

Acknowledgements

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ABSTRACT

The problem of electron-electron correlation and the methods for its consideration are briefly discussed. One of these methods, called "shell-opening", has gained some interest in recent years in calculations concerning radial correlation in simple atomic structures. These calculations are briefly outlined. The method of "shell-opening" is extended in the present work to the problem of radial correlation in molecular structure and applied to the determination of the energy of the  $\text{He}_2^+$  molecule ion by performing variational calculations. Two different molecular wave functions, both of the valence bond type, are constructed as approximations A and B. Each of these can be written as an algebraic sum of terms consisting of a Hylleraas-Eckart type wave function for a He atom multiplied by a wave function for a  $\text{He}^+$  ion. In approximation A open-shell configurations are introduced only for the filled ( $1s^2$ ) shell of the He atom. In approximation B the idea of the open-shells is further developed and applied also to the half-filled ( $1s$ ) shell of the  $\text{He}^+$  ion. As far as the author knows this latter idea is the first attempt of this kind in the literature. The wave function of approximation A is a linear combination of four determinants of the third order with three exponential variational parameters and that of approximation B is a superposition of eight determinants of the third order with two exponential and one linear variational parameters. Either one of the two present

open-shell wave functions contains the simpler closed-shell wave functions of other authors as special cases.

Theoretical considerations, based on the analysis of the idea of open-shell configurations, permit a new possibility for the interpretation of the three-electron bond and the quantum mechanical model of the binding. It is shown mathematically that the three-electron bond can be interpreted as the superposition of resonating Heitler-London type electron pair bonds. These results suggest the possibility for an eventual generalization both of approximations A and B but lead to wave functions of considerable complexity.

At  $R = 2a_0 = 1.058 \text{ \AA}$  the energy of the  $\text{He}_2^+$  molecular ion is found to be  $-4.935 e^2/a_0$ , lower than any previously calculated value.

In an appendix an approximate method suggested by Mulliken for the calculation of the two-center exchange integrals is analyzed mathematically. In another appendix a few other molecular systems such as  $\text{Li}_2$ ,  $\text{LiH}$ ,  $\text{BeH}^+$ ,  $\text{Li}_2^+$ ,  $\text{LiH}^+$ ,  $\text{BeH}^{++}$ , are also treated on the basis of a "valence electron approximation", i.e. by replacing the closed-shell electrons by an appropriate screening field.

Finally, it is noted that the numerical calculations were performed with the aid of an electric desk computer (MADAS).

## I. INTRODUCTION

### 1) The problem of correlation

In the quantum mechanical theory of atomic and molecular systems the treatment of the electron-electron correlation effect is an important problem. This problem originates from the fact that the many-electron Schrödinger equation cannot be solved exactly, due to the presence of interactions involving the interelectronic distances. For this reason, the quantum mechanical calculation of atomic and molecular structure is usually based upon the approximation in which a state is described as a linear combination of determinants of one-electron functions. In this representation, also referred to as the independent particle approximation, the effect of the repulsion between two electrons is not represented by a dependence of the wave function on the distances  $r_{12}$  between the electrons. Any means by which the effect of the positions of the electrons can be related to each other in the wave function of a system, thus allowing for a smaller probability of finding two electrons at small distances than at great distances, is called the inclusion of correlation.

### 2) Methods of considering correlation

The most straightforward method of considering correlation is the explicit introduction of the interelectronic distances into the wave function of the given system, as demonstrated by Hylleraas (1929) for the He atom and by James and Coolidge (1933) for the H<sub>2</sub> molecule. As these authors have found, this method leads to a good agreement between the calculated and the

empirical energy values, but it involves very lengthy calculations which render its generalization unpracticable for more than a two-electron problem. Its other disadvantage is the complete loss of the simple and very useful orbital picture.

Lennard-Jones and Pople (1952), following theoretical considerations, divided the correlation effect into radial and into angular correlation effects. It is said that the wave function of two electrons gives some account of the radial correlation if it is made dependent in addition to the radius vectors  $r_1$  and  $r_2$  also on their difference,  $r_1 - r_2$ . If  $\theta_{12}$ , the angle between the radius vectors is also considered in the wave function, then it is capable of giving some account of the angular correlation.

It has been found that a method based on the introduction of "open-shell" configurations is successful in giving some account of the radial correlation effect of two electrons with opposite spins. This method was first introduced by Hylleraas (1929) and independently by Eckart (1930) in connection with a variational calculation on the ground state energy of the He atom. Their function is based on the idea of assigning different radial functions for the electrons of the  $(1s^2)$  shell and thereby separating them into two concentric shells. The result obtained was considerably better than the simple variational product function of Frenkel (1929). The improvement is due to the fact that by the splitting of the originally closed shell into two half-filled open-shells the electrons are prevented from being close to each other in space.

Löwdin (1955), following theoretical arguments, concluded that the possibility of having different orbitals for different spins is a new degree of freedom in constructing wave functions and could be used to give some account of the radial correlation effect also in other many-electron systems. In the case of more than two electrons the situation is somewhat more complicated because there are electrons not only with antiparallel but also with parallel spins. It was, however, pointed out by Wigner and Seitz (1933) that applying an antisymmetrical, i.e. determinantal, wave function the occurrence of the exchange effect automatically includes the correlation effect between electrons having parallel spins, and the essential problem is then to consider the correlation between electrons with opposite spins. They have shown that the antisymmetry requirement of the Pauli principle leads to a correlation effect for two electrons with parallel spins which will strongly keep them apart. There is no such connection of the positions, however, for electrons with antiparallel spins and in constructing wave functions one has to apply physical considerations such as, for instance, the idea of open-shell configurations.

It may be noted that the introduction of open-shell configurations for a state of a system may be considered to be equivalent in a certain sense to the method of the configuration interaction. This latter method is also applicable to give account of the correlation since it has been shown by Green et al. (1954) in the case of the He atom that the

superposition of configurations of the proper symmetry is equivalent to the explicit introduction of the  $r_{12}$  term into the wave function. Although this method can be generalized for many-electron problems, the calculations of Taylor and Parr (1952) and of Shull and Löwdin (1955) concerning the radial correlation of the He atom demonstrated a not fast enough convergence towards the experimental energy.

### 3) Extension of the method of open-shell configurations

This method has been extended by Shull and Löwdin (1956) to a few He-like ions, by Pratt (1956) and Brigrman and Matsen (1957) to the Li atom, by Burke and Mulligan (1958) to a few Li-like ions and by Hurst et al. (1958) for all the three-electron atomic systems of the second period of the periodic table. In these calculations open-shell configurations are introduced only for the filled ( $1s^2$ ) shell. As a result, the above authors all find an improvement in comparison with energy values obtained with "closed-shell" configurations. This agrees with the opinion, emphasized earlier by Mulliken (1952) and by Taylor and Parr (1952), that "shell-opening" should lead to a significant improvement in the calculated energy values.

The purpose of the present work is to apply the method of the shell-opening to the simple molecular ion  $\text{He}_2^+$  by performing variational calculations. Two approximations were carried out. In approximation A open-shell configurations are introduced only for the filled ( $1s^2$ ) shell of the He atom. In approximation B the idea of open-shells is further

developed and applied also to the half-filled (1 s) shell of the  $\text{He}^+$  ion. As far as the author knows this latter idea is the first attempt of this kind in the literature.

Throughout the calculations the atomic units of Hartree (1928) ( $1 e^2/a_0 = 27.2 \text{ ev}$ ,  $1 a_0 = 0.529 \text{ \AA}$ ) are used unless explicitly stated otherwise. The energy calculation was carried out at the nuclear separation  $R = 2 a_0 = 1.058 \text{ \AA}$ . The experimental equilibrium value is  $2.04 a_0 = 1.080 \text{ \AA}$ , but the choice of  $R = 2 a_0$  instead of  $R = 2.04 a_0$  allows a considerable simplification in the numerical work.

## II. Experimental methods for the measurement of the molecular constants of the $\text{He}_2^+$ molecule ion

### 1) Spectroscopic measurements

According to Herzberg (1950) the experimental equilibrium value of the internuclear distance is  $1.080 \text{ \AA}$  and the dissociation energy is  $3.1 \text{ ev}$ . Herzberg's value is based on the measurements of Weizel and Pestel (1929), and the dissociation energy is listed as uncertain. The molecular constants were determined from the analysis of the band spectrum of the excited  $\text{He}_2$  molecule. The spectral data were measured partly by Weizel and Pestel and partly by others (see references in this regard in the paper of Weizel and Pestel (1929)). They have found that the bands can be interpreted on the assumption

that in the excited  $\text{He}_2$  molecule only one electron is excited. With increasing excitation of this electron all molecular constants of the excited  $\text{He}_2$  molecule converge to those of the  $\text{He}_2^+$  molecule ion. On this basis they were determined by extrapolation. It is difficult to say how accurate the extrapolated values are since no estimate is given in this regard in the quoted references. The value of the equilibrium internuclear distance can be considered as quite accurate since the equilibrium internuclear distances of the various excited states of the  $\text{He}_2$  molecule lie in a very narrow interval (see Herzberg (1950) p. 535, 536).

## 2) Ion scattering measurements

Very recently Mason and Vanderslice (1958) have determined the dissociation energy from a theoretical analysis of ion scattering data. They made use of the measurements of Cramer and Simons (1957), and give the dissociation energy as 2.16 ev. In the experiments of Cramer and Simons beams of  $\text{He}^+$  ions of a wide energy range (4 - 400 ev) are scattered in He gas and the elastic scattering cross section is determined. For the description of the interaction between the He atom and the  $\text{He}^+$  ion Mason and Vanderslice have chosen a Morse curve. Of the three disposable parameters of the Morse function the elastic cross section data determine only

two and for this reason in the calculation of the dissociation energy the spectroscopically determined value of the equilibrium internuclear distance, 1.080 Å, has been applied. Mason and Vanderslice have the opinion that the calculated dissociation energy, 2.16 ev, is likely to be too small because the Morse function does not represent well the actual interaction curves at larger nuclear separations. (Concerning theory and details see the references in the papers by Mason and Vanderslice (1958) and by Cramer and Simons (1957).)

### III. Calculations

#### 1) Approximation A

##### 1a) Derivation of the energy expression

A molecular wave function corresponding to the  $\sum_u^{2+}$  symmetry (Herzberg (1950) p. 536) of the ground state of the  $\text{He}_2^+$  molecule ion of the form

$$\Psi = \Psi_1 + \Psi_2 - \Psi_3 - \Psi_4 \quad (1)$$

has been chosen, where the  $\Psi'$ 's are the following determinants

$$\Psi_1 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z', 1) \alpha(1) & \psi_a(z'', 1) \beta(1) & \psi_f(z''', 1) \alpha(1) \\ \psi_a(z', 2) \alpha(2) & \psi_a(z'', 2) \beta(2) & \psi_f(z''', 2) \alpha(2) \\ \psi_a(z', 3) \alpha(3) & \psi_a(z'', 3) \beta(3) & \psi_f(z''', 3) \alpha(3) \end{vmatrix} \quad (2.1)$$

$$\Psi_2 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z'', 1) \alpha(1) & \psi_a(z', 1) \beta(1) & \psi_f(z''', 1) \alpha(1) \\ \psi_a(z'', 2) \alpha(2) & \psi_a(z', 2) \beta(2) & \psi_f(z''', 2) \alpha(2) \\ \psi_a(z'', 3) \alpha(3) & \psi_a(z', 3) \beta(3) & \psi_f(z''', 3) \alpha(3) \end{vmatrix} \quad (2.2)$$

$$\Psi_3 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_f(z', 1) \alpha(1) & \psi_f(z'', 1) \beta(1) & \psi_a(z''', 1) \alpha(1) \\ \psi_f(z', 2) \alpha(2) & \psi_f(z'', 2) \beta(2) & \psi_a(z''', 2) \alpha(2) \\ \psi_f(z', 3) \alpha(3) & \psi_f(z'', 3) \beta(3) & \psi_a(z''', 3) \alpha(3) \end{vmatrix} \quad (2.3)$$

$$\Psi_4 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_f(z'', 1) \alpha(1) & \psi_f(z', 1) \beta(1) & \psi_a(z''', 1) \alpha(1) \\ \psi_f(z'', 2) \alpha(2) & \psi_f(z', 2) \beta(2) & \psi_a(z''', 2) \alpha(2) \\ \psi_f(z'', 3) \alpha(3) & \psi_f(z', 3) \beta(3) & \psi_a(z''', 3) \alpha(3) \end{vmatrix} \quad (2.4)$$

In (2.1-4)  $\alpha$  and  $\beta$  are the spin wave functions, corresponding to  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$  respectively, and the  $\psi'$ 's are hydrogenic 1s functions, namely

$$\psi_x(\gamma, i) = \left(\frac{\gamma^3}{\pi}\right)^{\frac{1}{2}} e^{-\gamma r_{xi}}, \quad (3)$$

where  $\gamma = z', z'', z'''$  are the effective charges,  $x = a, b$  denote the nuclei and the indices  $i = 1, 2, 3$  refer to the three electrons.

It can easily be shown by expanding the determinants in (2.1-4) and rearranging certain terms in (1) that the molecular wave function  $\bar{\Psi}$  can alternatively be written as

$$\begin{aligned} \bar{\Psi} = \frac{1}{\sqrt{3!}} \{ & [\psi_a(z', 1) \psi_a(z'', 2) + \psi_a(z'', 1) \psi_a(z', 2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ & \times \psi_b(z''', 3) \alpha(3) \\ & + [\psi_a(z', 2) \psi_a(z'', 3) + \psi_a(z'', 2) \psi_a(z', 3)] [\alpha(2)\beta(3) - \beta(2)\alpha(3)] \\ & \times \psi_b(z''', 1) \alpha(1) \\ & + [\psi_a(z', 3) \psi_a(z'', 1) + \psi_a(z'', 3) \psi_a(z', 1)] [\alpha(3)\beta(1) - \beta(3)\alpha(1)] \\ & \times \psi_b(z''', 2) \alpha(2) \\ & - [\psi_b(z', 1) \psi_b(z'', 2) + \psi_b(z'', 1) \psi_b(z', 2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ & \times \psi_a(z''', 3) \alpha(3) \\ & - [\psi_b(z', 2) \psi_b(z'', 3) + \psi_b(z'', 2) \psi_b(z', 3)] [\alpha(2)\beta(3) - \beta(2)\alpha(3)] \\ & \times \psi_a(z''', 1) \alpha(1) \\ & - [\psi_b(z', 3) \psi_b(z'', 1) + \psi_b(z'', 3) \psi_b(z', 1)] [\alpha(3)\beta(1) - \beta(3)\alpha(1)] \\ & \times \psi_a(z''', 2) \alpha(2) \} . \end{aligned} \quad (4)$$

From (4) it is seen that the wave function  $\bar{\Psi}$  is an algebraic sum of terms consisting of an Hylleraas-Eckart type wave function for a He atom multiplied by the wave function of a  $\text{He}^+$  ion. It is also seen that the wave function of the He atom is symmetric in the spatial coordinates and anti-symmetric in the spin part. Eq. (4) clearly shows that there is no Heitler-London type bond between the He atom and the  $\text{He}^+$  ion. For this reason in this model the stability of the  $\text{He}_2^+$  molecule ion must be entirely due to the exchange effect of the electrons.

The Hamiltonian of the system  $\text{He}_2^+$  is

$$H = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{1}{2}\Delta_3 - \frac{2}{r_{a1}} - \frac{2}{r_{a2}} - \frac{2}{r_{a3}} \quad (5)$$

$$- \frac{2}{r_{b1}} - \frac{2}{r_{b2}} - \frac{2}{r_{b3}} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} + \frac{4}{R} ;$$

where  $\Delta_i$  is the Laplace operator,  $r_{ai}$  and  $r_{bi}$  ( $i = 1, 2, 3$ ) are the distances between the  $i^{\text{th}}$  electron and nucleus a and b respectively,  $r_{ij}$  is the distance between the  $i^{\text{th}}$  and  $j^{\text{th}}$  electron and  $R$  is the internuclear distance.

According to the variational method the energy of a system described by a trial wave function  $\bar{\Phi}$  with variational parameters  $c_1, c_2, \dots$  can be calculated as

$$E(c_1, c_2, \dots) = \frac{\int \bar{\Phi}^* H \bar{\Phi} d\tau}{\int \bar{\Phi}^* \bar{\Phi} d\tau}, \quad (6)$$

where the \* denotes the complex conjugate of  $\Phi$  and the integration is extended over all of the space coordinates and spin coordinates. The minimum energy of the system can be found from the conditions

$$\frac{\partial E}{\partial c_1} = 0, \quad \frac{\partial E}{\partial c_2} = 0, \quad \dots$$

It is well known that those trial functions which satisfy certain general quantum mechanical requirements never can lead to a lower energy value than the true one.

In our case the molecular wave function  $\Psi$  is real so (6) assumes the form

$$E(z', z'', z''') = \frac{\int \Psi H \Psi d\tau}{\int \Psi^2 d\tau} = \frac{W}{N}. \quad (7)$$

As the analytical differentiation of  $E$  with respect to the variational parameters is impracticable the energy minimum is found numerically.

The various molecular integrals arising from (7) (66 in number) have been calculated with the formulae of Roothaan (1951), except the exchange-coulomb and exchange integrals, which have been evaluated according to the works of Rüdénberg (1951), and Rüdénberg, Roothaan and Jaunzemis (1956)\*. The problem of the evaluation of the exchange-coulomb and exchange integrals will be discussed in more detail in Appendices 1, and 2.

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\*In references Roothaan (1951) and Rüdénberg (1951) there are some errors which were later corrected in a paper by Roothaan and Rüdénberg (1954).

