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I am submitting herewith a dissertation written by Robert V. Miller entitled "A Variational Calculation of the Repulsive Interaction Energy Between Two Helium Atoms Using United Atom Wave Functions." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

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We have read this dissertation and recommend its acceptance:

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A VARIATIONAL CALCULATION OF THE REPULSIVE INTERACTION ENERGY BETWEEN TWO HELIUM ATOMS USING UNITED ATOM WAVE FUNCTIONS

A Dissertation

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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by

Robert V. Miller

June 1962

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the guidance, encouragement, and patience of Professor R. D. Present throughout the course of this investigation. Discussions with Professor A. F. Saturno of the Department of Chemistry have been enlightening.

The financial support from a Dryzer Award by the University of Tennessee, from a National Science Foundation summer fellowship, and through a graduate teaching assistantship made the completion of this work possible.

Finally, gratitude must be expressed to the members of the University of Tennessee Computing Center, who rendered valuable assistance in the completion of the required calculations.

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CHAPTER I

BACKGROUND OF THE PROBLEM AND THE METHODS OF SOLUTION

In principle the energy of interaction between molecules can be determined exactly by the utilization of the Schrödinger equation and the Pauli exclusion principle for electrons. In practice the Schrödinger equation cannot be solved exactly. Approximation methods must be utilized, and the basic problem then becomes one of selecting methods appropriate to the particular physical situation under investigation.

In this chapter the problem is presented, and the qualitative theoretical background necessary for later considerations is given. The treatment of the problem is justified, the relevant experimental work described, and the discrepancy between experimental results and previous theoretical calculations noted. Material contained in later chapters is briefly outlined.

I. STATEMENT OF THE PROBLEM AND CONTRIBUTIONS PRESENTED TOWARD A SOLUTION

Present knowledge of the energy of interaction between two normal helium atoms is not sufficient to give agreement between theory and experiment over the complete

range of internuclear separations investigated. A significant difference between the theoretically calculated values of the interaction potential and the experimental values exists at small values of the internuclear separation (3,5). The discrepancy between theory and experiment increases with decreasing separation. The work presented in this thesis adds to the theoretical information by presenting new values for the calculated interaction energy for the small internuclear separations of 1 a.u. (0.529A.), 0.75 a.u., and 0.50 a.u. These calculations have been made by the variational method utilizing Slater type orbitals to form one-center wave functions characterizing electronic configurations of the united atom. Two-center wave functions have been used in the best previous variational calculations of the repulsive interaction (16, 24, 25). The results of the calculations with one-center wave functions tend to reduce, but do not remove, the discrepancy between the theoretical values and the energies given by the empirical equation of Buckingham (6). The equation of Buckingham reproduces the results from early atomic beam scattering experiments (1, 4).

The one-center calculations of this thesis also yield an indication of the range of internuclear separations over which one-center united atom wave functions may be expected to be superior to the two-center wave functions

which are most suitable for large separations. An approximate upper limit for the range of separations over which the one-center method is preferred has been obtained by determining the separation R_c at which the united atom configuration yielding the lowest energy changes from the $(1s^2 2s^2)$ configuration to the $(1s^2 2p\sigma^2)$ configuration. On the basis of the correlation of atomic and molecular states this point may be considered as separating the range of internuclear separations over which the wave function has an atomic character from the range over which the wave function has a predominantly molecular character.

II. ELECTRONIC STATES OF HOMONUCLEAR DIATOMIC MOLECULES

The Designation of States

The classification of the electronic states of a molecule is associated with the symmetries of the molecule. An isolated diatomic molecule may be rotated about the internuclear axis formed by a line between the two nuclei without changing the energy of the molecule. Such a symmetry indicates the existence of an ignorable coordinate in classical mechanics and indicates a separability of the Schrödinger equation with respect to a coordinate in wave mechanics. As a result of the rotational symmetry of the system of two atoms, the component of total orbital angular momentum of the electrons along the internuclear axis is

conserved. The quantum number Λ corresponding to this component of angular momentum takes on integral values 0, ±1, ±2, ···. The states for different Λ values are designated in a manner analogous to the designation of atomic angular momentum states; Greek letters are used as analogs to the Latin letters for atomic states. Thus the states corresponding to successive Λ values of 0, 1, and 2 are designated as Σ, Π, and Δ states.

A reflection of the electronic coordinates in any plane containing the internuclear axis leaves the energy unchanged, but the direction of the component of angular momentum along the internuclear axis is reversed. Two successive reflections in a given plane return all electrons to their original positions. Since two successive reflections are equivalent to the identity transformation, the effect of a single reflection on a Σ state wave function is to multiply the wave function by +1 or -1. There is no change in the angular momentum component under this operation, since the component along the internuclear axis is zero for a Σ state. Therefore Σ states may be designated as plus or minus Σ states, i.e. Σ^+ or Σ^-, on the basis of the respective presence or absence of a sign change in the wave function upon reflection of the electronic coordinates in a plane containing the internuclear axis.

When the two nuclei of a system composed of two identical atoms are identical, the distribution of electrons

relative to each nucleus is the same. The molecule then possesses symmetry with respect to the inversion of electron coordinates in a center located at the midpoint between nuclei. If the inversion produces no sign change in the wave function, the state of the system is termed gerade. The term ungerade is applied to states with wave functions which change sign upon inversion of the coordinates. The gerade and ungerade character are designated by the posterior subscripts g and u attached to the term symbol.

Finally, the total spin S is indicated by a superscript preceding the term symbol and indicating the term multiplicity as given by the value of the quantity (2S+1). The molecular states of interest in this thesis are all $^1\Sigma_g^+$ states corresponding to the symmetry of the ground state wave function for the system composed of two interacting helium atoms originally in their ground states.

