and the interpolation method (section 3) applied to calculate the root accurately. However once the coefficients b_n^m are determined the matrix solution of the polynomial equation is to be preferred for it leads at once to the dominant root and may be extended to the calculation of other roots with moderate amount of additional calculation.

In the concluding paragraphs of this section we will describe a method which was developed by Duncan and Collar and others (60,61,62). It provides, essentially, a means of finding the eigenvalues of characteristic matrices including as a special case the matrix corresponding to an algebraic equation.

Let M be the characteristic matrix whose eigenvalue is sought and let K be a completely arbitrary matrix. We form $M^m \times K$ and denote one of its typical elements by α_m. Then the following fundamental theorem may be applied for finding the dominant root λ_1, (that is, the root largest in absolute value):

$$\lim_{m \to \infty} \frac{\alpha_{m+1}}{\alpha_m} = \lambda_1$$

In practice, K is taken to be a matrix of one column so that $M^m K$ will likewise be a linear matrix. This reduces the number of new quantities which must be computed in performing one matrix multiplication, from n^2 to n.

In order to be able to apply the theorem to the solution of our secular equations for Li_2, we must find an equivalent secular equation in which the $d_{ij} = \delta_{ij}$ (Kronecker δ). The reduction to such an equation may be accomplished in two ways. First, we may introduce an orthonormal set of variation functions by a linear transformation as described previously (p. 55) these giving $d_{ij} = \delta_{ij}$ by definition. In the second place we may normalize each term in the molecular variation function thus making $d_{ii} = 1$, substitute an estimated value of $\lambda = \lambda_0$ in the non-diagonal terms, and solve the resulting secular equation by Duncan and Collar's method for a "root" λ_1. Then we may repeat the process using some systematically chosen mean of λ_0 and λ_1 as the approximating root in the non-diagonal terms. This method has been tried with some success and might be improved with further development. An unsettled question is whether by this method the dominant root is always obtained.

An important application of the general theorpm is to the solution of a polynomial equation.

$$D(\lambda) = \lambda^n + p_1 \lambda^{n-1} + \cdots + p_n = 0$$

This may be written in the form,

$$\begin{vmatrix} \lambda, & 1, & 0 & 0 & 0 & - & - & - & - & 0 \\ 0 & \lambda & 1 & 0 & 0 & & & & & 0 \\ 0 & 0 & \lambda & 1 & 0 & - & - & - & - & 0 \\ \vdots & & \vdots & & - & - & - & \vdots & & \\ \vdots & & \vdots & & & & & & \lambda_1, & 1 \\ -p_n, & -p_{n-1}, & -p_{n-2}, & -p_{n-3}, & -p_{n-4} & - & - & - & -p_2, & -p_1 \end{vmatrix}$$

and will therefore have as its characteristic matrix,

the same array with λ put $= 0$.

If we choose our arbitrary matrix K in the form $\begin{Vmatrix} \alpha_0 \\ \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_{n-1} \end{Vmatrix}$

then $MK = \begin{Vmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{Vmatrix}$ where $\alpha_n = -\sum_{j=0}^{n-1} p_{n-j} \alpha_j$.

Thus the only effect of multiplying K by M is to shift α_2 to the first row, α_3 to the second row, etc. and to add one new element α_m. Repeating this process, and applying the fundamental theorem, we find as before

$$\lim_{m \to \infty} \frac{\alpha_{m+1}}{\alpha_m} = \lambda_1$$

but now, each successive approximation to the root involves only the computation of the one sum, as in the eq. above, whereas in the case of the determinantal equation, n such sums must be calculated.