Defining the quantities

$$H_{ij} = \int \bar{\Psi}_i H \Psi_j d\tau \quad i = 1, 2, 3, 4 \quad (8)$$

$$S_{ij} = \int \bar{\Psi}_i \Psi_j d\tau \quad j = 1, 2, 3, 4$$

the energy expression (7) can be brought to the form

$$W = H_{11} + 2H_{12} + H_{22} - H_{13} - 2H_{14} - H_{24} \quad (9.1)$$

$$N = S_{11} + 2S_{12} + S_{22} - S_{13} - 2S_{14} - S_{24} \quad (9.2)$$

In deriving (9.1) and (9.2) it has been considered that by interchanging a and b

$$\begin{aligned} \bar{\Psi}_1 &\rightarrow \bar{\Psi}_3 & \Psi_3 &\rightarrow \Psi_1 \\ \bar{\Psi}_2 &\rightarrow \bar{\Psi}_4 & \Psi_4 &\rightarrow \Psi_2 \end{aligned} \quad (10)$$

and that the Hamiltonian (5) is hermitian and invariant under the interchange of a and b and under the permutation of 1, 2, 3. These symmetry properties together with (10) established the following simplifying relations

$$\begin{aligned} H_{11} &= H_{33} & S_{11} &= S_{33} \\ H_{22} &= H_{44} & S_{22} &= S_{44} \\ H_{12} &= H_{34} & S_{12} &= S_{34} \\ H_{23} &= H_{14} & S_{14} &= S_{23} \end{aligned} \quad (11)$$

As a next step, using (8), we integrate over the spin coordinates considering the following normality and orthogonality properties of the spin functions  $\alpha$  and  $\beta$

$$\int \alpha(i) \alpha(i) d\sigma_i = 1$$

$$\int \beta(i) \beta(i) d\sigma_i = 1 \quad i = 1, 2, 3.$$

(12)

$$\int \alpha(i) \beta(i) d\sigma_i = 0$$

After this integration the  $H_{ij}$  and  $S_{ij}$  quantities are only functions of the space coordinates and can be brought to the form

$$H_{11} = H_{aab, aab}^{123, 123} (z' z'' z''', z' z'' z''')$$

$$- H_{aab, aab}^{i23, 321} (z' z'' z''', z' z'' z''')$$

$$H_{22} = H_{aab, aab}^{123, 123} (z' z'' z''', z' z'' z''')$$

$$- H_{aab, aab}^{123, 132} (z' z'' z''', z' z'' z''')$$

$$H_{12} = H_{aab, aab}^{123, 213} (z' z'' z''', z' z'' z''')$$

$$- H_{aab, aab}^{123, 231} (z' z'' z''', z' z'' z''')$$

(13.1)

$$H_{13} = H_{aab, bba}^{123, 123} (z' z'' z''', z' z'' z''')$$

$$- H_{aab, bba}^{123, 321} (z' z'' z''', z' z'' z''')$$

$$H_{14} = H_{aab, bba}^{123, 213} (z' z'' z''', z' z'' z''')$$

$$- H_{aab, bba}^{123, 231} (z' z'' z''', z' z'' z''')$$

$$H_{24} = H_{aab, bba}^{123, 123} (z' z'' z''', z' z'' z''')$$

$$- H_{aab, bba}^{123, 132} (z' z'' z''', z' z'' z''')$$

and

$$S_{11} = S_{aab, aab}^{123, 123} (z'z''z''', z'z''z''') \\ - S_{aab, aab}^{123, 321} (z'z''z''', z'z''z''')$$

$$S_{22} = S_{aab, aab}^{123, 123} (z'z''z''', z'z''z''') \\ - S_{aab, aab}^{123, 132} (z'z''z''', z'z''z''')$$

$$S_{12} = S_{aab, aab}^{123, 213} (z'z''z''', z'z''z''') \\ - S_{aab, aab}^{123, 213} (z'z''z''', z'z''z''')$$

$$S_{13} = S_{aab, bba}^{123, 123} (z'z''z''', z'z''z''') \\ - S_{aab, bba}^{123, 321} (z'z''z''', z'z''z''')$$

(13.2)

$$S_{14} = S_{aab, bba}^{123, 213} (z'z''z''', z'z''z''') \\ - S_{aab, bba}^{123, 231} (z'z''z''', z'z''z''')$$

$$S_{24} = S_{aab, bba}^{123, 123} (z'z''z''', z'z''z''') \\ - S_{aab, bba}^{123, 132} (z'z''z''', z'z''z''') .$$

In eqs. (13.1) and (13.2) the quantities on the right hand side are defined by

$$H_{aab, aab}^{123, ijk} (z'z''z''', z'z''z''') = \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_f(z''', 3) H \psi_a(z', i) \psi_a(z'', j) \psi_f(z''', k) dv_1 dv_2 dv_3 \quad (14.1)$$

$$H_{aab, bba}^{123, ijk} (z'z''z''', z'z''z''') = \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_f(z''', 3) H \psi_f(z', i) \psi_f(z'', j) \psi_a(z''', k) dv_1 dv_2 dv_3$$

and

$$S_{aab, aab}^{123, ijk} (z'z''z''', z'z''z''') = \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_f(z''', 3) \cdot \psi_a(z', i) \psi_a(z'', j) \psi_f(z''', k) dv_1 dv_2 dv_3 \quad (14.2)$$

$$S_{aab, bba}^{123, ijk} (z'z''z''', z'z''z''') = \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_f(z''', 3) \cdot \psi_f(z', i) \psi_f(z'', j) \psi_a(z''', k) dv_1 dv_2 dv_3,$$

where both in (14.1) and (14.2)

$ijk = 123, 213, 321, 132, 231$  .

Inserting the Hamiltonian from (5) into (13.1) and integrating over the configurational space, of which the volume element is  $dv = dv_1 dv_2 dv_3$ , the energy expression can be expressed in terms of molecular integrals. The result is

$$\begin{aligned}
 H_{aab, aab}^{123, 123} (z^1 z^2 z^3, z^1 z^2 z^3) &= k_{aa} (z^1, z^1) + k_{aa} (z^2, z^2) + k_{aa} (z^3, z^3) \\
 &+ p_{aa}^a (z^1, z^1) + p_{aa}^a (z^2, z^2) + p_{aa}^a (z^3, z^3) + p_{bb}^a (z^1, z^1) + p_{bb}^a (z^2, z^2) + p_{bb}^a (z^3, z^3) \\
 &+ p_{aa, aa} (z^1 z^1, z^2 z^2) + p_{aa, bb} (z^1 z^1, z^3 z^3) + p_{aa, bb} (z^2 z^2, z^3 z^3) + \frac{4}{R}.
 \end{aligned} \tag{15.1}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 321} (z^1 z^2 z^3, z^1 z^2 z^3) &= 2 f_{ab} (z^1, z^3) \{ k_{ab} (z^1, z^3) + p_{ab}^a (z^1, z^3) + p_{ab}^a (z^3, z^1) \} \\
 &+ f_{ab}^2 (z^1, z^3) \{ k_{aa} (z^2, z^2) + p_{aa}^a (z^2, z^2) + p_{bb}^a (z^2, z^2) \} + 2 f_{ab} (z^1, z^3) p_{aa, ab} (z^2 z^2, z^1 z^1) \\
 &+ p_{ab, ab} (z^1 z^3, z^1 z^3) + f_{ab}^2 (z^1, z^3) \frac{4}{R}.
 \end{aligned} \tag{15.2}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 213} (z^1 z^2 z^3, z^1 z^2 z^3) &= 2 f_{aa} (z^1, z^2) \{ k_{aa} (z^1, z^2) + p_{aa}^a (z^1, z^2) + p_{bb}^a (z^1, z^2) \} \\
 &+ f_{aa}^2 (z^1, z^2) \{ k_{aa} (z^3, z^3) + p_{aa}^a (z^3, z^3) + p_{bb}^a (z^3, z^3) \} \\
 &+ 2 f_{aa} (z^1, z^2) p_{aa, bb} (z^1 z^1, z^3 z^3) + p_{aa, aa} (z^1 z^1, z^2 z^2) + f_{aa}^2 (z^1, z^2) \frac{4}{R}.
 \end{aligned} \tag{15.3}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 231} (z^1 z^2 z^3, z^1 z^2 z^3) &= f_{aa} (z^1, z^2) f_{ab} (z^1, z^3) \{ k_{ab} (z^2, z^3) \\
 &+ p_{ab}^a (z^2, z^3) + p_{ab}^a (z^3, z^2) \} + f_{ab} (z^2, z^3) f_{ab} (z^1, z^3) \{ k_{aa} (z^1, z^2) + p_{aa}^a (z^1, z^2) \\
 &+ p_{bb}^a (z^1, z^2) \} + f_{aa} (z^1, z^2) f_{ab} (z^2, z^3) \{ k_{ab} (z^1, z^3) + p_{ab}^a (z^1, z^3) + p_{ab}^a (z^3, z^1) \} \\
 &+ f_{ab} (z^1, z^3) p_{aa, ab} (z^1 z^2, z^2 z^3) + f_{ab} (z^2, z^3) p_{aa, ab} (z^1 z^1, z^1 z^3) \\
 &+ f_{aa} (z^1, z^2) p_{ab, ab} (z^1 z^3, z^2 z^3) + f_{aa} (z^1, z^2) f_{ab} (z^1, z^3) f_{ab} (z^2, z^3) \frac{4}{R}.
 \end{aligned} \tag{15.4}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 132} (z'z''z''', z'z''z''') &= 2f_{ab}(z'', z''') \{ k_{ab}(z'', z''') + p_{ab}^a(z'', z''') \\
 &+ p_{ab}^a(z''', z'') \} + f_{ab}^2(z'', z''') \{ k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z') \} \\
 &+ 2f_{ab}(z'', z''') p_{aa, ab}(z'z', z''z''') + p_{ab, ab}(z''z''', z''z''') + f_{ab}^2(z'', z''') \frac{4}{R}.
 \end{aligned} \tag{15.5}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 213} (z'z''z''', z'z''z''') &= 2f_{ab}(z', z'') f_{ab}(z''', z''') \{ k_{ab}(z', z'') \\
 &+ p_{ab}^a(z', z'') + p_{ab}^a(z''', z''') \} + f_{ab}^2(z', z'') \{ k_{ab}(z''', z''') + 2p_{ab}^a(z''', z''') \} \\
 &+ 2f_{ab}(z', z'') p_{ab, ab}(z'z'', z''z''') + f_{ab}(z''', z''') p_{ab, ab}(z'z'', z''z''') \\
 &+ f_{ab}^2(z', z'') f_{ab}(z''', z''') \frac{4}{R}.
 \end{aligned} \tag{15.6}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 231} (z'z''z''', z'z''z''') &= f_{aa}(z', z''') f_{ab}(z', z'') \{ k_{aa}(z'', z''') + p_{aa}^a(z'', z''') \\
 &+ p_{bb}^a(z'', z''') \} + f_{aa}(z', z''') f_{aa}(z'', z''') \{ k_{ab}(z', z'') + p_{ab}^a(z'', z') + p_{ab}^a(z', z'') \} \\
 &+ f_{aa}(z'', z''') f_{ab}(z', z'') \{ k_{aa}(z', z''') + p_{aa}^a(z', z''') + p_{bb}^a(z', z''') \} \\
 &+ f_{aa}(z', z''') p_{aa, ab}(z''z''', z'z'') + f_{ab}(z', z'') p_{aa, bb}(z'z''', z''z''') \\
 &+ f_{aa}(z'', z''') p_{aa, ab}(z'z''', z''z') + f_{aa}(z', z''') f_{aa}(z'', z''') f_{ab}(z', z'') \frac{4}{R}.
 \end{aligned} \tag{15.7}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 123} (z'z''z''', z'z''z''') &= f_{ab}(z'', z'') f_{ab}(z''', z''') \{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} \\
 &+ f_{ab}(z', z') f_{ab}(z'', z'') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} + f_{ab}(z', z') f_{ab}(z'', z'') \{k_{ab}(z''', z''') \\
 &+ 2p_{ab}^a(z''', z''')\} + f_{ab}(z', z') p_{ab, ab}(z''z'', z''z''') + f_{ab}(z'', z'') p_{ab, ab}(z'z', z''z''') \\
 &+ f_{ab}(z''', z''') p_{ab, ab}(z'z', z''z'') + f_{ab}(z', z') f_{ab}(z'', z'') f_{ab}(z''', z''') \frac{4}{R}.
 \end{aligned} \tag{15.8}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 321} (z'z''z''', z'z''z''') &= 2f_{aa}(z', z''') f_{ab}(z'', z'') \{k_{aa}(z', z''') \\
 &+ p_{aa}^a(z', z''') + p_{bb}^a(z', z''')\} + f_{aa}^2(z', z''') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} \\
 &+ 2f_{aa}(z', z''') p_{aa, ab}(z'z''', z''z'') + f_{ab}(z'', z'') p_{aa, bb}(z'z''', z'z''') \\
 &+ f_{aa}^2(z', z''') f_{ab}(z'', z'') \frac{4}{R}.
 \end{aligned} \tag{15.9}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 132} (z'z''z''', z'z''z''') &= 2f_{aa}(z'', z''') f_{ab}(z', z') \{k_{aa}(z'', z''') \\
 &+ p_{aa}^a(z'', z''') + p_{bb}^a(z'', z''')\} + f_{aa}^2(z'', z''') \{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} \\
 &+ 2f_{aa}(z'', z''') p_{aa, ab}(z''z''', z'z') + f_{ab}(z', z') p_{aa, bb}(z''z''', z''z''') \\
 &+ f_{aa}^2(z'', z''') f_{ab}(z', z') \frac{4}{R}.
 \end{aligned} \tag{15.10}$$

$$S_{aab, aab}^{123, 123} (z'z''z''', z'z''z''') = 1 \quad (16.1)$$

$$S_{aab, aab}^{123, 321} (z'z''z''', z'z''z''') = f_{ab}^2 (z', z''') \quad (16.2)$$

$$S_{aab, aab}^{123, 213} (z'z''z''', z'z''z''') = f_{aa}^2 (z', z'') \quad (16.3)$$

$$S_{aab, aab}^{123, 231} (z'z''z''', z'z''z''') = f_{aa} (z', z'') f_{ab} (z', z''') f_{ab} (z'', z''') \quad (16.4)$$

$$S_{aab, aab}^{123, 132} (z'z''z''', z'z''z''') = f_{ab}^2 (z'', z''') \quad (16.5)$$

$$S_{aab, bba}^{123, 213} (z'z''z''', z'z''z''') = f_{ab}^2 (z', z'') f_{ab} (z''', z''') \quad (16.6)$$

$$S_{aab, bba}^{123, 231} (z'z''z''', z'z''z''') = f_{aa} (z', z''') f_{aa} (z'', z''') f_{ab} (z', z'') \quad (16.7)$$

$$S_{aab, bba}^{123, 123} (z'z''z''', z'z''z''') = f_{ab} (z', z') f_{ab} (z'', z'') f_{ab} (z''', z''') \quad (16.8)$$

$$S_{aab, bba}^{123, 321} (z'z''z''', z'z''z''') = f_{aa}^2 (z', z''') f_{ab} (z'', z'') \quad (16.9)$$

$$S_{aab, bba}^{123, 132} (z'z''z''', z'z''z''') = f_{aa}^2 (z'', z''') f_{ab} (z', z'). \quad (16.10)$$

The molecular integrals in (15.1-10) and (16.1-10) belong to several types which are defined below. It is noted that in order to unify the notations extensive use has been made of the invariance properties of the Hamiltonian. The different integral types are defined so that they can be obtained as special cases of general arguments.\* The

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\*The arguments  $\alpha$  and  $\beta$  are not to be confused with the spin functions.

arguments denoted by a star refer to integrals which will appear only in the second approximation, discussed later on.

1b) Definition and classification of the integrals

A. Atomic types

1. One-electron one-center integrals

i) Non-orthogonality integrals:

$$f_{aa}(\alpha, \beta) = \int \psi_a(\alpha, i) \psi_a(\beta, i) dv_i \quad (17)$$

$$(\alpha, \beta) = (z', z''); (z', z'''); (z'', z''').$$

ii) Kinetic energy integrals:

$$k_{aa}(\alpha, \beta) = \int \psi_a(\alpha, i) \left(-\frac{1}{2} \Delta_i\right) \psi_a(\beta, i) dv_i \quad (18)$$

$$(\alpha, \beta) = (z', z'); (z'', z''); (z''', z'''); (z', z''); (z', z'''); (z'', z''').$$

iii) Nuclear attraction integrals:

$$p_{aa}^a(\alpha, \beta) = \int \psi_a(\alpha, i) \left(-\frac{2}{r_{ai}}\right) \psi_a(\beta, i) dv_i \quad (19)$$

$$(\alpha, \beta) = (z', z'); (z'', z''); (z''', z'''); (z', z''); (z', z'''); (z'', z''').$$

2. Two-electron one-center integrals

i) Coulomb integrals:

$$p_{aa,aa}(\alpha\alpha, \gamma\gamma) = \iint \psi_a(\alpha, i) \psi_a(\alpha, i) \left(\frac{1}{r_{ij}}\right) \psi_a(\gamma, j) \psi_a(\gamma, j) dv_i dv_j \quad (20)$$

$$(\alpha\alpha, \gamma\gamma) = (z'z', z''z'').$$

ii) Exchange integrals:

$$p_{aa,aa}(\alpha\beta, \gamma\delta) = \iint \psi_a(\alpha, i) \psi_a(\beta, i) \left(\frac{1}{r_{ij}}\right) \psi_a(\gamma, j) \psi_a(\delta, j) dv_i dv_j \quad (21)$$

$$(\alpha\beta, \gamma\delta) = (z'z'', z'z'').$$

B. Molecular types

1. One-electron two-center integrals

i) Overlap integrals:

$$f_{ab}(\alpha, \beta) = \int \psi_a(\alpha, i) \psi_b(\beta, i) dv_i \quad (22)$$

$$(\alpha, \beta) = (z', z'); (z'', z''); (z''', z'''); (z', z''); (z', z'''); (z'', z''').$$

ii) Kinetic energy integrals:

$$k_{ab}(\alpha, \beta) = \int \psi_a(\alpha, i) \left(-\frac{1}{2} \Delta_i\right) \psi_b(\beta, i) dv_i \quad (23)$$

$$(\alpha, \beta) = (z', z'); (z'', z''); (z''', z'''); (z', z''); (z', z'''); (z'', z''').$$

iii) Coulomb type nuclear attraction integrals:

$$p_{ab}^a(\alpha, \beta) = \int \psi_a(\alpha, i) \left(-\frac{Z}{r_{ai}}\right) \psi_b(\beta, i) dv_i \quad (24)$$

$$(\alpha, \beta) = (z', z'); (z'', z''); (z''', z'''); (z', z''); (z', z'''); (z'', z''').$$

iiii) Exchange type nuclear attraction integrals:

$$p_{ab}^a(\alpha, \beta) = \int \psi_a(\alpha, i) \left(-\frac{Z}{r_{ai}}\right) \psi_b(\beta, i) dv_i \quad (25)$$

$$(\alpha, \beta) = (z', z'); (z'', z''); (z''', z'''); (z', z''); (z'', z'); (z', z'''); (z''', z'); (z'', z'''); (z''', z'').$$

2. Two-electron two-center integrals

i) Coulomb integrals

$$p_{aa,bb}(\alpha\beta, \gamma\delta) = \iint \psi_a(\alpha, i) \psi_a(\beta, i) \left(\frac{1}{r_{ij}}\right) \psi_b(\gamma, j) \psi_b(\delta, j) dv_i dv_j \quad (26)$$

$$(\alpha\beta, \gamma\delta) = (z'z', z''z'''); (z''z'', z''z'''); (z'z'', z''z'''); (z'z''', z''z'''); (z'z'', z''z'''); (z'z', z'z')^*; (z'z', z''z'')^*; (z'z', z'z'')^*; (z'z'', z'z'')^*; (z''z'', z''z'')^*; (z'z'', z''z'')^*.$$

ii) Exchange-coulomb integrals:

$$P_{aa,ab}(\alpha\beta,\gamma\delta) = \iint \psi_a(\alpha,i) \psi_a(\beta,i) \left(\frac{1}{r_{ij}}\right) \psi_a(\gamma,j) \psi_b(\delta,j) dv_i dv_j \quad (27)$$

$$(\alpha\beta,\gamma\delta) = (z''z'', z'z'''); (z'z', z''z'''); (z'z'', z''z''');$$

$$(z'z'', z'z'''); (z''z''', z'z''); (z''z''', z'z');$$

$$(z'z''', z''z'); (z'z''', z''z''); (z''z'', z'z')^*;$$

$$(z'z', z''z')^*; (z'z'', z''z')^*; (z'z'', z'z')^*;$$

$$(z'z', z''z'')^*; (z'z'', z'z'')^*; (z''z'', z'z'')^*;$$

$$(z'z'', z''z'')^*.$$

iii) Exchange integrals:

$$P_{ab,ab}(\alpha\beta,\gamma\delta) = \iint \psi_a(\alpha,i) \psi_b(\beta,i) \left(\frac{1}{r_{ij}}\right) \psi_a(\gamma,j) \psi_b(\delta,j) dv_i dv_j \quad (28)$$

$$(\alpha\beta,\gamma\delta) = (z'z', z''z''); (z'z', z''z'''); (z''z'', z''z''');$$

$$(z''z''', z''z'''); (z'z''', z'z'''); (z'z'', z''z');$$

$$(z'z'', z''z'''); (z'z''', z''z'''); (z'z', z'z')^*;$$

$$(z'z'', z'z'')^*; (z'z', z''z')^*; (z''z'', z''z'')^*;$$

$$(z'z'', z''z'')^*.$$

The atomic type integrals are functions of only  $z', z'', z'''$  and can easily be evaluated in spherical polar coordinates. The molecular type integrals are functions of the variational parameters  $z', z'', z'''$  and of the internuclear distance  $R$  and can be evaluated in elliptic coordinates. Explicit formulae for the simpler ones are given in the quoted literature and these will not be discussed further here. However, no explicit formulae can be found in the literature for the exchange-coulomb and exchange integrals and for this reason they will be given in Appendices 1 and 2.