The great advantage of the Duncan Collar technique is that it is self-correcting. An error made in computing a sum of the type given in the eq. above merely delays convergence of the process but does not invalidate the limiting ratio

$$\lim \frac{\alpha_{m+1}}{\alpha_m} .$$

When two roots, λ_1, λ_2, are nearly or exactly equal, the limit is approached very slowly or not at all, respectively. The convergence in the first case may be considerably improved by finding the matrix M^2 which is then used to form M^2K_1, M^4K etc. thus speeding up the numerical approximation to the root. However, relatively simple extensions of the theory lead to expressions for $(\lambda_1+\lambda_2)$ and $\lambda_1\lambda_2$ which converge rapidly. It is interesting to note that the Duncan-Collar method may be applied to the determination of complex roots as well as using these expressions for the sum and difference of, in this case, conjugate complex roots.

The second great advantage is that the lowest root corresponding to the most stable state is obtained automatically for secular equations corresponding to attractive states since any possible positive roots are usually smaller in absolute value than the root corresponding to the ground state. In the case of all positive roots (repulsive state), where it is yet the root lowest in algebraic value which is desired, we may multiply each term in secular equation by $\lambda' = \frac{1}{\lambda}$ and solve the resulting determinantal equation for λ' by the Duncan and Collar technique. Finally, the matrix method is perfectly suited for machine computation since a sum of products, $\sum_{j=1}^{n} \alpha_{ij} \beta_{jk} = \gamma_{ik}$ as occurs in matrix multiplication, may be calculated on the machine directly from the α_{ij}, β_{jk} without it being necessary to record the intermediate steps.

Table I

Constants for the Ground State of H_2^+ ($1s\,^2\Sigma$)

Energies - v.e.	Burrau	Hylleraas	Sandeman	Birge	Richardson
		Theoretical		Experimental	
Vibrational Constants					
Y_{10}		.279	.28633	.281	.284
Y_{20}		-.0069	-.008360	-.0076	-.0074
$Y_{01} = B_e$			.003692		
Zero-point Vibrational Energy					
$\frac{1}{2} h\nu_0$	.14	.138	.1421	.140	.141
Electronic Dissociation Energy					
D_e	2.76	2.7773	2.7750		
True Dissociation Energy					
D_0		2.659	2.6329		2.6
Equilibrium Internuclear Distance					
R_e - Å	1.06	1.06	1.055	1.056	1.06

Assuming $R_H hc = 13.5300$ v.e.

Table I (Cont.)

Constants for the Ground State of H_2^+ ($1s\,^2\Sigma$)

	R_e - Å	D_e - v.e.
Pauling	1.32	1.77
Finkelstein and Horovitz	1.06	2.25
Dickinson	1.06	2.712
Guillemin and Zener	1.06	2.77
James		2.772
Sandeman	1.055	2.7750
Svartholm		2.777
Jaffé	1.06	2.7775

Table II

Constants for the Ground State of H_2 ($1s1s\,^1\Sigma$)

	Electronic Dissociation Energy D_e - v.e.	Zero-point Vibration Energy Cm^{-1}	Equilibrium Internuclear Distance R_e - °A
Heitler-London-Sugiura	3.14	4800	.80
Weinbaum (molecular-orbital)	3.47		.73
Conlson (Hartree field)	3.63		
Wang	3.76	4900	.76
Weinbaum (ionic)	4.00	4750	.77
Rosen	4.02	4260	.77
Inui	4.043	4390	.757
Weinbaum (ionic-polarization)	4.06		
James-Coolidge	4.722		.74
Experiment	4.72	4317.9	.7395

Table III

L Shell Energies of LiI and BeII

Spectroscopic Values*[*]	$-W_s$		$-W_p$		$W_p - W_s$	
	v.e.	$a.u._Z$	v.e.	$a.u._Z$	v.e.	$a.u._Z$
LiI, Z=1	5.3645	.19825	3.5260	.13030	1.8386	.06795
BeII, Z=2	18.120	.16740	14.180	.13101	3.9392	.03639
Computed Values						
$\Gamma_{Z=1} = 0.500$						
Unmodified Laplacian	5.6374	.20833	3.3825	.12500	2.2549	.08333
Modified Laplacian	3.3825	.12500	3.3825	.12500	0	0
Modified Hamiltonian	5.2212	.19295	3.3825	.12500	1.8386	.06795
$\Gamma_{Z=2} = .500$						
Unmodified Laplacian	22.550	.20833	13.530	.12500	9.0196	.08333
Modified Laplacian	13.530	.12500	13.530	.12500	0	0
Modified Hamiltonian	17.469	.16139	13.530	.12500	3.939	.03639
$\Gamma_{Z=2} = 0.544$						
Modified Hamiltonian	17.364	.16042	13.425	.12403	3.939	.03639
$\Gamma_{Z=1} = .588$						
Modified Hamiltonian	5.1165	.18908	3.2778	.12113	1.8386	.06795

[*] from R.F. Bacher and S. Goudsmit "Atomic Energy States" assuming $R_H hc = 13.5300$ v.e. $\quad a.u._Z = \frac{Z^2 e^2}{a_0}$

Table IV

Li$_2$ and Be$_2^{++}$ - Variation of D and k_1 with ρ

Li$_2$ Z=1 Energy unit = Z^2e^2/a_0 $\rho = \alpha R$

Orbitals	α		2	2.5	3	4	5
$s^2 s^2$	.500	D=	.01249	.03054	.03209	.01991	.00854
	.588		.01713	.03943	.04194	.02749	.01272
		(v.e.	.464	1.067	1.135	.744	.344)
$p^2 p^2$	.500		.03815	.04808	.03846	.01684	.00857
	.588		.04887	.05662	.04378	.02038	.00907
$s^2 s^2$, $s^2 sp$, $spsp$	.500		.03113	.04191	.03915	.02243	.00916
variation $\varepsilon = \varepsilon_{sp}$		(v.e.	.842	1.134	1.059	.607	.248)
		k_1=	.592	.400	.294	.133	.074
Be$_2^{++}$ Z=2							
$s^2 s^2$	.500	D=	.3080	.1802	.1206	.0848	.0799
	.544		.1664	.0964	.0636	.0487	.0422
$p^2 p^2$	.500		.2382	.1166	.0731	.0562	.0581
	.544		.1277	.0634	.0404	.0303	.0305
$s^2 s^2$, $s^2 sp$, $spsp$	5.00×10^{-1}		.0998	.0484	.0266	.0196	.0263
variation $\varepsilon = \varepsilon_{sp}$		(v.e.	10.80	5.24	2.88	2.12	2.84)
		k_1=	.74	.65	.60	.54	.48

Table V

Normalization and One-Electron Integrals-Definition

$S_1 = \int a_s b_s \, d\tau$ $\qquad$ $S_2 = \int a_p b_p \, d\tau$ $\qquad$ $S_3 = \int a_s b_p \, d\tau$

$$I_1 = \int \frac{a_s^2}{a} d\tau = \frac{\alpha}{2}$$

$$I_2 = \int \frac{a_s^2}{b} d\tau$$

$$I_3 = \int \frac{a_s b_s}{a} d\tau$$

$$I_4 = \int \frac{a_p b_p}{a} d\tau = \frac{\alpha}{2}$$

$$I_5 = \int \frac{a_p a_p}{b} d\tau$$

$$I_6 = \int \frac{a_p b_p}{a} d\tau$$

$$I_{10} = \int \frac{a_p a_s}{a} d\tau = 0$$

$$I_{11} = \int \frac{a_p a_s}{b} d\tau$$

$$I_{12} = \int \frac{a_p b_s}{a} d\tau$$

$$I_{13} = \int \frac{a_p b_s}{b} d\tau$$

Table VI

Two-Electron Integrals- Definition

$$I = \int A_{\tau_1} B_{\tau_1'} \frac{1}{r} C_{\tau_2} D_{\tau_2'} \, d\tau_1 \, d\tau_2$$