At this point it may be added that the wave function (1) describes only one of the doublet components of the ground state of the  $\text{He}_2^+$  molecule ion. Another doublet component is described by a similar wave function, differing from (1) only in the interchange of spin  $\alpha$  by spin  $\beta$  in the last column of determinants (2.1-4). Since no external magnetic field is present and the Hamiltonian (5) does not include the spin-orbit interaction the second doublet component leads to the same energy level. Due to the spin degeneracy the most general wave function is the superposition of the wave functions of the two doublet components. This, however, as a consequence of the orthogonality relations of the spin functions leads to the same energy level.

#### 1c) Discussion of the calculation

The molecular energy at  $R = 2 a_0$  was first calculated with the values of the parameters  $z_0^I, z_0^{II}, z_0^{III}$  that correspond to the system of a He atom and of a  $\text{He}^+$  ion at infinite separation. The energy so obtained is, of course, a very rough estimate and is useful only as a reference point. The energy at  $R = 2 a_0$  is then calculated by the variational method in which the effective charges  $z^I, z^{II}, z^{III}$  are varied.

The initial set of parameter values is denoted by  $z_0^I, z_0^{II}$  and  $z_0^{III}$  and the corresponding energy by  $E(z_0^I, z_0^{II}, z_0^{III})$ . In this work the  $z_0^I = 2.15$  and  $z_0^{II} = 1.19$  values are used for the He atom, as determined by P. Rosen (1950), and, of course,  $z_0^{III} = 2.00$  for the  $\text{He}^+$  ion.

Variation of  $z'$  only, while  $z_0''$ ,  $z_0'''$  are kept fixed, does not improve significantly the energy value obtained with the set  $z_0'$ ,  $z_0''$ ,  $z_0'''$ . The gain is only  $E(z_0', z_0'', z_0''') - E(z_0', z_0'', z_0''') = -0.03$  ev. This is understandable since the "inner shell", characterized by  $z'$ , is very tight around the nucleus and therefore it is only slightly effected in the binding.

Variation of  $z''$  only, while  $z_0'$ ,  $z_0'''$  are kept fixed, leads to a significant improvement compared with the value obtained with the set  $z_0'$ ,  $z_0''$ ,  $z_0'''$ . The gain is  $E(z_0', z_0'', z_0''') - E(z_0', z_0'', z_0''') = -0.38$  ev. The shell, characterized by  $z''$ , is the more loosely bound "outer shell" and therefore it enters in a more effective way in the binding.

One can observe a marked analogy with molecules consisting of atoms with closed electron shells. It is well known that in such cases the bond formation is restricted to the valence electrons and the orbits of the atomic core are not greatly affected. In the Hylleraas-Eckart type open-shell configuration for the He atom/<sup>the</sup>"inner shell", according to the results of the variation, plays the role of the core and the "outer shell" the role of the valence shell.

Variation of  $z'''$  only, with the fixed values of  $z_0'$  and  $z_0''$ , proves to be effective also. It leads to an improvement of  $E(z_0', z_0'', z_0''') - E(z_0', z_0'', z_0''') = -0.27$  ev.

The variational results are given in Tables 1, 2, 3 and 4. Table 4 gives an idea of the energy surface containing the data of Tables 2 and 3 together with a few energy values obtained with the simultaneous variation of  $z''$  and  $z'''$  while  $z_0'$  was kept fixed.

Table 1. The molecular energy (in units  $e^2/a_0$ )  
as a function of  $z'$   
 $R = 2 a_0$

$z'$	$E(z', z_0'', z_0''')$
2.10	-4.915
2.15 = $z_0'$	-4.921
2.20	-4.922*

\* Minimum, as can be shown by fitting a parabola.

Table 2. The molecular energy (in units  $e^2/a_0$ )  
as a function of  $z''$   
 $R = 2 a_0$

$z''$	$E(z_0', z'', z_0''')$
1.19 = $z_0''$	-4.921
1.28	-4.930
1.34	-4.934
1.40	-4.935*
1.55	-4.926

\* Best value obtained in Approximation A.

Table 3. The molecular energy (in units  $e^2/a_0$ )  
as a function of  $z'''$   
 $R = 2 a_0$

$z'''$	$E(z_0', z_0'', z''')$
1.75	-4.931
1.85	-4.929
2.00 = $z_0'''$	-4.921
2.15	-4.905

Table 4. The molecular energy (in units  $e^2/a_0$ )  
as a function of  $z''$  and  $z'''$

$$z'_0 = 2.15$$

$$R = 2 a_0$$

$z''$	$z'''$	1.75	1.85	1.90	2.00	2.15
1.19		-4.931	-4.929		-4.921	-4.905
1.28					-4.930	
1.32				-4.929		
1.34					-4.933	
1.40		-4.908			-4.935	
1.55					-4.926	

One definite result is the fact that the "correlation splitting" is less in the  $\text{He}_2^+$  molecule ion than in the He atom. According to Shull and Löwdin's (1956) terminology one can write

$$z' = \eta (1 + \nu)$$

$$z'' = \eta (1 - \nu)$$

and call  $\nu$  the "splitting factor". They have shown that this factor decreases from  $\text{H}^-$  to  $\text{C}^{4+}$  as the ratio of the negative charges to the positive charges decreases. For the free He atom  $\nu = 0.287$  (with P. Rosen's (1950) values) while for the  $\text{He}_2^+$  molecule  $\nu = 0.211$  with  $z' = 2.15$  and  $z'' = 1.40$ .

1d) Discussion of other authors' calculations on the  $\text{He}_2^+$

Previous works done on the  $\text{He}_2^+$  molecule ion are those of Pauling (1933) (in two approximations), Majorana (1931),

Weinbaum (1935), and Moiseiwitsch (1956). The molecular wave functions of these authors, except that of Moiseiwitsch (1956), are special cases of function (1). The calculations of Pauling, Majorana and Weinbaum are based on closed-shell configurations. Their wave function is of the form

$$\Psi = \Psi' - \Psi'' , \quad (29)$$

where

$$\Psi' = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z_a, 1)\alpha(1) & \psi_a(z_a, 1)\beta(1) & \psi_b(z_i, 1)\alpha(1) \\ \psi_a(z_a, 2)\alpha(2) & \psi_a(z_a, 2)\beta(2) & \psi_b(z_i, 2)\alpha(2) \\ \psi_a(z_a, 3)\alpha(3) & \psi_a(z_a, 3)\beta(3) & \psi_b(z_i, 3)\alpha(3) \end{vmatrix} \quad (30.1)$$

$$\Psi'' = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_b(z_a, 1)\alpha(1) & \psi_b(z_a, 1)\beta(1) & \psi_a(z_i, 1)\alpha(1) \\ \psi_b(z_a, 2)\alpha(2) & \psi_b(z_a, 2)\beta(2) & \psi_a(z_i, 2)\alpha(2) \\ \psi_b(z_a, 3)\alpha(3) & \psi_b(z_a, 3)\beta(3) & \psi_a(z_i, 3)\alpha(3) \end{vmatrix} . \quad (30.2)$$

The one-electron functions are defined by

$$\psi_x(z_y, i) = \left(\frac{z_y^3}{\pi}\right)^{\frac{1}{2}} e^{-z_y r_{xi}} \quad \begin{array}{l} i = 1, 2, 3 \\ x = a, b \end{array} \quad (31)$$

$$z_y = z_a, z_i,$$

where  $z_a$  is the effective charge for the electrons of the He atom and  $z_i$  is that one for the electron of the  $\text{He}^+$  ion.

(29) can easily be derived from (1) if one lets the two concentric shells coincide by putting  $z' = z'' = z_a$  and  $z''' = z_i$ . In this case

$$\Psi_1 = \Psi_2 = \Psi'$$

and

$$\Psi_3 = \Psi_4 = \Psi''$$

which leads to eq. (29).

By expanding the determinants on the right hand side of (29) the molecular wave function of the closed-shell approximations can be written as

$$\begin{aligned} \bar{\Psi} = \frac{1}{\sqrt{3!}} \{ & \psi_a(z_{a,1}) \psi_a(z_{a,2}) [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \times \psi_f(z_i,3) \alpha(3) \\ & + \psi_a(z_{a,2}) \psi_a(z_{a,3}) [\alpha(2)\beta(3) - \beta(2)\alpha(3)] \times \psi_f(z_i,1) \alpha(1) \\ & + \psi_a(z_{a,3}) \psi_a(z_{a,1}) [\alpha(3)\beta(1) - \beta(3)\alpha(1)] \times \psi_f(z_i,2) \alpha(2) \\ & - \psi_f(z_{a,1}) \psi_f(z_{a,2}) [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \times \psi_a(z_i,3) \alpha(3) \\ & - \psi_f(z_{a,2}) \psi_f(z_{a,3}) [\alpha(2)\beta(3) - \beta(2)\alpha(3)] \times \psi_a(z_i,1) \alpha(1) \\ & - \psi_f(z_{a,3}) \psi_f(z_{a,1}) [\alpha(3)\beta(1) - \beta(3)\alpha(1)] \times \psi_a(z_i,2) \alpha(2) \}. \end{aligned} \quad (32)$$

It is seen from (32) that the spatial wave function of the He atom is of the Frenkel type

$$\psi(z,1) \psi(z,2), \quad (33)$$

which is a special case of the Hylleraas-Eckart type spatial wave function

$$\psi(z',1) \psi(z'',2) + \psi(z'',1) \psi(z',2). \quad (34)$$

The earlier calculations of other authors are described as follows:

1) If  $z_a = z_i = 2.00$ , we have Pauling's (1933) first approximation. The  $E_{\text{calc}}(R_{\infty})$  value is that one which can be obtained for a He atom by a first order perturbation calculation (Pauling and Wilson (1935) p. 162), plus  $- 2.000 e^2/a_0$ , which is the energy of the  $\text{He}^+$  ion.

2) If  $z_a = z_i$  is varied, we have Pauling's (1933) second approximation. The  $E_{\text{calc}}(R_{\infty})$  value can be obtained if one minimizes the energy of the He atom and of the  $\text{He}^+$  ion when all one-electron functions have the same effective charge.

3) If  $z_a$  and  $z_i$  are taken as two independent variational parameters we have Weinbaum's (1935) result. In this case the  $E_{\text{calc}}(R_{\infty})$  value is the sum of the separately minimized energies of the He atom (Pauling and Wilson (1935) p. 184) and of the  $\text{He}^+$  ion.

4) Moiseiwitsch (1956) uses the same function as described by (1) and (2.1-4) but instead of varying the effective charges  $z'$ ,  $z''$  and  $z'''$  he assigns fixed values ( $z' = 2.19$ ,  $z'' = 1.18$ ,  $z''' = 2.00$ ) to them. His assumption that variation of the effective charges would only negligibly improve the value derived with  $z'_0$ ,  $z''_0$ ,  $z'''_0$ , is not borne out here since relative to  $E(z'_0, z''_0, z'''_0)$  a lowering of 0.38 ev is obtained by the variational method.

5) Majorana's (1931) work is the same as that of

Pauling's (1933) first approximation, except that he has chosen  $z' = z'' = z''' = 1.8$ , which seems to be arbitrary.

The molecular energy derived by closed-shell calculations is compared with the present open-shell calculation in Table 5.

TABLE 5. Molecular energy derived by closed-shell calculations and by the present calculation

Author	$E_{\text{calc}} (R_e)$ (in $e^2/a_0$ )	Nuclear separation (in Å)	$E_{\text{calc}} (R_\infty)$ (in $e^2/a_0$ )
Pauling 1st appr.	-4.865*	1.01	-4.750
Pauling 2nd appr.	-4.906	1.085	-4.815
Weinbaum	-4.930	1.097	-4.848
Present calc.	-4.935	1.058	-4.875

\* Pauling (1933) originally gave -4.857 but Moiseiwitsch (1956) after recalculation found -4.865.

The internuclear distance in Table 5 is nearly the same in every approximation. The listed values are calculated equilibrium values, except that of the present calculation, where the choice of the  $R = 2 a_0 = 1.058 \text{ Å}$  value makes the comparison possible. It is seen from

Table 5, that the more parameters the molecular wave function has, the lower is the value of the molecular energy, which is in accordance with the variational principle.

It is also seen from Table 5 that an improvement in the molecular wave function lowers the energy of the system at  $R = R_{\infty}$  more than that at  $R = R_e$ , which makes the calculation of the energy of the molecular system  $\text{He}_2^+$  more difficult than that of the atomic system He. This is shown in Table 6 for the various approximations.

TABLE 6. The improvement (in units ev) between subsequent approximations at equilibrium and at infinite internuclear distance

Between Approximations	$E_{\text{calc}} (R_e)$	$E_{\text{calc}} (R_{\infty})$
Pauling 2nd and Pauling 1st	-1.12	-1.77
Weinbaum and Pauling 2nd	-0.653	-0.898
Present calc. and Weinbaum	-0.136	-0.734

2) Approximation B

2a) Derivation of the energy expression

Another wave function of the form

$$\Psi = \Psi_{\text{I}} + \lambda \Psi_{\text{II}} \quad (35)$$

has also been tried where  $\lambda$  is a variational parameter and

$$\Psi_{\text{I}} = \Psi_1 + \Psi_2 - \Psi_3 - \Psi_4 \quad (36)$$

$$\Psi_{\text{II}} = \Psi_5 + \Psi_6 - \Psi_7 - \Psi_8 \quad (37)$$

with

$$\Psi_1 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z',1)\alpha(1) & \psi_a(z'',1)\beta(1) & \psi_f(z',1)\alpha(1) \\ \psi_a(z',2)\alpha(2) & \psi_a(z'',2)\beta(2) & \psi_f(z',2)\alpha(2) \\ \psi_a(z',3)\alpha(3) & \psi_a(z'',3)\beta(3) & \psi_f(z',3)\alpha(3) \end{vmatrix} \quad (38.1)$$

$$\Psi_2 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z'',1)\alpha(1) & \psi_a(z',1)\beta(1) & \psi_f(z',1)\alpha(1) \\ \psi_a(z'',2)\alpha(2) & \psi_a(z',2)\beta(2) & \psi_f(z',2)\alpha(2) \\ \psi_a(z'',3)\alpha(3) & \psi_a(z',3)\beta(3) & \psi_f(z',3)\alpha(3) \end{vmatrix} \quad (38.2)$$

$$\Psi_3 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_f(z',1)\alpha(1) & \psi_f(z'',1)\beta(1) & \psi_a(z',1)\alpha(1) \\ \psi_f(z',2)\alpha(2) & \psi_f(z'',2)\beta(2) & \psi_a(z',2)\alpha(2) \\ \psi_f(z',3)\alpha(3) & \psi_f(z'',3)\beta(3) & \psi_a(z',3)\alpha(3) \end{vmatrix} \quad (38.3)$$

$$\Psi_4 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_f(z'',1)\alpha(1) & \psi_f(z',1)\beta(1) & \psi_a(z',1)\alpha(1) \\ \psi_f(z'',2)\alpha(2) & \psi_f(z',2)\beta(2) & \psi_a(z',2)\alpha(2) \\ \psi_f(z'',3)\alpha(3) & \psi_f(z',3)\beta(3) & \psi_a(z',3)\alpha(3) \end{vmatrix} \quad (38.4)$$

$$\Psi_5 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z',1)\alpha(1) & \psi_a(z'',1)\beta(1) & \psi_f(z'',1)\alpha(1) \\ \psi_a(z',2)\alpha(2) & \psi_a(z'',2)\beta(2) & \psi_f(z'',2)\alpha(2) \\ \psi_a(z',3)\alpha(3) & \psi_a(z'',3)\beta(3) & \psi_f(z'',3)\alpha(3) \end{vmatrix} \quad (38.5)$$

$$\Psi_6 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z'',1)\alpha(1) & \psi_a(z',1)\beta(1) & \psi_f(z'',1)\alpha(1) \\ \psi_a(z'',2)\alpha(2) & \psi_a(z',2)\beta(2) & \psi_f(z'',2)\alpha(2) \\ \psi_a(z'',3)\alpha(3) & \psi_a(z',3)\beta(3) & \psi_f(z'',3)\alpha(3) \end{vmatrix} \quad (38.6)$$

$$\Psi_7 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_f(z',1)\alpha(1) & \psi_f(z'',1)\beta(1) & \psi_a(z'',1)\alpha(1) \\ \psi_f(z',2)\alpha(2) & \psi_f(z'',2)\beta(2) & \psi_a(z'',2)\alpha(2) \\ \psi_f(z',3)\alpha(3) & \psi_f(z'',3)\beta(3) & \psi_a(z'',3)\alpha(3) \end{vmatrix} \quad (38.7)$$

$$\Psi_8 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_f(z'',1)\alpha(1) & \psi_f(z',1)\beta(1) & \psi_a(z'',1)\alpha(1) \\ \psi_f(z'',2)\alpha(2) & \psi_f(z',2)\beta(2) & \psi_a(z'',2)\alpha(2) \\ \psi_f(z'',3)\alpha(3) & \psi_f(z',3)\beta(3) & \psi_a(z'',3)\alpha(3) \end{vmatrix}. \quad (38.8)$$

In (38.1-8) the one-electron functions are defined by

$$\psi_x(\gamma, i) = \left(\frac{\gamma^3}{\pi}\right)^{\frac{1}{2}} e^{-\gamma\sqrt{x}i} \quad \begin{array}{l} \gamma = z', z'' \\ x = a, f \\ i = 1, 2, 3. \end{array} \quad (39)$$

The molecular wave function (35) corresponds to the idea that the 1s orbital in the half-filled shell of the He<sup>+</sup> ion can also be decomposed into two concentric "shells" one of which is characterized by z' and the other one by z". Function  $\Psi_I$  in (36) describes the case when the He atom interacts with a He<sup>+</sup> ion whose "inner-shell" is occupied and function  $\Psi_{II}$  in (37) refers to the case when the "outer-shell" of the He<sup>+</sup> ion is occupied. Assuming resonance between these two structures one arrives at the general form expressed in (35).

It is easy to see that the second approximation includes the first approximation as a special case. If one assumes that for the He<sup>+</sup> ion z'=z''=z''' then

$$\Psi_1 = \Psi_5 ; \Psi_2 = \Psi_6 ; \Psi_3 = \Psi_7 ; \Psi_4 = \Psi_8$$

and  $\Psi$  in (35) can be written as

$$\Psi_{\text{appr. B}} = (1 + \lambda) \Psi_{\text{appr. A}}$$

where the  $(1 + \lambda)$  multiplier is an irrelevant constant.

To illuminate what the "resonance" means the molecular wave function (35) can be rewritten in the form

$$\begin{aligned} \Psi = \frac{1}{\sqrt{3!}} \{ & [\psi_a(z',1)\psi_a(z'',2) + \psi_a(z'',1)\psi_a(z',2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ & \times [\psi_f(z',3) + \lambda\psi_f(z'',3)] \alpha(3) \\ & + [\psi_a(z',2)\psi_a(z'',3) + \psi_a(z'',2)\psi_a(z',3)] [\alpha(2)\beta(3) - \beta(2)\alpha(3)] \\ & \times [\psi_f(z',1) + \lambda\psi_f(z'',1)] \alpha(1) \\ & + [\psi_a(z',3)\psi_a(z'',1) + \psi_a(z'',3)\psi_a(z',1)] [\alpha(3)\beta(1) - \beta(3)\alpha(1)] \\ & \times [\psi_f(z',2) + \lambda\psi_f(z'',2)] \alpha(2) \\ & - [\psi_f(z',1)\psi_f(z'',2) + \psi_f(z'',1)\psi_f(z',2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ & \times [\psi_a(z',3) + \lambda\psi_a(z'',3)] \alpha(3) \\ & - [\psi_f(z',2)\psi_f(z'',3) + \psi_f(z'',2)\psi_f(z',3)] [\alpha(2)\beta(3) - \beta(2)\alpha(3)] \\ & \times [\psi_a(z',1) + \lambda\psi_a(z'',1)] \alpha(1) \\ & - [\psi_f(z',3)\psi_f(z'',1) + \psi_f(z'',3)\psi_f(z',1)] [\alpha(3)\beta(1) - \beta(3)\alpha(1)] \\ & \times [\psi_a(z',2) + \lambda\psi_a(z'',2)] \alpha(2) \}. \end{aligned}$$

(40)

From (40) it is seen that there is no electron pair bond between the He atom and the He<sup>+</sup> ion and, as in the case of approximation A, the stability of the He<sub>2</sub><sup>+</sup> molecule ion is due to the exchange effect of the electrons.