	I_m	$A_{\tau_1} B_{\tau_1'} C_{\tau_2} D_{\tau_2'}$
m	14	$A_s A_s \quad B_s B_s$
	15	$A_s B_s \quad A_s B_s$
	16	$A_s A_s \quad B_s B_p$
	17	$A_s B_s \quad A_p B_p$
	18	$A_s A_s \quad B_p B_p$
	19	$A_s B_s \quad A_p B_p$
	22	$A_s A_p \quad B_s B_p$
	23	$A_s B_p \quad A_p B_s$
	24	$A_s A_p \quad B_p B_p$
	25	$A_s B_p \quad A_p B_p$
	28	$A_p A_p \quad B_p B_p$
	29	$A_p B_p \quad A_p B_p$
	54	$A_s B_p \quad A_s B_p$

Table VII

Normalization and One-Electron Integrals-Formulae

$$S_1 = \frac{e^{-\rho}}{3}\left\{3 + 3\rho + \frac{4\rho^2}{3} + \frac{\rho^3}{3} + \frac{\rho^5}{15}\right\}$$

$$S_2 = e^{-\rho}\left\{-1 - \rho - \frac{1}{5}\rho^2 + \frac{2}{15}\rho^3 + \frac{1}{15}\rho^4\right\}$$

$$S_3 = \frac{\rho e^{-\rho}}{2\sqrt{3}}\left\{1 + \rho + \frac{7}{15}\rho^2 + \frac{2}{15}\rho^3\right\}$$

$$I_2 = \frac{\alpha}{6\rho}\left\{6 - e^{-2\rho}\left[2\rho^3 + 6\rho^2 + 9\rho + 6\right]\right\}$$

$$I_3 = \frac{\alpha}{2}e^{-\rho}\left\{1 + \rho + \frac{4}{9}\rho^2 + \frac{1}{9}\rho^3\right\}$$

$$I_5 = \frac{\alpha}{\rho} + \frac{3\alpha}{\rho^3} - \alpha e^{-2\rho}\left[\rho^2 + 3\rho + \frac{11}{2} + \frac{7}{\rho} + \frac{6}{\rho^2} + \frac{3}{\rho^3}\right]$$

$$I_6 = \frac{\alpha}{2}e^{-\rho}\left(1 + \rho + \frac{\rho^3}{3}\right)$$

$$I_{11} = \frac{\alpha}{\sqrt{3}}\left\{\frac{5}{2\rho^2} - e^{-2\rho}\left[\rho^2 + 3\rho + 5 + \frac{5}{\rho} + \frac{5}{2\rho^2}\right]\right\}$$

$$\overline{I}_{12} = \frac{1}{2}\left(I_{12} + I_{13}\right) = \frac{\alpha\rho^4 e^{-\rho}}{6\sqrt{3}}\left\{\frac{1}{\rho} + \frac{2}{\rho^2} + \frac{2}{\rho^3}\right\}$$

Table VIII

Two-Electron Integrals-Formulae

$$I_{14} = \frac{\alpha}{144}\left\{\frac{144}{\rho} - e^{-2\rho}\left[\frac{4}{35}\rho^6 + \frac{6}{5}\rho^5 + \frac{36}{5}\rho^4 + 30\rho^3 + \frac{357}{4}\rho^2 + \frac{1467}{8}\rho + \frac{3771}{16} + \frac{144}{\rho}\right]\right\}$$

$$I_{15} = \frac{\alpha\rho^9}{136080}\left\{27H_{00} - 216H_{20} + 306H_{40} + 468H_{22} - 1296H_{42} + 903H_{44} + 51S_{10}\right.$$
$$\left. -117S_{30} - 294S_{12} + 666S_{32} + 379S_{14} - 861S_{34}\right\}$$

$$I_{16} = \frac{\alpha\rho^2}{192\sqrt{3}}\left\{\frac{480}{\rho^4} - e^{-2\rho}\left[\frac{16}{35}\rho^4 + \frac{472}{105}\rho^3 + \frac{76}{3}\rho^2 + 100\rho + 291 + \frac{1251}{2\rho} + \frac{960}{\rho^2} + \frac{960}{\rho^3} + \frac{480}{\rho^4}\right]\right\}$$

$$I_{17} = \frac{\alpha\rho^9}{90720\sqrt{3}}\left\{-27H_{10} + 108H_{30} + 63H_{50} + 90H_{21} - 135H_{41} - 288H_{32} - 378H_{52} + 468H_{43}\right.$$
$$+483H_{54} - 3S_{11} + 9S_{31} - 3S_{20} - 6S_{22} + S_{24} - 78S_{13} + 162S_{33}$$
$$\left. -63S_{40} + 378S_{42} - 483S_{44} + 217S_{15} - 483S_{35}\right\}$$

$$I_{18} = \frac{\alpha}{96}\left\{12\left(\frac{8}{\rho} + \frac{24}{\rho^3}\right) - e^{-2\rho}\left[\frac{8}{35}\rho^6 + \frac{44}{21}\rho^5 + \frac{396}{35}\rho^4 + \frac{224}{5}\rho^3 + 126\rho^2\right.\right.$$
$$\left.\left. + \frac{1257}{4}\rho + \frac{4329}{8} + \frac{672}{\rho} + \frac{576}{\rho^2} + \frac{288}{\rho^3}\right]\right\}$$

$$I_{19} = \frac{\alpha\rho^9}{90720}\left\{-81H_{00} + 603H_{20} - 576H_{40} + 63H_{60} - 1134H_{22} + 2259H_{42}\right.$$
$$-378H_{62} - 855H_{44} + 483H_{64} - 108S_{10} + 177S_{30} + 501S_{12} - 789S_{32}$$
$$\left. -618S_{14} + 919S_{34} - 63S_{50} + 378S_{52} - 483S_{54} + 217S_{16} - 483S_{36}\right\}$$

$$I_{22} = \frac{\alpha\rho^5}{80640}\left\{\frac{336000}{\rho^8} - e^{-2\rho}\left(192\rho + 1760 + \frac{9280}{\rho} + \frac{34720}{\rho^2} + \frac{100660}{\rho^3}\right.\right.$$
$$\left.\left. + \frac{236950}{\rho^4} + \frac{454475}{\rho^5} + \frac{672000}{\rho^6} + \frac{672000}{\rho^7} + \frac{336000}{\rho^8}\right)\right\}$$

$$I_{23} = \frac{\alpha \rho^9}{90720} \Big\{ 9 H_{11} - 90 H_{31} + 252 H_{33} - 126 H_{53} + 147 H_{55} + 6 S_{21}$$

$$- 42 S_{23} + 28 S_{25} + 126 S_{43} - 294 S_{45} \Big\} - \frac{1}{2} I_{54}$$

$$I_{54} = \frac{\alpha \rho^9}{45360} \Big\{ 90 H_{11} - 522 H_{31} + 270 H_{51} + 828 H_{33} - 846 H_{53} + 372 H_{55}$$

$$- 135 S_{01} + 360 S_{03} - 225 S_{05} + 411 S_{21} - 270 S_{41} - 112 S_{23} + 846 S_{43} + 703 S_{25} - 744 S_{45} \Big\}$$

$$I_{24} = \frac{\alpha \rho^5}{32\sqrt{3}} \Big\{ \frac{80}{\rho^7} + \frac{720}{\rho^9} - e^{-2\rho} \Big[\frac{8}{35}\rho + \frac{68}{35} + \frac{206}{21\rho} + \frac{782}{21\rho^2} + \frac{691}{6\rho^3} + \frac{3571}{12\rho^4}$$

$$+ \frac{640}{\rho^5} + \frac{1120}{\rho^6} + \frac{1520}{\rho^7} + \frac{1440}{\rho^8} + \frac{720}{\rho^9} \Big] \Big\}$$

$$I_{25} = \frac{\alpha \rho^9}{30240\sqrt{3}} \Big\{ 45 H_{01} - 162 H_{21} + 45 H_{41} - 198 H_{03} + 702 H_{23} - 90 H_{43} - 126 H_{63}$$