Substitution of (35) into the energy expression (6) with the Hamiltonian (5) leads to

$$E = \frac{W}{N}, \quad (41)$$

where

$$W = H_{\text{II}} + 2\lambda H_{\text{I}\bar{\text{I}}} + \lambda^2 H_{\bar{\text{I}}\bar{\text{I}}} \quad (42.1)$$

$$N = S_{\text{II}} + 2\lambda S_{\text{I}\bar{\text{I}}} + \lambda^2 S_{\bar{\text{I}}\bar{\text{I}}} \quad (42.2)$$

with

$$H_{xY} = \int \Psi_x H \Psi_Y d\tau \quad x = \text{I}, \bar{\text{I}}$$

$$S_{xY} = \int \Psi_x \Psi_Y d\tau \quad Y = \bar{\text{I}}, \bar{\bar{\text{I}}}.$$

Considering (36), (37) and (38.1-8), and using the invariance properties of the Hamiltonian and the following symmetry properties of the  $\Psi$ 's under the interchange of a and b

$$\Psi_1 \rightarrow \Psi_3$$

$$\Psi_5 \rightarrow \Psi_7$$

$$\Psi_2 \rightarrow \Psi_4$$

$$\Psi_6 \rightarrow \Psi_8$$

$$\Psi_3 \rightarrow \Psi_1$$

$$\Psi_7 \rightarrow \Psi_5$$

$$\Psi_4 \rightarrow \Psi_2$$

$$\Psi_8 \rightarrow \Psi_6$$

one can prove the following equalities

$$\begin{array}{ll}
 S_{11} = S_{33} & S_{17} = S_{35} \\
 S_{22} = S_{44} & S_{18} = S_{36} \\
 S_{14} = S_{23} & S_{15} = S_{37} \\
 S_{12} = S_{34} & S_{16} = S_{38} \\
 S_{55} = S_{77} & S_{27} = S_{45} \\
 S_{66} = S_{88} & S_{28} = S_{46} \\
 S_{56} = S_{78} & S_{25} = S_{47} \\
 S_{58} = S_{67} & S_{26} = S_{48}
 \end{array} \tag{43.1}$$

and

$$\begin{array}{ll}
 H_{11} = H_{33} & H_{17} = H_{35} \\
 H_{22} = H_{44} & H_{18} = H_{36} \\
 H_{14} = H_{23} & H_{15} = H_{37} \\
 H_{12} = H_{34} & H_{16} = H_{38} \\
 H_{55} = H_{77} & H_{27} = H_{45} \\
 H_{66} = H_{88} & H_{28} = H_{46} \\
 H_{56} = H_{78} & H_{25} = H_{47} \\
 H_{58} = H_{67} & H_{26} = H_{48} .
 \end{array} \tag{43.2}$$

With these simplifying relations the quantities on the right hand side of (42.1) and (42.2) can be expressed as

$$\begin{array}{l}
 H_{I \ I} = H_{11} + 2H_{12} + H_{22} - H_{13} - 2H_{14} - H_{24} \\
 H_{II \ II} = H_{55} + 2H_{56} + H_{66} - H_{57} - 2H_{58} - H_{68} \\
 H_{I \ II} = H_{15} + H_{16} - H_{17} - H_{18} + H_{25} + H_{26} - H_{27} - H_{28}
 \end{array} \tag{44}$$

and

$$S_{I I} = S_{11} + 2S_{12} + S_{22} - S_{13} - 2S_{14} - S_{24} \quad (45)$$

$$S_{II II} = S_{55} + 2S_{56} + S_{66} - S_{57} - 2S_{58} - S_{68}$$

$$S_{I II} = S_{15} + S_{16} - S_{17} - S_{18} + S_{25} + S_{26} - S_{27} - S_{28} \cdot$$

In (43.1), (43.2), (44) and (45) the  $H_{ij}$  and  $S_{ij}$  quantities are defined by

$$H_{ij} = \int \Psi_i H \Psi_j d\tau \quad i = 1, 2, 3, 4, 5, 6, 7, 8$$

$$S_{ij} = \int \Psi_i \Psi_j d\tau \quad j = 1, 2, 3, 4, 5, 6, 7, 8$$

and those which appear in (44) and (45) can be expressed as follows

$$H_{11} = H_{aab, aab}^{123, 123} (z'z''z', z'z''z') - H_{aab, aab}^{123, 321} (z'z''z', z'z''z') \quad (46.1)$$

$$H_{22} = H_{aab, aab}^{123, 123} (z'z''z', z'z''z') - H_{aab, aab}^{123, 132} (z'z''z', z'z''z') \quad (46.2)$$

$$H_{12} = H_{aab, aab}^{123, 213} (z'z''z', z'z''z') - H_{aab, aab}^{123, 231} (z'z''z', z'z''z') \quad (46.3)$$

$$H_{13} = H_{aab, bba}^{123, 123} (z'z''z', z'z''z') - H_{aab, bba}^{123, 321} (z'z''z', z'z''z') \quad (46.4)$$

$$H_{14} = H_{aab, bba}^{123, 213} (z'z''z', z'z''z') - H_{aab, bba}^{123, 231} (z'z''z', z'z''z') \quad (46.5)$$

$$H_{24} = H_{aab, bba}^{123, 123} (z'z''z', z'z''z') - H_{aab, bba}^{123, 132} (z'z''z', z'z''z') \quad (46.6)$$

$$H_{55} = H_{aab, aab}^{123, 123} (z'z''z'', z'z''z'') - H_{aab, aab}^{123, 321} (z'z''z'', z'z''z'') \quad (46.7)$$

$$H_{56} = H_{aab, aab}^{123, 213} (z'z''z''', z'z''z''') - H_{aab, aab}^{123, 231} (z'z''z''', z'z''z''') \quad (46.8)$$

$$H_{66} = H_{aab, aab}^{123, 123} (z'z''z''', z'z''z''') - H_{aab, aab}^{123, 132} (z'z''z''', z'z''z''') \quad (46.9)$$

$$H_{57} = H_{aab, bba}^{123, 123} (z'z''z''', z'z''z''') - H_{aab, bba}^{123, 321} (z'z''z''', z'z''z''') \quad (46.10)$$

$$H_{58} = H_{aab, bba}^{123, 213} (z'z''z''', z'z''z''') - H_{aab, bba}^{123, 231} (z'z''z''', z'z''z''') \quad (46.11)$$

$$H_{68} = H_{aab, bba}^{123, 123} (z'z''z''', z'z''z''') - H_{aab, bba}^{123, 132} (z'z''z''', z'z''z''') \quad (46.12)$$

$$H_{15} = H_{aab, aab}^{123, 123} (z'z''z''', z'z''z''') - H_{aab, aab}^{123, 321} (z'z''z''', z'z''z''') \quad (46.13)$$

$$H_{16} = H_{aab, aab}^{123, 213} (z'z''z''', z'z''z''') - H_{aab, aab}^{123, 231} (z'z''z''', z'z''z''') \quad (46.14)$$

$$H_{17} = H_{aab, bba}^{123, 123} (z'z''z''', z'z''z''') - H_{aab, bba}^{123, 321} (z'z''z''', z'z''z''') \quad (46.15)$$

$$H_{18} = H_{aab, bba}^{123, 213} (z'z''z''', z'z''z''') - H_{aab, bba}^{123, 231} (z'z''z''', z'z''z''') \quad (46.16)$$

$$H_{25} = H_{aab, aab}^{123, 213} (z'z''z''', z'z''z''') - H_{aab, aab}^{123, 312} (z'z''z''', z'z''z''') \quad (46.17)$$

$$H_{26} = H_{aab, aab}^{123, 123} (z'z''z''', z'z''z''') - H_{aab, aab}^{123, 132} (z'z''z''', z'z''z''') \quad (46.18)$$

$$H_{27} = H_{aab, bba}^{123, 213} (z'z''z''', z'z''z''') - H_{aab, bba}^{123, 312} (z'z''z''', z'z''z''') \quad (46.19)$$

$$H_{28} = H_{aab, bba}^{123, 123} (z'z''z''', z'z''z''') - H_{aab, bba}^{123, 132} (z'z''z''', z'z''z''') \quad (46.20)$$

and

$$S_{11} = S_{aab, aab}^{123, 123} (z'z''z', z'z''z') - S_{aab, aab}^{123, 321} (z'z''z', z'z''z') \quad (47.1)$$

$$S_{22} = S_{aab, aab}^{123, 123} (z'z''z', z'z''z') - S_{aab, aab}^{123, 132} (z'z''z', z'z''z') \quad (47.2)$$

$$S_{12} = S_{aab, aab}^{123, 213} (z'z''z', z'z''z') - S_{aab, aab}^{123, 231} (z'z''z', z'z''z') \quad (47.3)$$

$$S_{13} = S_{aab, bba}^{123, 123} (z'z''z', z'z''z') - S_{aab, bba}^{123, 321} (z'z''z', z'z''z') \quad (47.4)$$

$$S_{14} = S_{aab, bba}^{123, 213} (z'z''z', z'z''z') - S_{aab, bba}^{123, 231} (z'z''z', z'z''z') \quad (47.5)$$

$$S_{24} = S_{aab, bba}^{123, 123} (z'z''z', z'z''z') - S_{aab, bba}^{123, 132} (z'z''z', z'z''z') \quad (47.6)$$

$$S_{55} = S_{aab, aab}^{123, 123} (z'z''z'', z'z''z'') - S_{aab, aab}^{123, 321} (z'z''z'', z'z''z'') \quad (47.7)$$

$$S_{56} = S_{aab, aab}^{123, 213} (z'z''z'', z'z''z'') - S_{aab, aab}^{123, 231} (z'z''z'', z'z''z'') \quad (47.8)$$

$$S_{66} = S_{aab, aab}^{123, 123} (z'z''z'', z'z''z'') - S_{aab, aab}^{123, 132} (z'z''z'', z'z''z'') \quad (47.9)$$

$$S_{57} = S_{aab, bba}^{123, 123} (z'z''z'', z'z''z'') - S_{aab, bba}^{123, 321} (z'z''z'', z'z''z'') \quad (47.10)$$

$$S_{58} = S_{aab, bba}^{123, 213} (z'z''z'', z'z''z'') - S_{aab, bba}^{123, 231} (z'z''z'', z'z''z'') \quad (47.11)$$

$$S_{68} = S_{aab, bba}^{123, 123} (z'z''z'', z'z''z'') - S_{aab, bba}^{123, 132} (z'z''z'', z'z''z'') \quad (47.12)$$

$$S_{15} = S_{aab, aab}^{123, 123} (z'z''z', z'z''z'') - S_{aab, aab}^{123, 321} (z'z''z', z'z''z'') \quad (47.13)$$

$$S_{16} = S_{aab, aab}^{123, 213} (z'z''z', z'z''z'') - S_{aab, aab}^{123, 231} (z'z''z', z'z''z'') \quad (47.14)$$

$$S_{17} = S_{aab, bba}^{123, 123} (z'z''z', z'z''z'') - S_{aab, bba}^{123, 321} (z'z''z', z'z''z'') \quad (47.15)$$

$$S_{18} = S_{aab, bba}^{123, 213} (z'z''z', z'z''z'') - S_{aab, bba}^{123, 231} (z'z''z', z'z''z'') \quad (47.16)$$

$$S_{25} = S_{aab, aab}^{123, 213} (z'z''z', z'z''z'') - S_{aab, aab}^{123, 312} (z'z''z', z'z''z'') \quad (47.17)$$

$$S_{26} = S_{aab, aab}^{123, 123} (z'z''z', z'z''z'') - S_{aab, aab}^{123, 132} (z'z''z', z'z''z'') \quad (47.18)$$

$$S_{27} = S_{aab, bba}^{123, 213} (z'z''z', z'z''z'') - S_{aab, bba}^{123, 312} (z'z''z', z'z''z'') \quad (47.19)$$

$$S_{28} = S_{aab, bba}^{123, 123} (z'z''z', z'z''z'') - S_{aab, bba}^{123, 132} (z'z''z', z'z''z''). \quad (47.20)$$

The quantities on the right hand side of (46.1-20) and

(47.1-20) are defined by

$$H_{aab, aab}^{123, ij k} (z'z''z', z'z''z'') = \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z', 3) H \psi_a(z', i) \psi_a(z'', j) \psi_b(z', k) dv_1 dv_2 dv_3 \quad (48.1)$$

$$H_{aab, bba}^{123, ij k} (z'z''z', z'z''z'') = \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z', 3) H \psi_b(z', i) \psi_b(z'', j) \psi_a(z', k) dv_1 dv_2 dv_3 \quad (48.2)$$

$$H_{aab, aab}^{123, ij k} (z'z''z'', z'z''z'') = \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z'', 3) H \psi_a(z', i) \psi_a(z'', j) \psi_b(z'', k) dv_1 dv_2 dv_3 \quad (48.3)$$

$$H_{a a b, b b a}^{123, i j k} (z' z'' z'', z' z'' z'') \quad (48.4)$$

$$= \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z'', 3) H \psi_b(z', i) \psi_b(z'', j) \psi_a(z'', k) dv_1 dv_2 dv_3$$

$$i j k = 123; 213; 321; 132; 231 \quad \text{for } (48.1-4)$$

$$H_{a a b, a a b}^{123, i j k} (z' z'' z', z' z'' z'') \quad (48.5)$$

$$= \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z', 3) H \psi_a(z', i) \psi_a(z'', j) \psi_b(z'', k) dv_1 dv_2 dv_3$$

$$H_{a a b, b b a}^{123, i j k} (z' z'' z', z' z'' z'') \quad (48.6)$$

$$= \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z', 3) H \psi_b(z', i) \psi_b(z'', j) \psi_a(z'', k) dv_1 dv_2 dv_3$$

$$i j k = 123; 213; 321; 231; 312; 132 \quad \text{for } (48.5-6)$$

and

$$S_{a a b, a a b}^{123, i j k} (z' z'' z', z' z'' z') \quad (49.1)$$

$$= \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z', 3) \cdot \psi_a(z', i) \psi_a(z'', j) \psi_b(z', k) dv_1 dv_2 dv_3$$

$$S_{a a b, b b a}^{123, i j k} (z' z'' z', z' z'' z') \quad (49.2)$$

$$= \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z', 3) \cdot \psi_b(z', i) \psi_b(z'', j) \psi_a(z', k) dv_1 dv_2 dv_3$$

$$S_{a a b, a a b}^{123, i j k} (z' z'' z'', z' z'' z'') \quad (49.3)$$

$$= \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z'', 3) \cdot \psi_a(z', i) \psi_a(z'', j) \psi_b(z'', k) dv_1 dv_2 dv_3$$

$$S_{a a b, b b a}^{123, i j k} (z' z'' z'', z' z'' z'') \quad (49.4)$$

$$= \iiint \psi_a(z', 1) \psi_a(z'', 2) \psi_b(z'', 3) \cdot \psi_b(z', i) \psi_b(z'', j) \psi_a(z'', k) dv_1 dv_2 dv_3$$

$$i j k = 123; 213; 321; 132; 231 \quad \text{for } (49.1-4)$$

$$S_{aab, aab}^{123, ijk} (z'z''z', z'z''z'') \quad (49.5)$$

$$= \iiint \psi_a(z', i) \psi_a(z'', j) \psi_b(z', k) \cdot \psi_a(z', i) \psi_a(z'', j) \psi_b(z'', k) dv_1 dv_2 dv_3$$

$$S_{aab, bba}^{123, ijk} (z'z''z', z'z''z'') \quad (49.6)$$

$$= \iiint \psi_a(z', i) \psi_a(z'', j) \psi_b(z', k) \cdot \psi_b(z', i) \psi_b(z'', j) \psi_a(z'', k) dv_1 dv_2 dv_3$$

$ijk = 123; 213; 321; 231; 312; 132$  for (49.5-6).

The next step is to express these quantities in terms of individual molecular integrals. Considering the Hamiltonian in (5) the resulting expressions are

$$H_{aab, aab}^{123, 123} (z'z''z', z'z''z') = 2 \{ k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z') \} \quad (50.1)$$

$$+ \{ k_{aa}(z'', z'') + p_{aa}^a(z'', z'') + p_{bb}^a(z'', z'') \} + p_{aa, aa}(z'z', z''z'')$$

$$+ p_{aa, bb}(z'z', z'z') + p_{aa, bb}(z'z', z''z'') + \frac{4}{R}.$$

$$H_{aab, aab}^{123, 321} (z'z''z', z'z''z') = 2 f_{ab}(z', z') \{ k_{ab}(z', z') + 2 p_{ab}^a(z', z') \}$$

$$+ f_{ab}^2(z', z') \{ k_{aa}(z'', z'') + p_{aa}^a(z'', z'') + p_{bb}^a(z'', z'') \} + 2 f_{ab}(z', z') p_{aa, ab}(z''z'', z'z')$$