$$- 63 H_{05} + 252 H_{25} - 315 H_{45} + 294 H_{65} + 9 S_{11} - 3 S_{31} + 9 S_{20} - 30 S_{22}$$

$$- 15 S_{24} + 36 S_{13} + 28 S_{26} - 78 S_{33} + 126 S_{53} + 63 S_{40} - 252 S_{42} + 315 S_{44}$$

$$- 294 S_{46} - 189 S_{15} + 217 S_{35} - 294 S_{55} \Big\}$$

$$I_{28} = \frac{\alpha \rho^5}{64} \Big\{ \frac{64}{\rho^6} + \frac{384}{\rho^8} + \frac{3456}{\rho^{10}} - e^{-2\rho} \Big[\frac{16}{35}\rho + \frac{376}{105} + \frac{608}{35\rho} + \frac{7144}{105\rho^2} + \frac{23809}{105\rho^3}$$

$$+ \frac{6411}{10\rho^4} + \frac{30731}{20\rho^5} + \frac{3136}{\rho^6} + \frac{5376}{\rho^7} + \frac{7296}{\rho^8} + \frac{6912}{\rho^9} + \frac{3456}{\rho^{10}} \Big] \Big\}$$

$$I_{29} = \frac{\alpha \rho^9}{30240} \Big\{ 126 H_{00} - 918 H_{20} + 360 H_{40} - 126 H_{60} + 1674 H_{22} - 1350 H_{42}$$

$$+ 504 H_{62} + 450 H_{44} - 630 H_{64} + 294 H_{66} + 126 S_{10} - 108 S_{30} + 126 S_{50}$$

$$- 486 S_{12} + 426 S_{32} - 504 S_{52} + 450 S_{14} - 480 S_{34} + 630 S_{54} - 378 S_{16}$$

$$+ 434 S_{36} - 588 S_{56} \Big\}$$

Table IX Integrals

Numerical Values

S_1	.815019	.729074	.637274	.456263	.302459
S_2	-.225559	-.005130	.159318	.318691	.318927
S_3	.463605	.503539	.508779	.444133	.333904
F_2	.402317	.356316	.313916	.246282	.199318
F_3	.383450	.328911	.273830	.176035	.104438
F_5	.492661	.435666	.378482	.284908	.221859
F_6	-.0225573	.0701133	.124468	.149577	.120160
F_{11}	.169180	.148663	.124677	.0835472	.0565267
F_{12}	.260453	.261642	.244329	.183292	.119946
$\frac{1}{2}(F_{12}+F_{13})$					
F_{14}	.31782	.296843	.27472	.23161	.19458
F_{15}	.23816	.18923	.14318	.071434	.030301
F_{16}	.066000	.070755	.070883	.062219	.070755
F_{17}	.15034	.14455	.12582	.075653	.035982
F_{18}	.33875	.31855	.29679	.25191	.21066
F_{19}	-.032249	.032932	.065951	.067104	.039373
F_{22}	-.017884	-.000507	.0117207	.021780	.020407
F_{23}	-.13904	-.15077	.14488	-.098510	-.050072
F_{24}	.051680	.063109	.069750	.068970	.057441
F_{25}	-.008171	.037215	.068032	.076059	.048592
F_{28}	.34588	.33118	.31454	.27418	.23051
F_{29}	.04400	.04327	.06143	.07850	.05694
F_{54}	.37717	.41581	.40372	.27878	.14346