$$+ p_{ab, ab}(z'z', z'z') + f_{ab}^2(z', z') \frac{4}{R}. \quad (50.2)$$

$$\begin{aligned}
 H_{aab, aab}^{123, 132} (z'z''z', z'z''z') &= 2f_{ab}(z', z'') \{k_{ab}(z', z'') + p_{ab}^a(z', z'') + p_{ab}^a(z'', z')\} \\
 &+ f_{ab}^2(z', z'') \{k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z')\} + 2f_{ab}(z', z'') p_{aa, ab}(z'z', z''z') \\
 &+ p_{ab, ab}(z'z'', z'z'') + f_{ab}^2(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.3}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 213} (z'z''z', z'z''z') &= 2f_{aa}(z', z'') \{k_{aa}(z', z'') + p_{aa}^a(z', z'') + p_{bb}^a(z', z'')\} \\
 &+ f_{aa}^2(z', z'') \{k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z')\} + p_{aa, aa}(z'z'', z'z'') \\
 &+ 2f_{aa}(z', z'') p_{aa, bb}(z'z', z'z'') + f_{aa}^2(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.4}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 231} (z'z''z', z'z''z') &= f_{aa}(z', z'') f_{ab}(z', z') \{k_{ab}(z', z'') + p_{ab}^a(z', z'') + p_{ab}^a(z'', z')\} \\
 &+ f_{ab}(z', z'') f_{ab}(z', z') \{k_{aa}(z', z'') + p_{aa}^a(z', z'') + p_{bb}^a(z', z'')\} \\
 &+ f_{ab}(z', z'') f_{aa}(z', z'') \{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} + f_{ab}(z', z') p_{aa, ab}(z'z'', z''z') \\
 &+ f_{aa}(z', z'') p_{ab, ab}(z'z', z''z') + f_{ab}(z', z'') p_{aa, ab}(z'z'', z'z') \\
 &+ f_{ab}(z', z'') f_{aa}(z', z'') f_{ab}(z', z') \frac{4}{R}.
 \end{aligned} \tag{50.5}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 123} (z'z''z', z'z''z') &= 2f_{ab}(z', z') f_{ab}(z'', z'') \{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} \\
 &+ f_{ab}^2(z', z') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} + 2f_{ab}(z', z') p_{ab, ab}(z'z', z''z'') \\
 &+ f_{ab}(z'', z'') p_{ab, ab}(z'z', z'z') + f_{ab}^2(z', z') f_{ab}(z'', z'') \frac{4}{R}.
 \end{aligned} \tag{50.6}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 321} (z'z''z', z'z''z') &= 2f_{ab}(z'', z'') \{k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z')\} \\
 &+ \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} + 2p_{aa, ab}(z'z', z''z'') \\
 &+ f_{ab}(z'', z'') p_{aa, bb}(z'z', z'z') + f_{ab}(z'', z'') \frac{4}{R}.
 \end{aligned} \tag{50.7}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 132} (z'z''z', z'z''z') &= 2f_{ab}(z', z') f_{aa}(z', z'') \{k_{aa}(z', z'') + p_{aa}^a(z', z'') \\
 &+ p_{bb}^a(z', z'')\} + f_{aa}^2(z', z'') \{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} + 2f_{aa}(z', z'') p_{aa, ab}(z'z'', z'z') \\
 &+ f_{ab}(z', z') p_{aa, bb}(z'z'', z'z'') + f_{aa}^2(z', z'') f_{ab}(z', z') \frac{4}{R}.
 \end{aligned} \tag{50.8}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 213} (z'z''z', z'z''z') &= 2f_{ab}(z', z'')f_{ab}(z', z')\{k_{ab}(z', z'') \\
 &+ p_{ab}^a(z', z'') + p_{ab}^a(z'', z')\} + f_{ab}^2(z', z'')\{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} \\
 &+ f_{ab}(z', z')p_{ab, ab}(z'z'', z'z') + f_{ab}(z', z'')p_{ab, ab}(z'z', z''z') \\
 &+ f_{ab}(z', z'')p_{ab, ab}(z'z', z''z') + f_{ab}^2(z', z'')f_{ab}(z', z')\frac{4}{R}.
 \end{aligned} \tag{50.9}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 231} (z'z''z', z'z''z') &= f_{ab}(z', z'')\{k_{aa}(z', z'') + p_{aa}^a(z', z'') + p_{bb}^a(z', z'')\} \\
 &+ f_{aa}(z', z'')\{k_{ab}(z', z'') + p_{ab}^a(z', z'') + p_{ab}^a(z'', z')\} + f_{aa}(z', z'')f_{ab}(z', z'')\{k_{aa}(z', z') \\
 &+ p_{aa}^a(z', z') + p_{bb}^a(z', z')\} + p_{aa, ab}(z'z'', z'z'') + f_{ab}(z', z'')p_{aa, bb}(z'z', z'z'') \\
 &+ f_{aa}(z', z'')p_{aa, ab}(z'z', z''z') + f_{aa}(z', z'')f_{ab}(z', z'')\frac{4}{R}.
 \end{aligned} \tag{50.10}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 123} (z'z''z'', z'z''z'') &= \{k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z')\} \\
 &+ 2\{k_{aa}(z'', z'') + p_{aa}^a(z'', z'') + p_{bb}^a(z'', z'')\} + p_{aa, aa}(z'z', z''z'') \\
 &+ p_{aa, bb}(z'z', z''z'') + p_{aa, bb}(z''z'', z''z'') + \frac{4}{R}.
 \end{aligned} \tag{50.11}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 321} (z'z''z'', z'z''z'') &= 2f_{ab}(z', z'')\{k_{ab}(z', z'') + p_{ab}^a(z', z'') + p_{ab}^a(z'', z')\} \\
 &+ f_{ab}^2(z', z'')\{k_{aa}(z'', z'') + p_{aa}^a(z'', z'') + p_{bb}^a(z'', z'')\} + 2f_{ab}(z', z'')p_{aa, ab}(z''z'', z'z'') \\
 &+ p_{ab, ab}(z'z'', z'z'') + f_{ab}^2(z', z'')\frac{4}{R}.
 \end{aligned} \tag{50.12}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 132} (z'z''z'', z'z''z'') &= 2f_{ab}(z'', z'') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} \\
 &+ f_{ab}^2(z'', z'') \{k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z')\} + p_{ab, ab}(z''z'', z''z'') \\
 &+ 2f_{ab}(z'', z'') p_{aa, ab}(z'z', z''z'') + f_{ab}^2(z'', z'') \frac{4}{R}.
 \end{aligned} \tag{50.13}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 213} (z'z''z'', z'z''z'') &= 2f_{aa}(z', z'') \{k_{aa}(z', z'') + p_{aa}^a(z', z'') + p_{bb}^a(z', z'')\} \\
 &+ f_{aa}^2(z', z'') \{k_{aa}(z'', z'') + p_{aa}^a(z'', z'') + p_{bb}^a(z'', z'')\} + p_{aa, aa}(z'z'', z'z'') \\
 &+ 2f_{aa}(z', z'') p_{aa, bb}(z'z'', z''z'') + f_{aa}^2(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.14}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 231} (z'z''z'', z'z''z'') &= f_{aa}(z', z'') f_{ab}(z', z'') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} \\
 &+ f_{ab}(z'', z'') f_{ab}(z', z'') \{k_{aa}(z', z'') + p_{aa}^a(z', z'') + p_{bb}^a(z', z'')\} \\
 &+ f_{ab}(z'', z'') f_{aa}(z', z'') \{k_{ab}(z', z'') + p_{ab}^a(z', z'') + p_{ab}^a(z'', z')\} \\
 &+ f_{ab}(z', z'') p_{aa, ab}(z'z'', z''z'') + f_{aa}(z', z'') p_{ab, ab}(z'z'', z''z'') \\
 &+ f_{ab}(z'', z'') p_{aa, ab}(z'z'', z'z'') + f_{ab}(z'', z'') f_{aa}(z', z'') f_{ab}(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.15}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 123} (z'z''z'', z'z''z'') &= f_{ab}^2(z'', z'') \{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} \\
 &+ 2f_{ab}(z', z') f_{ab}(z'', z'') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} + 2f_{ab}(z'', z'') p_{ab, ab}(z'z', z''z'') \\
 &+ f_{ab}(z', z') p_{ab, ab}(z''z'', z''z'') + f_{ab}(z', z') f_{ab}^2(z'', z'') \frac{4}{R}.
 \end{aligned} \tag{50.16}$$

$$\begin{aligned}
 H_{a a b, b b a}^{123, 321} (z' z'' z''', z' z'' z''') &= 2 f_{a b} (z'', z'') f_{a a} (z', z'') \{ k_{a a} (z', z'') + p_{a a}^a (z', z'') \\
 &+ p_{b b}^a (z', z'') \} + f_{a a}^2 (z', z'') \{ k_{a b} (z'', z'') + 2 p_{a b}^a (z'', z'') \} + 2 f_{a a} (z', z'') p_{a a, a b} (z' z'' z'' z''') \\
 &+ f_{a b} (z'', z'') p_{a a, b b} (z' z'', z' z'') + f_{a a}^2 (z', z'') f_{a b} (z'', z'') \frac{4}{R}. \quad (50.17)
 \end{aligned}$$

$$\begin{aligned}
 H_{a a b, b b a}^{123, 132} (z' z'' z''', z' z'' z''') &= 2 f_{a b} (z', z') \{ k_{a a} (z'', z'') + p_{a a}^a (z'', z'') + p_{b b}^a (z'', z'') \} \\
 &+ \{ k_{a b} (z', z') + 2 p_{a b}^a (z', z') \} + f_{a b} (z', z') p_{a a, b b} (z'' z'', z'' z'') \\
 &+ 2 p_{a a, a b} (z'' z'', z' z') + f_{a b} (z', z') \frac{4}{R}. \quad (50.18)
 \end{aligned}$$

$$\begin{aligned}
 H_{a a b, b b a}^{123, 213} (z' z'' z''', z' z'' z''') &= 2 f_{a b} (z'', z'') f_{a b} (z', z'') \{ k_{a b} (z', z'') \\
 &+ p_{a b}^a (z', z'') + p_{a b}^a (z'', z') \} + f_{a b}^2 (z', z'') \{ k_{a b} (z'', z'') + 2 p_{a b}^a (z'', z'') \} \\
 &+ f_{a b} (z'', z'') p_{a b, a b} (z' z'', z'' z') + 2 f_{a b} (z', z'') p_{a b, a b} (z' z'', z'' z'') \\
 &+ f_{a b}^2 (z', z'') f_{a b} (z'', z'') \frac{4}{R}. \quad (50.19)
 \end{aligned}$$

$$\begin{aligned}
 H_{a a b, b b a}^{123, 231} (z' z'' z''', z' z'' z''') &= f_{a b} (z', z'') f_{a a} (z', z'') \{ k_{a a} (z'', z'') \\
 &+ p_{a a}^a (z'', z'') + p_{b b}^a (z'', z'') \} + f_{a a} (z', z'') \{ k_{a b} (z', z'') + p_{a b}^a (z', z'') + p_{a b}^a (z'', z') \} \\
 &+ f_{a b} (z', z'') \{ k_{a a} (z', z'') + p_{a a}^a (z', z'') + p_{b b}^a (z', z'') \} + f_{a a} (z', z'') p_{a a, a b} (z'' z'', z' z'') \\
 &+ f_{a b} (z', z'') p_{a a, b b} (z' z'', z'' z'') + p_{a a, a b} (z' z'', z'' z') \\
 &+ f_{a b} (z', z'') f_{a a} (z', z'') \frac{4}{R}. \quad (50.20)
 \end{aligned}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 123} (z'z''z', z'z''z'') &= f_{aa}(z', z'') \{ k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z') \} \\
 &+ f_{aa}(z', z'') \{ k_{aa}(z'', z'') + p_{aa}^a(z'', z'') + p_{bb}^a(z'', z'') \} + \{ k_{aa}(z', z'') \\
 &+ p_{aa}^a(z', z'') + p_{bb}^a(z', z'') \} + f_{aa}(z', z'') p_{aa, aa}(z'z', z''z'') \\
 &+ p_{aa, bb}(z'z', z'z'') + p_{aa, bb}(z'z'', z''z'') + f_{aa}(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.21}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 321} (z'z''z', z'z''z'') &= f_{ab}(z', z'') \{ k_{ab}(z', z') + 2p_{ab}^a(z', z') \} \\
 &+ f_{ab}(z', z') f_{ab}(z', z'') \{ k_{aa}(z'', z'') + p_{aa}^a(z'', z'') + p_{bb}^a(z'', z'') \} \\
 &+ f_{ab}(z', z') \{ k_{ab}(z', z'') + p_{ab}^a(z', z'') + p_{ab}^a(z'', z') \} + f_{ab}(z', z'') p_{aa, ab}(z'z'', z'z') \\
 &+ p_{ab, ab}(z'z', z''z') + f_{ab}(z', z') p_{aa, ab}(z''z'', z'z'') + f_{ab}(z', z') f_{ab}(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.22}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 213} (z'z''z', z'z''z'') &= 3f_{aa}^2(z', z'') \{ k_{aa}(z', z'') + p_{aa}^a(z', z'') \\
 &+ p_{bb}^a(z', z'') \} + f_{aa}(z', z'') p_{aa, aa}(z'z'', z'z'') + 2f_{aa}(z', z'') p_{aa, bb}(z'z'', z'z'') \\
 &+ f_{aa}^3(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.23}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 231} (z'z''z', z'z''z'') &= 2f_{aa}(z', z'') f_{ab}(z', z'') \{ k_{ab}(z', z'') \\
 &+ p_{ab}^a(z', z'') + p_{ab}^a(z'', z') \} + f_{ab}^2(z', z'') \{ k_{aa}(z', z'') + p_{aa}^a(z', z'') + p_{bb}^a(z', z'') \} \\
 &+ f_{ab}(z', z'') p_{aa, ab}(z'z'', z''z') + f_{ab}(z', z'') p_{aa, ab}(z'z'', z'z'') \\
 &+ f_{aa}(z', z'') p_{ab, ab}(z'z'', z''z') + f_{ab}^2(z', z'') f_{aa}(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.24}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 312} (z'z''z', z'z''z'') &= f_{aa}(z', z'') f_{ab}(z'', z'') \{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} \\
 &+ f_{ab}(z', z') f_{ab}(z'', z'') \{k_{aa}(z', z'') + p_{aa}^a(z', z'') + p_{bb}^a(z', z'')\} \\
 &+ f_{ab}(z', z') f_{aa}(z', z'') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} + f_{ab}(z'', z'') p_{aa, ab}(z'z'', z'z') \\
 &+ f_{aa}^2(z', z'') p_{ab, ab}(z'z', z''z'') + f_{ab}(z', z') p_{aa, ab}(z'z'', z''z'') \\
 &+ f_{ab}(z', z') f_{aa}(z', z'') f_{ab}(z'', z'') \frac{4}{R}.
 \end{aligned} \tag{50.25}$$

$$\begin{aligned}
 H_{aab, aab}^{123, 132} (z'z''z', z'z''z'') &= f_{ab}(z'', z'') \{k_{ab}(z', z'') + p_{ab}^a(z', z'') \\
 &+ p_{ab}^a(z'', z')\} + f_{ab}(z', z'') f_{ab}(z'', z'') \{k_{aa}(z', z') + p_{aa}^a(z', z') + p_{bb}^a(z', z')\} \\
 &+ f_{ab}(z', z'') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} + f_{ab}(z'', z'') p_{aa, ab}(z'z', z''z'') \\
 &+ p_{ab, ab}(z'z'', z''z'') + f_{ab}(z', z'') p_{aa, ab}(z'z', z''z'') \\
 &+ f_{ab}(z', z'') f_{ab}(z'', z'') \frac{4}{R}.
 \end{aligned} \tag{50.26}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 123} (z'z''z', z'z''z'') &= f_{ab}(z', z'') f_{ab}(z'', z'') \{k_{ab}(z', z') + 2p_{ab}^a(z', z')\} \\
 &+ f_{ab}(z', z'') f_{ab}(z', z') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} + f_{ab}(z', z') f_{ab}(z'', z'') \{k_{ab}(z', z'') \\
 &+ p_{ab}^a(z', z'') + p_{ab}^a(z'', z')\} + f_{ab}(z', z'') p_{ab, ab}(z'z', z''z'') \\
 &+ f_{ab}(z'', z'') p_{ab, ab}(z'z', z''z') + f_{ab}(z', z') p_{ab, ab}(z'z'', z''z'') \\
 &+ f_{ab}(z', z') f_{ab}(z'', z'') f_{ab}(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.27}$$

$$\begin{aligned}
 H_{aab, bba}^{123, 321} (z'z''z', z'z''z'') &= f_{aa}(z', z'') f_{ab}(z'', z'') \{k_{aa}(z', z') + p_{aa}^a(z', z') \\
 &+ p_{bb}^a(z', z')\} + f_{aa}(z', z'') \{k_{ab}(z'', z'') + 2p_{ab}^a(z'', z'')\} + f_{ab}(z'', z'') \{k_{aa}(z', z'') \\
 &+ p_{aa}^a(z', z'') + p_{bb}^a(z', z'')\} + f_{aa}(z', z'') p_{aa, ab}(z'z', z''z'') + p_{aa, ab}(z'z'', z''z'') \\
 &+ f_{ab}(z'', z'') p_{aa, bb}(z'z', z'z'') + f_{ab}(z'', z'') f_{aa}(z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.28}$$

$$\begin{aligned}
 H_{a a b, b b a}^{123, 213} (z' z'' z', z' z'' z'') &= 3 f_{a b}^2 (z', z'') \{ k_{a b} (z', z'') + p_{a b}^a (z', z'') \\
 &+ p_{a b}^a (z'', z') \} + 2 f_{a b} (z', z'') p_{a b, a b} (z' z'', z'' z') + f_{a b} (z', z'') p_{a b, a b} (z' z'', z' z'') \\
 &+ f_{a b}^3 (z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.29}$$

$$\begin{aligned}
 H_{a a b, b b a}^{123, 231} (z' z'' z', z' z'' z'') &= 2 f_{a b} (z', z'') f_{a a} (z', z'') \{ k_{a a} (z', z'') + p_{a a}^a (z', z'') \\
 &+ p_{b b}^a (z', z'') \} + f_{a a}^2 (z', z'') \{ k_{a b} (z', z'') + p_{a b}^a (z', z'') + p_{a b}^a (z'', z') \} \\
 &+ f_{a a} (z', z'') p_{a a, a b} (z' z'', z' z'') + f_{a a} (z', z'') p_{a a, a b} (z' z'', z'' z') \\
 &+ f_{a b} (z', z'') p_{a a, b b} (z' z'', z' z'') + f_{a a}^2 (z', z'') f_{a b} (z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.30}$$

$$\begin{aligned}
 H_{a a b, b b a}^{123, 312} (z' z'' z', z' z'' z'') &= f_{a b} (z', z'') \{ k_{a a} (z', z') + p_{a a}^a (z', z') + p_{b b}^a (z', z') \} \\
 &+ \{ k_{a b} (z', z'') + p_{a b}^a (z', z'') + p_{a b}^a (z'', z') \} + f_{a b} (z', z'') \{ k_{a a} (z'', z'') \\
 &+ p_{a a}^a (z'', z'') + p_{b b}^a (z'', z'') \} + p_{a a, a b} (z' z', z'' z') + f_{a b} (z', z'') p_{a a, b b} (z' z', z'' z'') \\
 &+ p_{a a, a b} (z'' z'', z' z'') + f_{a b} (z', z'') \frac{4}{R}.
 \end{aligned} \tag{50.31}$$

$$\begin{aligned}
 H_{a a b, b b a}^{123, 132} (z' z'' z', z' z'' z'') &= f_{a b} (z', z') \{ k_{a a} (z', z'') + p_{a a}^a (z', z'') \\
 &+ p_{b b}^a (z', z'') \} + f_{a a} (z', z'') \{ k_{a b} (z', z') + 2 p_{a b}^a (z', z') \} \\
 &+ f_{a a} (z', z'') f_{a b} (z', z') \{ k_{a a} (z'', z'') + p_{a a}^a (z'', z'') + p_{b b}^a (z'', z'') \} \\
 &+ p_{a a, a b} (z' z'', z' z') + f_{a b} (z', z') p_{a a, b b} (z' z'', z'' z'') \\
 &+ f_{a a} (z', z'') p_{a a, a b} (z'' z'', z' z') + f_{a a} (z', z'') f_{a b} (z', z') \frac{4}{R}.
 \end{aligned} \tag{50.32}$$

$$S_{aab, aab}^{123, 123} (z'z''z', z'z''z') = 1 \quad (51.1)$$

$$S_{aab, aab}^{123, 321} (z'z''z', z'z''z') = f_{ab}^2 (z', z') \quad (51.2)$$

$$S_{aab, aab}^{123, 132} (z'z''z', z'z''z') = f_{ab}^2 (z', z'') \quad (51.3)$$

$$S_{aab, aab}^{123, 213} (z'z''z', z'z''z') = f_{aa}^2 (z', z'') \quad (51.4)$$

$$S_{aab, aab}^{123, 231} (z'z''z', z'z''z') = f_{ab} (z', z'') f_{aa} (z', z'') f_{ab} (z', z') \quad (51.5)$$

$$S_{aab, bba}^{123, 123} (z'z''z', z'z''z') = f_{ab}^2 (z', z') f_{ab} (z'', z'') \quad (51.6)$$

$$S_{aab, bba}^{123, 321} (z'z''z', z'z''z') = f_{ab} (z'', z'') \quad (51.7)$$

$$S_{aab, bba}^{123, 132} (z'z''z', z'z''z') = f_{aa}^2 (z', z'') f_{ab} (z', z') \quad (51.8)$$

$$S_{aab, bba}^{123, 213} (z'z''z', z'z''z') = f_{ab}^2 (z', z'') f_{ab} (z', z') \quad (51.9)$$

$$S_{aab, bba}^{123, 231} (z'z''z', z'z''z') = f_{aa} (z', z'') f_{ab} (z', z'') \quad (51.10)$$

$$S_{aab, aab}^{123, 123} (z'z''z'', z'z''z'') = 1 \quad (51.11)$$

$$S_{aab, aab}^{123, 321} (z'z''z'', z'z''z'') = f_{ab}^2 (z', z'') \quad (51.12)$$

$$S_{aab, aab}^{123, 132} (z'z''z'', z'z''z'') = f_{ab}^2 (z'', z'') \quad (51.13)$$

$$S_{aab, aab}^{123, 213} (z'z''z'', z'z''z'') = f_{aa}^2 (z', z'') \quad (51.14)$$

$$S_{aab, aab}^{123, 231} (z'z''z'', z'z''z'') = f_{ab}(z'', z'') f_{aa}(z', z'') f_{ab}(z', z'') \quad (51.15)$$

$$S_{aab, bba}^{123, 123} (z'z''z'', z'z''z'') = f_{ab}(z', z') f_{ab}^2(z'', z'') \quad (51.16)$$

$$S_{aab, bba}^{123, 321} (z'z''z'', z'z''z'') = f_{aa}^2(z', z'') f_{ab}(z'', z'') \quad (51.17)$$

$$S_{aab, bba}^{123, 132} (z'z''z'', z'z''z'') = f_{ab}(z', z') \quad (51.18)$$

$$S_{aab, bba}^{123, 213} (z'z''z'', z'z''z'') = f_{ab}^2(z', z'') f_{ab}(z'', z'') \quad (51.19)$$

$$S_{aab, bba}^{123, 231} (z'z''z'', z'z''z'') = f_{ab}(z', z'') f_{aa}(z', z'') \quad (51.20)$$

$$S_{aab, aab}^{123, 123} (z'z''z', z'z''z'') = f_{aa}(z', z'') \quad (51.21)$$

$$S_{aab, aab}^{123, 321} (z'z''z', z'z''z'') = f_{ab}(z', z') f_{ab}(z', z'') \quad (51.22)$$

$$S_{aab, aab}^{123, 213} (z'z''z', z'z''z'') = f_{aa}^3(z', z'') \quad (51.23)$$

$$S_{aab, aab}^{123, 231} (z'z''z', z'z''z'') = f_{ab}^2(z', z'') f_{aa}(z', z'') \quad (51.24)$$

$$S_{aab, aab}^{123, 312} (z'z''z', z'z''z'') = f_{ab}(z', z') f_{aa}(z', z'') f_{ab}(z'', z'') \quad (51.25)$$

$$S_{aab, aab}^{123, 132} (z'z''z', z'z''z'') = f_{ab}(z', z'') f_{ab}(z'', z'') \quad (51.26)$$

$$S_{aab, bba}^{123, 123} (z'z''z', z'z''z'') = f_{ab}(z', z') f_{ab}(z'', z'') f_{ab}(z', z'') \quad (51.27)$$

$$S_{aab, bba}^{123, 321} (z'z''z', z'z''z'') = f_{ab}(z', z'') f_{aa}(z', z'') \quad (51.28)$$

$$S_{aab, bba}^{123, 213} (z'z''z', z'z''z'') = f_{ab}^3(z', z'') \quad (51.29)$$

$$S_{aab, bba}^{123, 231} (z'z''z', z'z''z'') = f_{aa}^2(z', z'') f_{ab}(z', z'') \quad (51.30)$$

$$S_{aab, bba}^{123, 312} (z'z''z', z'z''z'') = f_{ab}(z', z'') \quad (51.51)$$

$$S_{aab, bba}^{123, 132} (z'z''z', z'z''z'') = f_{aa}(z', z'') f_{ab}(z', z'). \quad (51.32)$$

Some of the integrals in (50.1-32) and (51.1-32) are identical with those of the first approximation and some are new (19 in number). They are already defined in eqs. (17-28) where the integrals appearing only in the second approximation are distinguished by a star.

### 2b) Discussion of the calculation

The numerical calculation of the dissociation energy has been carried out at  $R = 2a_0$  with  $z'_0 = 2.15$  and  $z''_0 = 1.19$ . By applying the condition of minimum

$$\frac{\partial E(\lambda)}{\partial \lambda} = 0$$

for the energy expression in (41), the optimal value of the variational parameter,  $\lambda_0$ , can be determined analytically as

$$\lambda_0 = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A},$$

where

$$A = S_{I II} H_{II II} - H_{I II} S_{II II}$$

$$B = S_{I I} H_{II II} - H_{I I} S_{II II}$$

$$C = S_{I I} H_{I II} - H_{I I} S_{I II} .$$

The resulting energy is  $-4.924 e^2/a_0$ . This is shown in Table 7 together with the optimal value of the variational parameter,  $\lambda_0$ . Also shown are the quantities denoted by  $E_I = \frac{H_{I I}}{S_{I I}}$  and  $E_{II} = \frac{H_{II II}}{S_{II II}}$ , which can be interpreted as the energy of the  $\text{He}_2^+$  molecular ion when the electron of the  $\text{He}^+$  ion occupies the "inner shell" or the "outer shell", respectively.

TABLE 7. The energy of the  $\text{He}_2^+$  molecule ion (in units  $e^2/a_0$ ) with and without resonance

$$z'_0 = 2.15, z''_0 = 1.19$$

E	$E_I$	$E_{II}$	$\lambda_0$
-4.924	-4.905	-4.593	0.26

It is seen that consideration of  $\Psi_I$  alone leads to  $-4.905 e^2/a_0$  and that of  $\Psi_{II}$  alone to  $-4.593 e^2/a_0$ . The assumption of resonance however is fruitful and leads to a more stable state than  $E_I$  or  $E_{II}$ .

### 3) New interpretation of the three-electron bond

#### 3a) Approximation A

In this section it is pointed out that the introduction of open-shell configurations for the discussion of the  $\text{He}_2^+$  molecular ion leads to interesting consequences concerning the quantum mechanical model of the binding. Let us consider the following two configurations

$$\Psi_5 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z',1)\alpha(1) & \psi_a(z'',1)\alpha(1) & \psi_b(z''',1)\beta(1) \\ \psi_a(z',2)\alpha(2) & \psi_a(z'',2)\alpha(2) & \psi_b(z''',2)\beta(2) \\ \psi_a(z',3)\alpha(3) & \psi_a(z'',3)\alpha(3) & \psi_b(z''',3)\beta(3) \end{vmatrix} \quad (52.1)$$

and

$$\Psi_6 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_b(z',1)\alpha(1) & \psi_b(z'',1)\alpha(1) & \psi_a(z''',1)\beta(1) \\ \psi_b(z',2)\alpha(2) & \psi_b(z'',2)\alpha(2) & \psi_a(z''',2)\beta(2) \\ \psi_b(z',3)\alpha(3) & \psi_b(z'',3)\alpha(3) & \psi_a(z''',3)\beta(3) \end{vmatrix} \quad (52.2)$$

which by interchanging a and b obey the relations

$$\Psi_5 \rightarrow \Psi_6 \quad ; \quad \Psi_6 \rightarrow \Psi_5 .$$

These configurations can arise only when open-shells are introduced for the He atom, because in case of closed-shells  $z' = z''$  and the determinants in (52.1) and (52.2) would have two identical columns and would consequently vanish.

Introducing the functions

$$\Psi(z''', z' - z'') = \Psi_1 + \Psi_2 - \Psi_3 - \Psi_4 \quad (53)$$

$$\Psi(z', z'' - z''') = \Psi_1 - \Psi_5 - \Psi_3 + \Psi_6 \quad (54)$$

$$\Psi(z'', z' - z''') = \Psi_2 + \Psi_5 - \Psi_4 - \Psi_6 \quad (55)$$

the molecular wave function of approximation A can be written as

$$\Psi(z''', z' - z'') = \Psi(z', z'' - z''') + \Psi(z'', z' - z'''), \quad (56)$$

which evidently is identical with that given in (1).

With the aid of "structures" (56) can be expressed symbolically as

$$\left[ \text{He} \begin{array}{c} z' \\ | \\ z'' \end{array} \begin{array}{c} z''' \\ \diagdown \\ \text{He}^+ \end{array} \right] = \left[ \text{He} \begin{array}{c} z' \\ | \\ z'' \end{array} \begin{array}{c} z''' \\ \diagdown \\ \text{He}^+ \end{array} \right] + \left[ \text{He} \begin{array}{c} z' \\ | \\ z'' \end{array} \begin{array}{c} z''' \\ \diagdown \\ \text{He}^+ \end{array} \right]. \quad (57)$$

Expanding the determinants on the right hand side of (54) and rearranging certain terms  $\Psi(z', z'' - z''')$  can be written as

$$\begin{aligned} \Psi(z', z'' - z''') = & \frac{1}{\sqrt{3!}} \left\{ \psi_a(z', 1) \alpha(1) \times [\psi_a(z'', 2) \psi_f(z''', 3) + \psi_f(z'', 2) \psi_a(z'', 3)] \right. \\ & \times [\beta(2) \alpha(3) - \alpha(2) \beta(3)] \\ & + \psi_a(z', 2) \alpha(2) \times [\psi_a(z'', 3) \psi_f(z''', 1) + \psi_f(z'', 3) \psi_a(z'', 1)] \\ & \times [\beta(3) \alpha(1) - \alpha(3) \beta(1)] \\ & + \psi_a(z', 3) \alpha(3) \times [\psi_a(z'', 1) \psi_f(z''', 2) + \psi_f(z'', 1) \psi_a(z'', 2)] \\ & \times [\beta(1) \alpha(2) - \alpha(1) \beta(2)] \\ & - \psi_f(z', 1) \alpha(1) \times [\psi_f(z'', 2) \psi_a(z''', 3) + \psi_a(z'', 2) \psi_f(z'', 3)] \\ & \times [\beta(2) \alpha(3) - \alpha(2) \beta(3)] \\ & - \psi_f(z', 2) \alpha(2) \times [\psi_f(z'', 3) \psi_a(z''', 1) + \psi_a(z''', 3) \psi_f(z'', 1)] \\ & \times [\beta(3) \alpha(1) - \alpha(3) \beta(1)] \\ & \left. - \psi_f(z', 3) \alpha(3) \times [\psi_f(z'', 1) \psi_a(z''', 2) + \psi_a(z''', 1) \psi_f(z'', 2)] \right\}. \quad (58) \end{aligned}$$

Following an analogous treatment on the right hand side of (55) the function  $\bar{\Psi}(z'', z' - z''')$  can be brought to the form

$$\begin{aligned}
 \bar{\Psi}(z'', z' - z''') = & \frac{1}{\sqrt{3!}} \left\{ \psi_a(z'', 1) \alpha(1) \times [\psi_a(z', 2) \psi_f(z''', 3) + \psi_f(z''', 2) \psi_a(z', 3)] \right. \\
 & \times [\beta(2) \alpha(3) - \alpha(2) \beta(3)] \\
 & + \psi_a(z'', 2) \alpha(2) \times [\psi_a(z', 3) \psi_f(z''', 1) + \psi_f(z''', 3) \psi_a(z', 1)] \\
 & \times [\beta(3) \alpha(1) - \alpha(3) \beta(1)] \\
 & + \psi_a(z'', 3) \alpha(3) \times [\psi_a(z', 1) \psi_f(z''', 2) + \psi_f(z''', 1) \psi_a(z', 2)] \\
 & \times [\beta(1) \alpha(2) - \alpha(1) \beta(2)] \\
 & - \psi_f(z'', 1) \alpha(1) \times [\psi_f(z', 2) \psi_a(z''', 3) + \psi_a(z''', 2) \psi_f(z', 3)] \\
 & \times [\beta(2) \alpha(3) - \alpha(2) \beta(3)] \\
 & - \psi_f(z'', 2) \alpha(2) \times [\psi_f(z', 3) \psi_a(z''', 1) + \psi_a(z''', 3) \psi_f(z', 1)] \\
 & \times [\beta(3) \alpha(1) - \alpha(3) \beta(1)] \\
 & \left. - \psi_f(z'', 3) \alpha(3) \times [\psi_f(z', 1) \psi_a(z''', 2) + \psi_a(z''', 1) \psi_f(z', 2)] \right\} \times [\beta(1) \alpha(2) - \alpha(1) \beta(2)] \quad (59)
 \end{aligned}$$

Evidently (58) describes a Heitler-London type electron pair bond between the "outer" electron of the He atom and the electron of the He<sup>+</sup> ion. Quite similarly (59) describes a Heitler-London type electron pair bond between the "inner" electron of the He atom and the electron of the He<sup>+</sup> ion.

(58) and (59) show that the three-electron bond described by (1) can be interpreted as the superposition of two resonating electron pair bonds as expressed in (56) or symbolically in (57).

It is also seen from (58) and (59) that the Heitler-London type electron pair bonds are of the heteronuclear type because of the inequality of the effective nuclear charges  $z'$ ,  $z''$  and  $z'''$ , respectively. In case of heteronuclear electron pair bonds it is pointed out (Coulson, 1952) that the bond is the stronger the smaller is the difference in the energy of the participating electrons. Our results of variation, shown in Tables 1, 2 and 3, correspond nicely to this theorem. Evidently the smaller is the difference between  $z''$  and  $z'''$ , for instance, the smaller is the difference in the energy of the electrons having these effective nuclear charges. Since the difference between  $z''$  and  $z'''$  can be made smaller either by increasing  $z''$  or by decreasing  $z'''$ , in both cases the binding energy must be larger. Indeed, this is exactly what has been found.

### 3b) Possibility of generalizing approximation A

The fact that the structure in which there is no Heitler-London type electron pair bond is equivalent to the superposition of two structures in both of which the electron pair bond is between the He atom and  $\text{He}^+$  ion is in agreement with Rumer's rule (see Pauling and Wilson (1935) p. 375). This rule states that only those structures are independent which, when superimposed, do not exhibit bonds crossing each other.

However, this situation can be modified by allowing different weight factors for the structures shown in (57). In this case the three structures become canonical, i.e. independent, and one may assume that the ground state of the  $\text{He}_2^+$  molecule ion can be described by the wave function

$$\Phi_g = c_1 \Psi(z''', z' - z'') + c_2 \Psi(z', z'' - z''') + c_3 \Psi(z'', z' - z'''), \quad (60)$$

or symbolically by

$$\Phi_g = c_1 \left[ \text{He}_{\frac{z''}{z'''}}^{z'} z''' \text{He}^+ \right] + c_2 \left[ \text{He}_{\frac{z''}{z'''}}^{z'} z''' \text{He}^+ \right] + c_3 \left[ \text{He}_{\frac{z''}{z'''}}^{z'} z''' \text{He}^+ \right], \quad (61)$$

where g means generalized and  $c_1, c_2, c_3$  are variational parameters.

Considering (54) and (55) one can rewrite (60) in the form

$$\begin{aligned} \Phi_g = & (c_1 + c_2) \Psi_1 + (c_1 + c_3) \Psi_2 - (c_1 + c_2) \Psi_3 \\ & - (c_1 + c_3) \Psi_4 - (c_2 - c_3) \Psi_5 + (c_2 - c_3) \Psi_6, \end{aligned} \quad (62)$$

from which by putting  $c_1 = c_2 = c_3$ , the original form of approximation A is obtained. One can prove that the generalized wave function in (62) satisfies the  $\sum_u^2$  molecular symmetry and for the first time, due to the different weight factors, the configurations described by  $\Psi_5$  and  $\Psi_6$  appear explicitly in the molecular wave function.

### 3c) Approximation B

Similar conclusions to those derived concerning approximation A can be drawn also for approximation B. However, some additional features appear.

In order to investigate the mechanism of the binding let us consider the following configurations which exist only when the concept of shell-opening is introduced:

$$\Psi_9 = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z',1)\alpha(1) & \psi_a(z'',1)\alpha(1) & \psi_f(z',1)\beta(1) \\ \psi_a(z',2)\alpha(2) & \psi_a(z'',2)\alpha(2) & \psi_f(z',2)\beta(2) \\ \psi_a(z',3)\alpha(3) & \psi_a(z'',3)\alpha(3) & \psi_f(z',3)\beta(3) \end{vmatrix} \quad (63.1)$$

$$\Psi_{10} = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_f(z',1)\alpha(1) & \psi_f(z'',1)\alpha(1) & \psi_a(z',1)\beta(1) \\ \psi_f(z',2)\alpha(2) & \psi_f(z'',2)\alpha(2) & \psi_a(z',2)\beta(2) \\ \psi_f(z',3)\alpha(3) & \psi_f(z'',3)\alpha(3) & \psi_a(z',3)\beta(3) \end{vmatrix} \quad (63.2)$$

$$\Psi_{11} = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(z',1)\alpha(1) & \psi_a(z'',1)\alpha(1) & \psi_f(z'',1)\beta(1) \\ \psi_a(z',2)\alpha(2) & \psi_a(z'',2)\alpha(2) & \psi_f(z'',2)\beta(2) \\ \psi_a(z',3)\alpha(3) & \psi_a(z'',3)\alpha(3) & \psi_f(z'',3)\beta(3) \end{vmatrix} \quad (63.3)$$

$$\Psi_{12} = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_f(z',1)\alpha(1) & \psi_f(z'',1)\alpha(1) & \psi_a(z'',1)\beta(1) \\ \psi_f(z',2)\alpha(2) & \psi_f(z'',2)\alpha(2) & \psi_a(z'',2)\beta(2) \\ \psi_f(z',3)\alpha(3) & \psi_f(z'',3)\alpha(3) & \psi_a(z'',3)\beta(3) \end{vmatrix} \quad (63.4)$$

By interchanging a by b these functions obey the following relations

$$\begin{aligned} \Psi_9 &\rightarrow \Psi_{10} & \Psi_{10} &\rightarrow \Psi_9 \\ \Psi_{11} &\rightarrow \Psi_{12} & \Psi_{12} &\rightarrow \Psi_{11}. \end{aligned}$$

Introducing the notations

$$\Psi(z'_i, z'_a - z''_a) = \Psi_1 + \Psi_2 - \Psi_3 - \Psi_4 \quad (64)$$

$$\Psi(z''_i, z'_a - z''_a) = \Psi_5 + \Psi_6 - \Psi_7 - \Psi_8 \quad (65)$$

$$\Psi(z'_a, z''_a - z'_i) = \Psi_1 - \Psi_9 - \Psi_3 + \Psi_{10} \quad (66)$$

$$\Psi(z''_a, z'_a - z'_i) = \Psi_2 + \Psi_9 - \Psi_4 - \Psi_{10} \quad (67)$$

$$\Psi(z'_a, z''_a - z''_i) = \Psi_5 - \Psi_{11} - \Psi_7 + \Psi_{12} \quad (68)$$

$$\Psi(z''_a, z'_a - z''_i) = \Psi_6 + \Psi_{11} - \Psi_8 - \Psi_{12}, \quad (69)$$

where the a and i subscripts of the effective charges refer to the He atom and He<sup>+</sup> ion, respectively, one can express (36) and (37) as

$$\Psi(z'_i, z'_a - z''_a) = \Psi(z'_a, z''_a - z'_i) + \Psi(z''_a, z'_a - z'_i) \quad (70)$$

$$\Psi(z''_i, z'_a - z''_a) = \Psi(z'_a, z''_a - z''_i) + \Psi(z''_a, z'_a - z''_i). \quad (71)$$

It is obvious from (70) and (71) that  $\Psi_9$ ,  $\Psi_{10}$ ,  $\Psi_{11}$  and  $\Psi_{12}$  do not appear explicitly in the molecular wave function.

Symbolizing an electron pair bond again by a solid line the "structures" described by eqs. (64) - (69) are



One may note that, as a consequence of the introduction of open-shell configurations for the  $\text{He}^+$  ion there appear not only heteronuclear but also homonuclear electron pair bonds in the molecular wave function.