Table X

Formulae for $\mathcal{H}_{ij}$ and $\mathcal{R}_{ij}$

$$\mathcal{H}_{11} = \gamma_0 - 2F_2 - 2\delta_1 F_3 \qquad \mathcal{R}_{11} = F_{14} + F_{15}$$

$$\mathcal{H}_{12} = -F_{11} - \delta_3 F_3 - \delta_1 \overline{F}_{12} \qquad \mathcal{R}_{12} = F_{16} + F_{17}$$

$$\mathcal{H}_{13} = -2\delta_3 \overline{F}_{12} \qquad \mathcal{R}_{13} = F_{22} + F_{23}$$

$$\mathcal{H}_{22} = \frac{1}{2}\left(\gamma_0 - F_2 - F_5 - \delta_2 F_3 - \delta_1 F_6 - 2\delta_3 \overline{F}_{12}\right) \qquad \mathcal{R}_{22} = \frac{1}{2}\left(F_{18} + F_{19} + F_{54} + F_{22}\right)$$

$$\mathcal{H}_{23} = -F_{11} - \delta_2 \overline{F}_{12} - \delta_3 F_6 \qquad \mathcal{R}_{23} = F_{24} + F_{25}$$

$$\mathcal{H}_{33} = \gamma_0 - 2F_5 - 2\delta_2 F_6 \qquad \mathcal{R}_{33} = F_{28} + F_{29}$$

Figure 1 Energy Curves for a Diatomic Molecule

for curve 1a see
Part A, Fig. 3

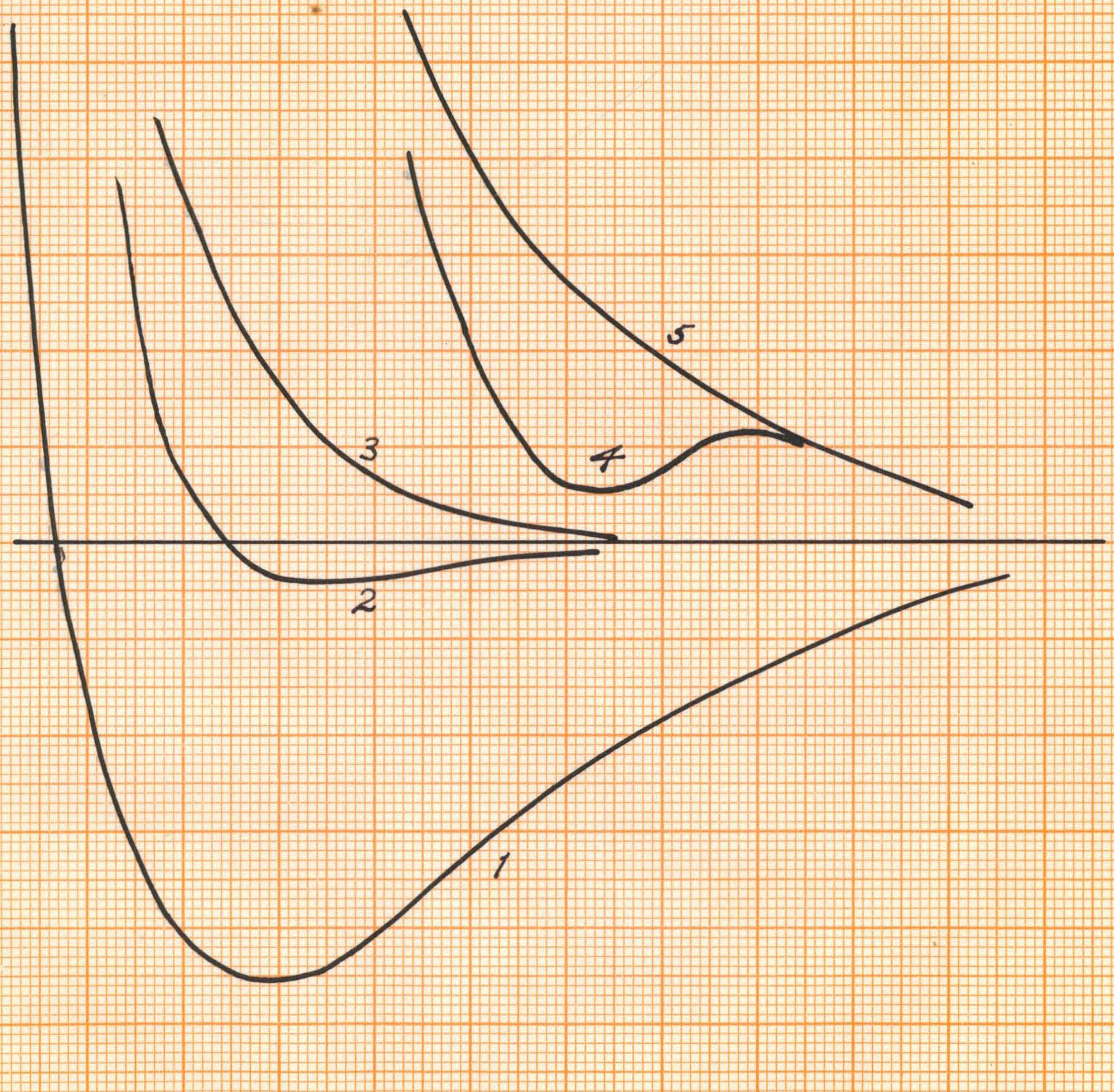
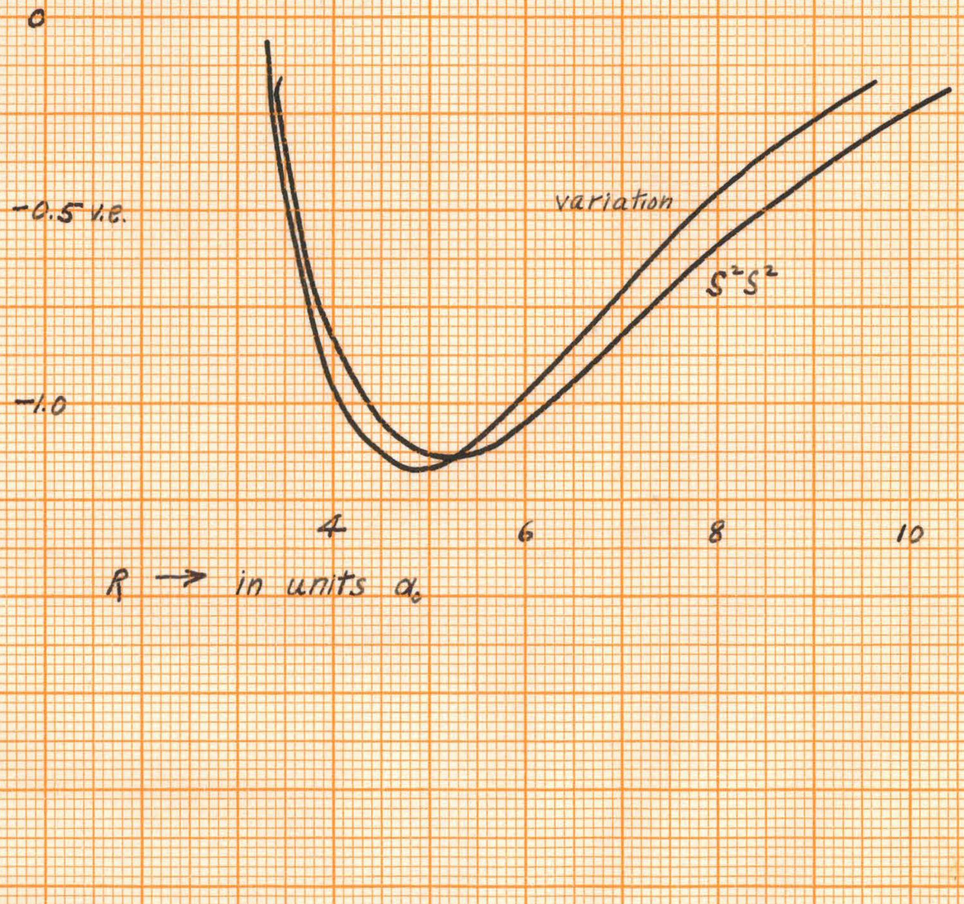


Figure 2 Energy Curves for Li_2



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