The molecular wave function (35) of approximation B can be rewritten as

$$\Psi = [ \Psi(z'_a, z''_a - z'_i) + \lambda \Psi(z'_a, z''_a - z''_i) ] + [ \Psi(z''_a, z'_a - z'_i) + \lambda \Psi(z''_a, z'_a - z''_i) ], \quad (73)$$

where illustrating the meaning of "resonance", the quantities in the square brackets can be expressed as follows

$$\begin{aligned}
 & \sqrt{3!} [\Psi(z'_a, z''_a - z'_i) + \lambda \Psi(z'_a, z''_a - z''_i)] \\
 &= \psi_a(z'_1, 1) \alpha(1) \times \{ \psi_a(z''_2, 2) [\psi_f(z'_3, 3) + \lambda \psi_f(z''_3, 3)] \\
 &\quad + [\psi_f(z'_2, 2) + \lambda \psi_f(z''_2, 2)] \psi_a(z''_3, 3) \} [\beta(2) \alpha(3) - \alpha(2) \beta(3)] \\
 &+ \psi_a(z'_2, 2) \alpha(2) \times \{ \psi_a(z''_3, 3) [\psi_f(z'_1, 1) + \lambda \psi_f(z''_1, 1)] \\
 &\quad + [\psi_f(z'_3, 3) + \lambda \psi_f(z''_3, 3)] \psi_a(z''_1, 1) \} [\beta(3) \alpha(1) - \alpha(3) \beta(1)] \\
 &+ \psi_a(z'_3, 3) \alpha(3) \times \{ \psi_a(z''_1, 1) [\psi_f(z'_2, 2) + \lambda \psi_f(z''_2, 2)] \\
 &\quad + [\psi_f(z'_1, 1) + \lambda \psi_f(z''_1, 1)] \psi_a(z''_2, 2) \} [\beta(1) \alpha(2) - \alpha(1) \beta(2)] \\
 &- \psi_f(z'_1, 1) \alpha(1) \times \{ \psi_f(z''_2, 2) [\psi_a(z'_3, 3) + \lambda \psi_a(z''_3, 3)] \\
 &\quad + [\psi_a(z'_2, 2) + \lambda \psi_a(z''_2, 2)] \psi_f(z''_3, 3) \} [\beta(2) \alpha(3) - \alpha(2) \beta(3)] \\
 &- \psi_f(z'_2, 2) \alpha(2) \times \{ \psi_f(z''_3, 3) [\psi_a(z'_1, 1) + \lambda \psi_a(z''_1, 1)] \\
 &\quad + [\psi_a(z'_3, 3) + \lambda \psi_a(z''_3, 3)] \psi_f(z''_1, 1) \} [\beta(3) \alpha(1) - \alpha(3) \beta(1)] \\
 &- \psi_f(z'_3, 3) \alpha(3) \times \{ \psi_f(z''_1, 1) [\psi_a(z'_2, 2) + \lambda \psi_a(z''_2, 2)] \\
 &\quad + [\psi_a(z'_1, 1) + \lambda \psi_a(z''_1, 1)] \psi_f(z''_2, 2) \} [\beta(1) \alpha(2) - \alpha(1) \beta(2)]
 \end{aligned} \tag{74}$$

and

$$\begin{aligned}
 & \sqrt{3}! [\Psi(z''_a, z'_a - z'_i) + \lambda \Psi(z''_a, z'_a - z''_i)] \\
 &= \psi_a(z''_1) \alpha(1) \times \{ \psi_a(z'_2) [\psi_\beta(z'_3) + \lambda \psi_\beta(z''_3)] \\
 &\quad + [\psi_\beta(z'_2) + \lambda \psi_\beta(z''_2)] \psi_a(z'_3) \} [\beta(2) \alpha(3) - \alpha(2) \beta(3)] \\
 &+ \psi_a(z''_2) \alpha(2) \times \{ \psi_a(z'_3) [\psi_\beta(z'_1) + \lambda \psi_\beta(z''_1)] \\
 &\quad + [\psi_\beta(z'_3) + \lambda \psi_\beta(z''_3)] \psi_a(z'_1) \} [\beta(3) \alpha(1) - \alpha(3) \beta(1)] \\
 &+ \psi_a(z''_3) \alpha(3) \times \{ \psi_a(z'_1) [\psi_\beta(z'_2) + \lambda \psi_\beta(z''_2)] \\
 &\quad + [\psi_\beta(z'_1) + \lambda \psi_\beta(z''_1)] \psi_a(z'_2) \} [\beta(1) \alpha(2) - \alpha(1) \beta(2)] \\
 &- \psi_\beta(z''_1) \alpha(1) \times \{ \psi_\beta(z'_2) [\psi_a(z'_3) + \lambda \psi_a(z''_3)] \\
 &\quad + [\psi_a(z'_2) + \lambda \psi_a(z''_2)] \psi_\beta(z'_3) \} [\beta(2) \alpha(3) - \alpha(2) \beta(3)] \\
 &- \psi_\beta(z''_2) \alpha(2) \times \{ \psi_\beta(z'_3) [\psi_a(z'_1) + \lambda \psi_a(z''_1)] \\
 &\quad + [\psi_a(z'_3) + \lambda \psi_a(z''_3)] \psi_\beta(z'_1) \} [\beta(3) \alpha(1) - \alpha(3) \beta(1)] \\
 &- \psi_\beta(z''_3) \alpha(3) \times \{ \psi_\beta(z'_1) [\psi_a(z'_2) + \lambda \psi_a(z''_2)] \\
 &\quad + [\psi_a(z'_1) + \lambda \psi_a(z''_1)] \psi_\beta(z'_2) \} [\beta(1) \alpha(2) - \alpha(1) \beta(2)].
 \end{aligned}$$

(75)

3d) Possibility of generalizing approximation B

$$[\text{He}_{\substack{z'' \\ z'}}^{\substack{z' \\ z'}} \text{He}^+] = [\text{He}_{\substack{z'' \\ z'}}^{\substack{z' \\ z'}} \text{He}^+] + [\text{He}_{\substack{z'' \\ z'}}^{\substack{z' \\ z'}} \text{He}^+] \quad (76)$$

$$[\text{He}_{\substack{z'' \\ z''}}^{\substack{z' \\ z''}} \text{He}^+] = [\text{He}_{\substack{z'' \\ z''}}^{\substack{z' \\ z''}} \text{He}^+] + [\text{He}_{\substack{z'' \\ z''}}^{\substack{z' \\ z''}} \text{He}^+], \quad (77)$$

(76) and (77) are the symbolical forms of (70) and (71) which show again that Rumer's rule (see Pauling and Wilson, 1935 p.375) is confirmed. Removing the restriction that the structures in (76) and (77) contribute with equal weight to the molecular wave function, one may assume the following generalized wave functions

$$\Phi_{\text{I}g} = c_1 \Psi(z'_i, z'_a - z''_a) + c_2 \Psi(z'_a, z''_a - z'_i) + c_3 \Psi(z''_a, z'_a - z'_i) \quad (78)$$

$$\Phi_{\text{II}g} = c_4 \Psi(z''_i, z'_a - z''_a) + c_5 \Psi(z'_a, z''_a - z''_i) + c_6 \Psi(z''_a, z'_a - z''_i) \quad (79)$$

and write the molecular wave function as

$$\Phi_g = \Phi_{\text{I}g} + \Phi_{\text{II}g}. \quad (80)$$

In (80) the idea is expressed that all the six conceivable structures contribute to the ground state of the  $\text{He}_2^+$  molecule ion, or symbolically

$$\begin{aligned} \Phi_g = & c_1 [\text{He}_{\substack{z'' \\ z'}}^{\substack{z' \\ z'}} \text{He}^+] + c_2 [\text{He}_{\substack{z'' \\ z'}}^{\substack{z' \\ z'}} \text{He}^+] \\ & + c_3 [\text{He}_{\substack{z'' \\ z''}}^{\substack{z' \\ z''}} \text{He}^+] + c_4 [\text{He}_{\substack{z'' \\ z''}}^{\substack{z' \\ z''}} \text{He}^+] \\ & + c_5 [\text{He}_{\substack{z'' \\ z''}}^{\substack{z' \\ z''}} \text{He}^+] + c_6 [\text{He}_{\substack{z'' \\ z''}}^{\substack{z' \\ z''}} \text{He}^+]. \end{aligned} \quad (81)$$

By putting  $c_1 = c_2 = c_3$ ,  $c_4 = c_5 = c_6$  and  $\lambda = c_1/c_2$  the original form of approximation B is obtained.

#### 4) Conclusions

From the experimental value of the dissociation energy of the  $\text{He}_2^+$  molecular ion, and from the known energies of the He atom and  $\text{He}^+$  ion (measured from the state when the electrons and nucleus of the He atom and the electron and nucleus of the  $\text{He}^+$  ion, respectively, are infinitely separated) one can calculate the experimental energy,  $E_{\text{exp}}(R_e)$ , of the system  $\text{He}_2^+$ . With the value of Mason and Vanderslice ( $D_{\text{exp}} = 2.16$  ev) one obtains  $E_{\text{exp}}(R_e) = -4.983 e^2/a_0$ , and with Herzberg's value ( $D_{\text{exp}} = 3.1$  ev) one gets  $E_{\text{exp}}(R_e) = -5.018 e^2/a_0$ .\* Our calculated value ( $-4.935 e^2/a_0$ ), although better than any previously calculated value, is still not as close as one would like to the above experimental values. One may remark that the nuclear separation,  $R = 2.0 a_0 = 1.058 \text{ \AA}$ , that we have chosen to simplify the numerical work and to make comparisons with other authors' work possible, is not the actual equilibrium value. For this reason, the energy obtainable at the true minimum of the potential curve would be lower than our calculated value. A correction of that kind, however, would not fill the gap between the calculated and measured value, since the potential curve is "flat" in the neighbourhood of its minimum. In order to obtain a closer agreement one could try to apply more complicated functions for a better description of the radial correlation.

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\* It is remarked that  $1 e^2/a_0 = 27.2$  ev!

As more complicated wave functions one might consider the generalized wave functions of approximations A and B. Since they have more adjustable variational parameters than approximations A and B there is some reason to suppose that they would lead to an improvement in the calculated energy of the  $\text{He}_2^+$  molecular ion.

Another possibility for a better description of the radial correlation would be the inclusion of 2s, 3s, etc. terms in the wave function of the He atom, essentially following the works of Taylor and Parr (1952) and Shull and Löwdin (1955), with the modification that instead of closed-shell configurations the Hylleraas-Eckart type wave functions should be generalized also to the ns functions.

It seems, however, very probable that considerable improvement in the calculated energy of the  $\text{He}_2^+$  molecular ion could only be obtained by considering simultaneously with the radial, also the angular correlation. The first step in this direction could be the construction of wave functions with angular dependence capable to give account of the polarization energy (see Pauling and Wilson (1935) p. 383) of the He atom. One may note in this regard, as pointed out by Cramer and Simons (1957), on the basis of the work of Simons, Muschlitz and Unger (1943), that at 1.1 Å the polarization energy of the He atom in the field of the  $\text{He}^+$  ion is  $\sim 1$  ev. Considering that the obtained  $\sim 1$  ev is approximately the difference between the calculated and the experimental value of the molecular energy, the inclusion of polarization seems to be the most probable way of obtaining further improvement.

Appendix 1

Evaluation and explicit formulae for  
the exchange-coulomb integrals

The general exchange-coulomb integral of 1s functions

$$P_{aa,ab}(\alpha\beta, \gamma\delta) = \iint \psi_a(\alpha, i) \psi_a(\beta, i) \left(\frac{1}{r_{ij}}\right) \psi_a(\gamma, j) \psi_b(\delta, j) dv_i dv_j \quad (1)$$

can be written as

$$P_{aa,ab}(\alpha\beta, \gamma\delta) = \int V(\alpha, \beta, r_{aj}) \psi_a(\gamma, r_{aj}) \psi_b(\delta, r_{bj}) dv_j, \quad (2)$$

where

$$V(\alpha, \beta, r_{aj}) = \int \frac{\psi_a(\alpha, r_{ai}) \psi_a(\beta, r_{ai})}{r_{ij}} dv_i \quad (3)$$

is considered as a potential. It may be determined in spherical polar coordinates with the aid of a theorem in electrostatic theory as

$$V(\alpha, \beta, r_{aj}) = \frac{1}{r_{aj}} \int_0^{r_{aj}} \psi_a(\alpha, r_{ai}) \psi_a(\beta, r_{ai}) dv_i + \int_{r_{aj}}^{\infty} \frac{\psi_a(\alpha, r_{ai}) \psi_a(\beta, r_{ai})}{r_{ai}} dv_i. \quad (4)$$

Having determined  $V(\alpha, \beta, r_{aj})$  the integral in (2) can be evaluated without difficulty in confocal elliptic coordinates  $\mu, \nu, \varphi$ , defined by

$$\mu = \frac{r_{aj} + r_{bj}}{R}; \quad \nu = \frac{r_{aj} - r_{bj}}{R}; \quad \varphi = \varphi_a = \varphi_b.$$

These coordinates are defined in the intervals

$$1 \leq \mu \leq \infty; \quad -1 \leq \nu \leq 1; \quad 0 \leq \varphi \leq 2\pi,$$

and in terms of them the volume element is

$$dv_j = \frac{R^3}{8} (\mu^2 - \nu^2) d\mu d\nu d\varphi.$$

The resulting general expression, from which the 16 different integrals involved in the calculations can be derived as special cases, is of the form

$$P_{\alpha\alpha, \alpha\beta}(\alpha, \beta, \gamma, \delta) = \frac{\alpha^{3/2} \beta^{3/2} \gamma^{3/2} \delta^{3/2} R^3}{(\alpha + \beta)^3} \times \left\{ -(\alpha + \beta) [A_2(x) B_0(y) - A_0(x) B_2(y)] - \frac{4}{R} [A_1(x) B_0(y) - A_0(x) B_1(y)] + \frac{4}{R} [A_1(\bar{x}) B_0(\bar{y}) - A_0(\bar{x}) B_1(\bar{y})] \right\} \quad (5)$$

with variables

$$x = \frac{1}{2} R (\alpha + \beta + \gamma + \delta)$$

$$y = \frac{1}{2} R (\alpha + \beta + \gamma - \delta)$$

$$\bar{x} = \frac{1}{2} R (\gamma + \delta)$$

$$\bar{y} = \frac{1}{2} R (\gamma - \delta).$$

The quantities  $A_n$  and  $B_n$  are defined by

$$A_n(s) = \int_0^\infty \mu^n e^{-s\mu} d\mu = \frac{n!}{s^{n+1}} e^{-s} \sum_{k=0}^n \frac{s^k}{k!} \quad s = x, \bar{x} \quad (6)$$

and

$$B_n(s) = \int_{-1}^{+1} \nu^n e^{-s\nu} d\nu = -A_n(\bar{s}) - (-1)^n A_n(-\bar{s}) \quad \bar{s} = y, \bar{y}. \quad (7)$$

In deriving the formulae for the individual integrals one must consider the following additional relations

$$B_0(0) = 2$$

$$B_1(0) = 0$$

and

$$B_0(-\bar{y}) = B_0(\bar{y})$$

$$B_1(-\bar{y}) = -B_1(\bar{y}) .$$

It should be noted that the above outline of the evaluation of the exchange-coulomb integrals practically agrees with the work of Rüdénberg, Roothaan and Jaunzemis (1956), except that for convenience different variables  $(x, \bar{x}, y, \bar{y})$  were introduced.

#### Appendix 2

#### Evaluation and explicit formulae of the exchange integrals

The evaluation of the exchange integrals is one of the toughest problems of molecular quantummechanics. Until recently, when Rüdénberg (1951) presented a general but tedious method, only special cases were treated even for exchange integrals composed only of 1s functions. The importance of Rüdénberg's method is, that with its aid, exchange integrals composed of functions with unequal effective charges can also be calculated.

Omitting details of the very lengthy and difficult derivation of the formulae we may only mention that Rüdénberg's work is based on the

Neumann expansion of  $\frac{1}{r_{ij}}$  in terms of elliptic coordinates.

Accepting Rüdénberg's notations let us redefine the general exchange integral, composed of 1s functions with unequal effective nuclear charges, as

$$P_{ab,ab}(\xi_a, \xi_b, \bar{\xi}_a, \bar{\xi}_b) = \iint \psi_a(\xi_a, i) \psi_b(\xi_b, i) \left( \frac{1}{r_{ij}} \right) \psi_a(\bar{\xi}_a, j) \psi_b(\bar{\xi}_b, j) dv_i dv_j. \quad (1)$$

Rüdénberg has proved that (1) can be written as

$$P_{ab,ab}(\xi_a, \xi_b, \bar{\xi}_a, \bar{\xi}_b) = R^5 \xi_a^{3/2} \xi_b^{3/2} \bar{\xi}_a^{-3/2} \bar{\xi}_b^{-3/2} \sum_{l=0}^{\infty} J_l, \quad (2)$$

where

$$J_l = \sum_{n=0}^2 \sum_{\bar{n}=0}^2 \omega_n^l(\beta) \bar{\omega}_{\bar{n}}^l(\bar{\beta}) \phi_{n\bar{n}}^{0l}(\alpha, \bar{\alpha}) \quad (3)$$

with variables

$$\alpha = \frac{1}{2} R (\xi_a + \xi_b)$$

$$\beta = \frac{1}{2} R (\xi_a - \xi_b)$$

and

$$\bar{\alpha} = \frac{1}{2} R (\bar{\xi}_a + \bar{\xi}_b)$$

$$\bar{\beta} = \frac{1}{2} R (\bar{\xi}_a - \bar{\xi}_b).$$

In words, the general expression (2) is built up from two kinds of functions. From the one-parameter functions  $\omega_n^l(\beta)$  and  $\bar{\omega}_{\bar{n}}^l(\bar{\beta})$  and from the two-parameter function  $\phi_{n\bar{n}}^{0l}(\alpha, \bar{\alpha})$ .

The one-parameter functions are defined by

$$\omega_n^l(\beta) = \sum_{j=0}^2 \omega_{nj} B_j^{ol}(\beta) \quad (4)$$

$$\bar{\omega}_{\bar{n}}^l(\bar{\beta}) = \sum_{\bar{j}=0}^2 \bar{\omega}_{\bar{n}\bar{j}} B_{\bar{j}}^{ol}(\bar{\beta}), \quad (5)$$

where

$$B_j^{ol}(\beta) = \frac{1}{2} [2(2l+1)]^{1/2} \int_{-1}^{+1} dt P_l(t) e^{\beta t} t^j \quad (6)$$

$$B_{\bar{j}}^{ol}(\bar{\beta}) = \frac{1}{2} [2(2l+1)]^{1/2} \int_{-1}^{+1} dt P_l(t) e^{\bar{\beta} t} t^{\bar{j}}. \quad (7)$$

In (6) and (7)  $P_l(t)$  is the Legendre polynomial

$$P_l(t) = \frac{1}{2^l l!} \frac{d^l}{dt^l} (t^2 - 1)^l. \quad (8)$$

Before defining the much more complicated two-parameter function  $\phi_{n\bar{n}}^{ol}(\alpha, \bar{\alpha})$ , we recall that the integral (1) is presented in form of an infinite series, as given in (2). With certain rules given in Rüdénberg's paper one can determine which of the  $\omega_{nj}$  and  $\bar{\omega}_{\bar{n}\bar{j}}$  coefficients in (4) and (5) are zero and which have given numerical values. Applying these rules one can write

$$\begin{aligned} \gamma_l = \frac{1}{4} \{ & B_2^{ol}(\beta) B_2^{ol}(\bar{\beta}) \phi_{00}^{ol}(\alpha, \bar{\alpha}) - B_2^{ol}(\beta) B_0^{ol}(\bar{\beta}) \phi_{02}^{ol}(\alpha, \bar{\alpha}) \\ & - B_0^{ol}(\beta) B_2^{ol}(\bar{\beta}) \phi_{20}^{ol}(\alpha, \bar{\alpha}) + B_0^{ol}(\beta) B_0^{ol}(\bar{\beta}) \phi_{22}^{ol}(\alpha, \bar{\alpha}) \}. \end{aligned} \quad (9)$$

To illustrate the procedure let us stop at the first term of the series (2) and write

$$P_{ab, ab}(\{a\}_b, \{\bar{a}\}_{\bar{b}}) \approx R^5 \{a\}_a^{3/2} \{b\}_b^{3/2} \{\bar{a}\}_{\bar{a}}^{3/2} \{\bar{b}\}_{\bar{b}}^{3/2} J_0. \quad (10)$$

Defining

$$\phi_{00}^{00}(\alpha, \bar{\alpha}) = \frac{1}{\alpha \bar{\alpha}} \left\{ e^{-\alpha} G_0(\bar{\alpha}) + e^{-\bar{\alpha}} G_0(\alpha) - G_0(\alpha + \bar{\alpha}) \right\} \quad (11)$$

one can compute  $\phi_{n\bar{n}}^{00}(\alpha, \bar{\alpha})$  as

$$\begin{aligned} \phi_{n\bar{n}}^{00}(\alpha, \bar{\alpha}) = \frac{1}{\alpha \bar{\alpha}} \left\{ \bar{\alpha} n \phi_{(n-1)\bar{n}}^{00}(\alpha, \bar{\alpha}) + \alpha \bar{n} \phi_{n(\bar{n}-1)}^{00}(\alpha, \bar{\alpha}) \right. \\ \left. - n \bar{n} \phi_{(n-1)(\bar{n}-1)}^{00}(\alpha, \bar{\alpha}) + e^{-\alpha} G_{\bar{n}}(\bar{\alpha}) + e^{-\bar{\alpha}} G_n(\alpha) - G_{n+\bar{n}}(\alpha + \bar{\alpha}) \right\}, \end{aligned} \quad (12)$$

where introducing  $G_0$  and  $G_1$  defined by

$$G_0(x) = \frac{1}{2} e^{-x} \left\{ C + \log 2x - e^{2x} Ei(-2x) \right\} \quad (13)$$

$$G_1(x) = \frac{1}{2} e^x \left\{ C + \log 2x + e^{2x} Ei(-2x) \right\} \quad (14)$$

the  $G_n$  quantities are calculated as

$$G_n(x) = G_{n-2}(x) - A_{n-2}(x). \quad (15)$$

In (13) and (14)  $C$  is Euler's constant and  $Ei$  is the exponential integral for which tables are available. In (15)

$$A_n(x) = (-1)^n \frac{d^n}{dx^n} A_0(x) \quad (16)$$

with

$$A_0(x) = \frac{1}{x} e^{-x}. \quad (17)$$

In order to calculate  $\mathcal{J}_1$ , the second term of the infinite series (2), one needs the  $\phi_{n\bar{n}}^{01}(\alpha, \bar{\alpha})$  quantities.

These can be calculated according to

$$\phi_{n\bar{n}}^{01}(\alpha, \bar{\alpha}) = \phi_{(n+1)(\bar{n}+1)}^{00}(\alpha, \bar{\alpha}) - A_n(\alpha) A_{\bar{n}}(\bar{\alpha}) - A_{n\bar{n}}(\alpha, \bar{\alpha}), \quad (18)$$

where

$$A_{n\bar{n}}(\alpha, \bar{\alpha}) = \frac{1}{\alpha + \bar{\alpha}} \left\{ n A_{(n-1)\bar{n}}(\alpha, \bar{\alpha}) + \bar{n} A_{n(\bar{n}-1)}(\alpha, \bar{\alpha}) + A_n(\alpha) A_{\bar{n}}(\bar{\alpha}) \right\} \quad (19)$$

with

$$A_{00}(\alpha, \bar{\alpha}) = \frac{1}{\alpha + \bar{\alpha}} A_0(\alpha) A_0(\bar{\alpha}). \quad (20)$$

The above discussion shows well that this is a very lengthy method when numerical calculations are concerned. Evaluation of higher terms becomes much more complicated. We only add, for the sake of generality, that the method in case of integrals composed of more complicated functions (for instance angular dependence) is also applicable but it becomes much more complex.

For this reason, much work has been done to find fairly accurate approximations which can be handled more easily. One of these methods is known as the Mulliken (1949) approximation. The investigations of the author (1958) concerning the accuracy of this method are presented in Appendix 3.

Appendix 3

Approximation of two-center exchange integrals

Mulliken's (1949) intuitively found approximation gives for the four-center integral

$$L_{ABCD} = \iint \phi_A^{(1)} \phi_B^{(1)} \left( \frac{1}{r_{12}} \right) \phi_C^{(2)} \phi_D^{(2)} dv_1 dv_2$$

$$\approx \frac{1}{4} J_{AB} J_{CD} \{ L_{AACC} + L_{AADD} + L_{BBCC} + L_{BBDD} \}, \quad (1)$$

where  $\phi_A$ ,  $\phi_B$ ,  $\phi_C$  and  $\phi_D$  are general atomic orbitals of electrons 1 and 2 centered on the nuclei A, B, C and D.

The overlap integrals  $J_{AB}$  and  $J_{CD}$  are defined by

$$J_{AB} = \int \phi_A \phi_B dv \quad \text{and} \quad J_{CD} = \int \phi_C \phi_D dv,$$

while the two-center Coulomb integrals  $L_{AACC}$ ,  $L_{AADD}$ ,  $L_{BBCC}$  and  $L_{BBDD}$  are defined by (1).

For the simplest "symmetric" case of two-center exchange integrals when  $\phi_A$  and  $\phi_B$  are hydrogenic 1s functions, with the same "effective nuclear charge" Z, the corresponding expression can be derived from (1) by putting C = A and D = B. It is

$$L_{ABAB} = \iint \phi_A^{(1)} \phi_B^{(1)} \left( \frac{1}{r_{12}} \right) \phi_A^{(2)} \phi_B^{(2)} dv_1 dv_2$$

$$\approx \frac{1}{2} J_{AB}^2 \{ L_{AAAA} + L_{AABB} \}. \quad (2)$$

Since Sugiura (1927) has evaluated in this case the integral (2) exactly, it is possible to compare the exact values with the approximate ones. In Table 1,  $L_{ABAB}^S$  gives

the exact values of the integral (2) for various internuclear distances  $R$  when  $Z = 1$ , taken from a paper of Hirschfelder and Weigandt (1938).

Table I. The exact and approximate values of the exchange integral at various nuclear separations in atomic units  $e^2/a_0$  and  $a_0$ . The percentage errors are in parentheses.

R	$L^S_{ABAB}$	$L^M_{ABAB}$		$L^I_{ABAB}$		$L^{II}_{ABAB}$	
1.0	0.436651	0.434550	(-0.481)	0.460516	(+5.47)	0.408585	(-6.43)
1.5	0.296835	0.293265	(-1.20)	0.328673	(+10.7)	0.257857	(-13.1)
2.0	0.184156	0.180729	(-1.86)	0.214954	(+16.7)	0.146504	(-20.4)
2.5	0.106622	0.104329	(-2.15)	0.131279	(+23.1)	0.0773784	(-27.4)
3.0	0.0585083	0.0573773	(-1.93)	0.0759118	(+29.8)	0.0388429	(-33.6)
4.0	0.0156272	0.0156274	(0.00)	0.0223875	(+43.3)	0.00886737	(-43.3)
5.0	0.00371704	0.00384461	(+3.43)	0.00582948	(+56.8)	0.00185973	(-50.0)
6.0	0.03814027	0.03877901	(+7.85)	0.02138629	(+70.3)	0.03369513	(-54.6)
8.0	0.04328959	0.04388292	(+18.0)	0.04647154	(+96.7)	0.04129429	(-60.7)
12.0	0.07354836	0.07497508	(+40.2)	0.07877954	(+147)	0.07117061	(-67.0)

Column  $L^M_{ABAB}$  of Table I gives the approximate values of the integral (2) evaluated with the help of expression  $\frac{1}{2}I^2_{AB}\{L_{AAAA} + L_{AABB}\}$ . The corresponding percentage deviations from the exact values are given in parentheses. The agreement is very good except at large internuclear distances. The Mulliken approximation was obtained by Rüdénberg (1951) by expanding the wave functions of one electron centered at a given nucleus in terms of a complete orthonormal set of functions of unspecified nature centered at another nucleus and neglecting all but the largest term of the expression.

The fact that a single term of an infinite expansion gives such good agreement is due to the following circumstances. The Mulliken formula in (2) is the arithmetic mean of two approximations, each of which is based on the same expansion theorem mentioned before.

In one approximation, one sets

$$\phi_{A1s}(j) = \sum_{i=1}^{\infty} J_{AB_i} \psi_{B_i}(j) \quad \begin{matrix} j = 1, 2 \\ i = 1s, 2s, \dots \end{matrix} \quad (3)$$

where the  $\psi_{B_i}$ 's are hydrogenic functions with  $Z = 1$  and  $J_{AB_i} = \int \phi_A \psi_{B_i} dV$ . Keeping only the first term of each series after substitution in the integral in (2), one obtains

$$L_{ABAB} \approx I_{AB1}^2 L_{BBBB}$$

Column  $L^I_{ABAB}$  of Table 1 gives the values obtained from this expression. The errors have positive signs and are given in parentheses.

In the other approximation, one sets

$$\phi_{A1s}(1) = \sum_{i=1}^{\infty} J_{AB_i} \psi_{B_i}(1) \quad (4)$$

and

$$\phi_{B1s}(2) = \sum_{i=1}^{\infty} J_{AB_i} \psi_{A_i}(2).$$

Keeping again only the first term of each series after substitution in the integral in (2), one obtains

$$L_{ABAB} \approx I_{AB1}^2 L_{AABB}$$

The values obtained from this expression are listed in column  $L^{II}_{ABAB}$  of Table 1. The errors have negative signs

and are given in parentheses.

The fact that the errors of  $L_{ABAB}^I$  and  $L_{ABAB}^{II}$  are not of the same sign suggests the possibility that inclusion of the second term of the Rüdénberg series may not improve the result, because the convergence of one series may be much better than that of the other. It would be difficult to say whether the same situation arises in the case of exchange integrals composed of functions other than  $1s$  functions.

One may state that the Mulliken approximation will give a good result when the two approximations (3) and (4) give errors with opposite signs. If both approximations give errors with the same sign, then one of them would be better than the Mulliken approximation.

It is noteworthy that recently a new approach has been worked out by Tauber (1958) for the evaluation of homonuclear exchange integrals which is based on the solution of Poisson's equation.

Appendix 4

Valence electron approximation

1) General remarks

In calculating the binding energy of molecules the question as to whether the electrons of filled inner shells may or may not be neglected is important. If the simplification of omitting the cores is allowed then the calculation of the binding energy of most diatomic molecules is reduced to a one-, two- or three-electron problem.

In this section an attempt has been made to reinvestigate this problem and to work out such a method which will be referred to as Valence Electron Approximation (VEA).

2) Discussion

a) The  $\text{Li}_2$  molecule. (Homonuclear two-electron bond).

In the early stage of molecular quantum mechanics, based on the assumption that only the valence electrons outside of closed shells are responsible for the binding, several molecules were discussed in an approximation that explicitly considered only the valence electrons. In this type of calculation the orbital exponents of the wave functions of the valence electrons usually have the value obtained by a variational calculation on the infinitely separated component atoms when all electrons are considered. James (1933, 1934) criticized these calculations and pointed out that the omission of the inner shells leads to a serious error in the calculated energy of the molecules since by the omission of

the cores their repulsive effect is neglected. It is also believed by Coulson (1952, p. 95) that the repulsion is the only role that the inner shells play in the binding. For this reason if one wants to omit the inner shells and to deal only with the valence electrons, a method must be found which includes the repulsion of the cores.

Let us demonstrate the rightness of James' criticism in the case of the  $\text{Li}_2$  molecules which was discussed by Bartlett and Furry (1931) as a two-electron problem. For the molecular wave function they have chosen a Heitler-London type wave function. Their energy expression, derived with a two-electron Hamiltonian, at  $R = \infty$  goes over into the expression

$$E_{\text{calc.}}(R_{\infty}) = 2E_{\text{Li}2s} = 2 \int \varphi_{\text{Li}2s} H_{\text{Li}2s} \varphi_{\text{Li}2s} dv. \quad (1)$$

Calculation of  $E_{\text{Li}2s}$  with

$$H_{\text{Li}2s} = -\frac{1}{2} \Delta - \frac{1}{r}$$

and with the Guillemin and Zener (1930) type function\*

$$\varphi_{\text{Li}2s} = \left(\frac{\gamma^5}{3\pi}\right)^{1/2} r e^{-\gamma r},$$

used by Bartlett and Furry, gives

$$E_{\text{Li}2s} = \frac{1}{6} \gamma^2 - \frac{1}{2} \gamma. \quad (2)$$

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\* Apart from the numerical value of the orbital exponent it is the same as the nodeless 2s function of Slater (1930)

We must now interpret what  $E_{Li2s}$  means. Since the inner shell of the Li atom is not considered,  $E_{Li2s}$  is the energy necessary to remove the 2s electron from the Li atom, because in this model a  $Li^+$  ion has no energy. Eq. (2) upon substitution of  $\zeta = 0.63$  as applied by Bartlett and Furry yields

$$E_{Li2s} = -0.2489 e^2/a_0 ,$$

for the ionization energy of the valence electron of the Li atom. This value is wrong because according to Landolt-Börnstein (1950) the measured value is  $-0.1985 e^2/a_0$ . The too low value is due to the fact that the repulsion between the core and the valence electron is neglected when the inner shell electrons are omitted. For similar reasons the molecular energy calculated by Bartlett and Furry is also too large.

Knowing the experimental value of the ionization energy, the repulsion between the core and the 2s valence electron of the Li atom can be taken care of. The solution of the equation

$$\int \psi_{Li2s} H_{Li2s} \psi_{Li2s} dv = \frac{1}{6} \zeta^2 - \frac{1}{2} \zeta = E_{Li2s} \text{ exp.} \quad (3)$$

yields the  $\zeta = 0.4709$  value which is much smaller than the  $\zeta = 0.63$  used by Bartlett and Furry. The wave function with the orbital exponent  $\zeta = 0.4709$  describes an electron which is centered at a nucleus of single positive charge and moves in the Coulomb field of this

point-like attractive center occupying a 2s orbit of the same energy as that of the 2s electron of the Li atom in the superimposed field of a triply charged point-like nucleus and a doubly charged centrosymmetric but not Coulomb-like core. Due to the repulsion between the core and the valence electron the latter is pushed to an orbit which is of larger diameter.

A calculation has been carried out for the Li<sub>2</sub> molecule by the author with the Heitler-London type function

$$\Psi = \varphi_{A2s} (1) \varphi_{B2s} (2) + \varphi_{B2s} (1) \varphi_{A2s} (2),$$

where the one-electron functions are Slater type nodeless functions of the form

$$\varphi_{x2s} (i) = \left( \frac{\gamma^5}{3\pi} \right)^{1/2} r_{xi} e^{-\gamma r_{xi}} \quad \begin{array}{l} i = 1, 2 \\ x = A, B \end{array}$$

with orbital exponent  $\gamma = 0.4709$  as determined from (3).

The molecular energy is calculated from

$$E = \frac{\int \Psi H \Psi dv}{\int \Psi^2 dv}, \quad (4)$$

where

$$H = -\frac{1}{2} \Delta_1 - \frac{1}{2} \Delta_2 - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{R}. \quad (5)$$

All integrals were determined exactly except the exchange integral which was calculated in the Mulliken

approximation. The potential curve has been determined and the values corresponding to its minimum are shown and compared with the experimental values in Table 2. The experimental energy of the  $\text{Li}_2$  molecule is calculated from the measured ionization energy (Landolt-Börnstein, 1950) of the 2s electron of the Li atom and from the measured dissociation energy (Herzberg, 1950) of the  $\text{Li}_2$  molecule. (In the following paragraphs of this appendix all the empirical data are taken from the previously quoted two sources and for this reason they will not be quoted again.)

TABLE 2. The calculated and experimental constants of the  $\text{Li}_2$  molecule

	Molecular energy (in ev)	Equilibrium internuclear distance (in Å)
Experimental	-11.83	3.02
Calculated	-11.50	2.67

Comparison of the experimental values with our values shows a satisfactory character, insomuch that the calculated energy value is higher than the empirical one and the calculated  $R_e$  value is larger than the empirical one as expected using a Heitler-London type function. In our approximation it is assumed that the interaction between the valence electron of one atom and the superimposed field of the nucleus and core of the other atom is very much the same

as that between the valence electron and the reduced charge (nuclear charge minus charge of K-shell) of the other atom.

b) The LiH molecule. (Heteronuclear two-electron bond).

A calculation has been carried out with the wave function

$$\psi = \varphi_{A1s}^{(1)} \varphi_{B2s}^{(2)} + \varphi_{B2s}^{(1)} \varphi_{A1s}^{(2)}, \quad (6)$$

and Hamiltonian (5), where A and B represent the nuclei of the H and Li atoms respectively, and the 1s and 2s functions are Slater-type nodeless functions with orbital exponents  $\lambda_A = 1$  and  $\lambda_B = 0.4709$ . The calculated and experimental values of the molecular constants are shown and compared in Table 3.

TABLE 3. The calculated and experimental constants of the LiH molecule

	Molecular energy (in ev)	Equilibrium internuclear distance (in Å)
Experimental	-21.42 *	1.60
Calculated	-20.32	1.53

\* In calculating the experimental molecular energy Velasco's (1958) dissociation energy has been used.

c) The BeH<sup>+</sup> molecule. (Heteronuclear two-electron bond).

The results of a calculation of the author with the Hamiltonian

$$H = -\frac{1}{2} \Delta_1 - \frac{1}{2} \Delta_2 - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{2}{r_{B1}} - \frac{2}{r_{B2}} + \frac{1}{r_{12}} + \frac{2}{R}$$

and wave function (6) with orbital exponents  $\lambda_A = 1$  and  $\lambda_B = 0.7567$  as determined from

$$E_{\text{Be}^+2s \text{ exp.}} = \int \psi_{\text{Be}^+2s} H_{\text{Be}^+2s} \psi_{\text{Be}^+2s} d\nu$$

where

$$H_{\text{Be}^+2s} = -\frac{1}{2} \Delta - \frac{Z}{r},$$

is compared with the experimental values in Table 4.

TABLE 4. The calculated and experimental constants of the  $\text{BeH}^+$  molecule

	Molecular energy (in ev)	Equilibrium internuclear distance (in Å)
Experimental	-35.0	1.31
Calculated	-33.9	1.35

d) The  $\text{Li}_2^+$  molecule. (Homonuclear one-electron bond).

The calculated values of the author, using the wave function

$$\Psi_{\text{I}} = \psi_{A2s} + \psi_{B2s}$$

with orbital exponents  $\lambda_A = \lambda_B = 0.4709$  and the Hamiltonian

$$H = -\frac{1}{2} \Delta - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

are shown in Table 5. Unfortunately no comparison is possible with the experimental values since the dissociation energy and the equilibrium internuclear distance have not been measured.

TABLE 5. The calculated constants of the  $\text{Li}_2^+$  molecule

	Molecular energy (in ev)	Equilibrium internuclear distance (in Å)
Calculated I	-5.66	4.23
Calculated II	-6.52	2.70

A second calculation of the author, which includes also the polarization of the valence electron, is based on the function

$$\Psi_{\text{II}} = \varphi_{A2s} + \varphi_{B2s} + \lambda (\varphi_{A2p_z} + \varphi_{B2p_z}),$$

where the  $2p_z$  functions are of the Slater-type and have the same orbital exponent (0.4709) as the  $2s$  functions. The results obtained when the variational parameter  $\lambda$  has the optimal value of 1.26 are also shown in Table 5.

e) The  $\text{BeH}^{++}$  and  $\text{LiH}^+$  molecules. (Heteronuclear one-electron bonds).

Calculations of the author using the wave function

$$\psi = \varphi_{A1s} + \lambda \varphi_{B2s}$$

and Hamiltonian

$$H = -\frac{1}{2} \Delta - \frac{1}{r_A} - \frac{2}{r_B} + \frac{2}{R}$$

indicated no stability of these molecules in a large interval of nuclear separations.

As far as the author knows these molecular ions have not yet been observed experimentally either.

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