The Correlation of States

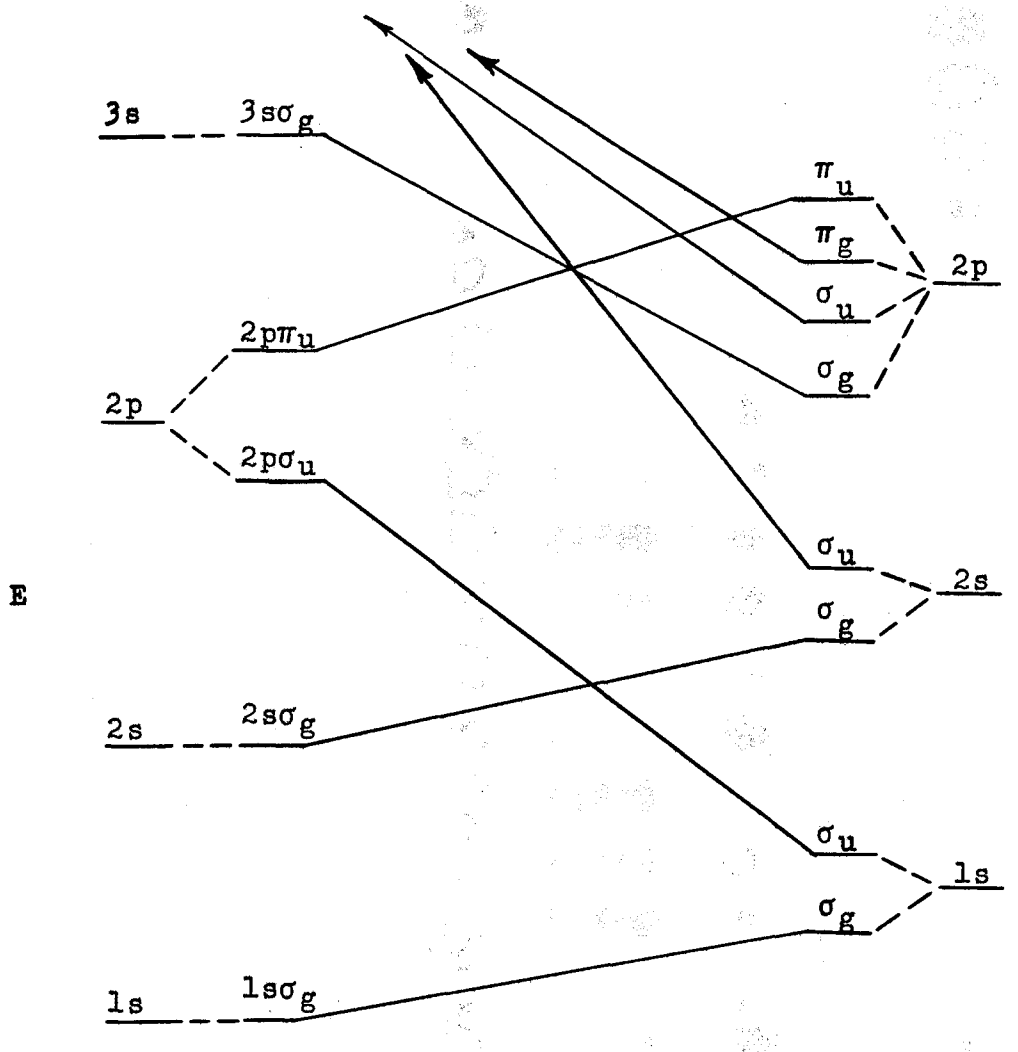
The symmetry properties of molecules are retained independently of a variation in the internuclear distance. A given molecular state therefore becomes, in the limit of zero internuclear separation, an atomic state with the same symmetry belonging to the united atom. The molecular states corresponding to two interacting helium atoms thus pass into states of the united atom beryllium as the separation is decreased.

The application of this principle of symmetry invariance is not sufficient by itself to give a one-to-one correspondence between the united atom states and the molecular states. One must also apply the theorem that the energy levels corresponding to states with the same symmetry properties cannot cross as the internuclear separation is varied (17). While the value of the energy of a state at a given internuclear separation is not indicated by these procedures, it is possible to obtain information with regard to the relative ordering of states.

Both in the united atom limit and for the individual separated atoms approximate solutions of the Schrödinger equation are used which associate an orbital wave function with each electron of the atom. Likewise the concept of one electron orbital functions may be applied as a first approximation to the molecular wave function. The one electron orbitals are designated in a manner analogous to the nomenclature for the complete molecular state. The component of angular momentum along the internuclear axis corresponding to a given one electron orbital is indicated by a small Greek letter. Thus the axial component of angular momentum for σ, π, and δ type orbitals is 0, ± 1, and ± 2 respectively. By application of the symmetry rules and the non-crossing theorem for states of the same symmetry, a correspondence may be established between orbital states of

the electrons in a molecule and the orbital states in the separated atoms and in the united atom. This correspondence between orbitals is displayed by means of correlation diagrams. A correlation diagram which shows the correspondence of united atom, molecular, and separated atom orbitals for a homonuclear diatomic molecule is given in Fig. 1 (12). By application of the exclusion principle limiting the number of electrons assigned to an orbital to two electrons of opposite spin, a correlation diagram may be prepared showing the correspondence between the many electron states of the united atom, the molecule, and the separated atoms. The correlation diagram for two states of the system composed of two ground state helium atoms is given in Fig. 2 (12). In these diagrams the scales of energy and distance are arbitrary. A line between states of the separated atoms and states of the united atom indicates correlated states. The molecular states are indicated by term symbols adjacent to the lines showing correlations.

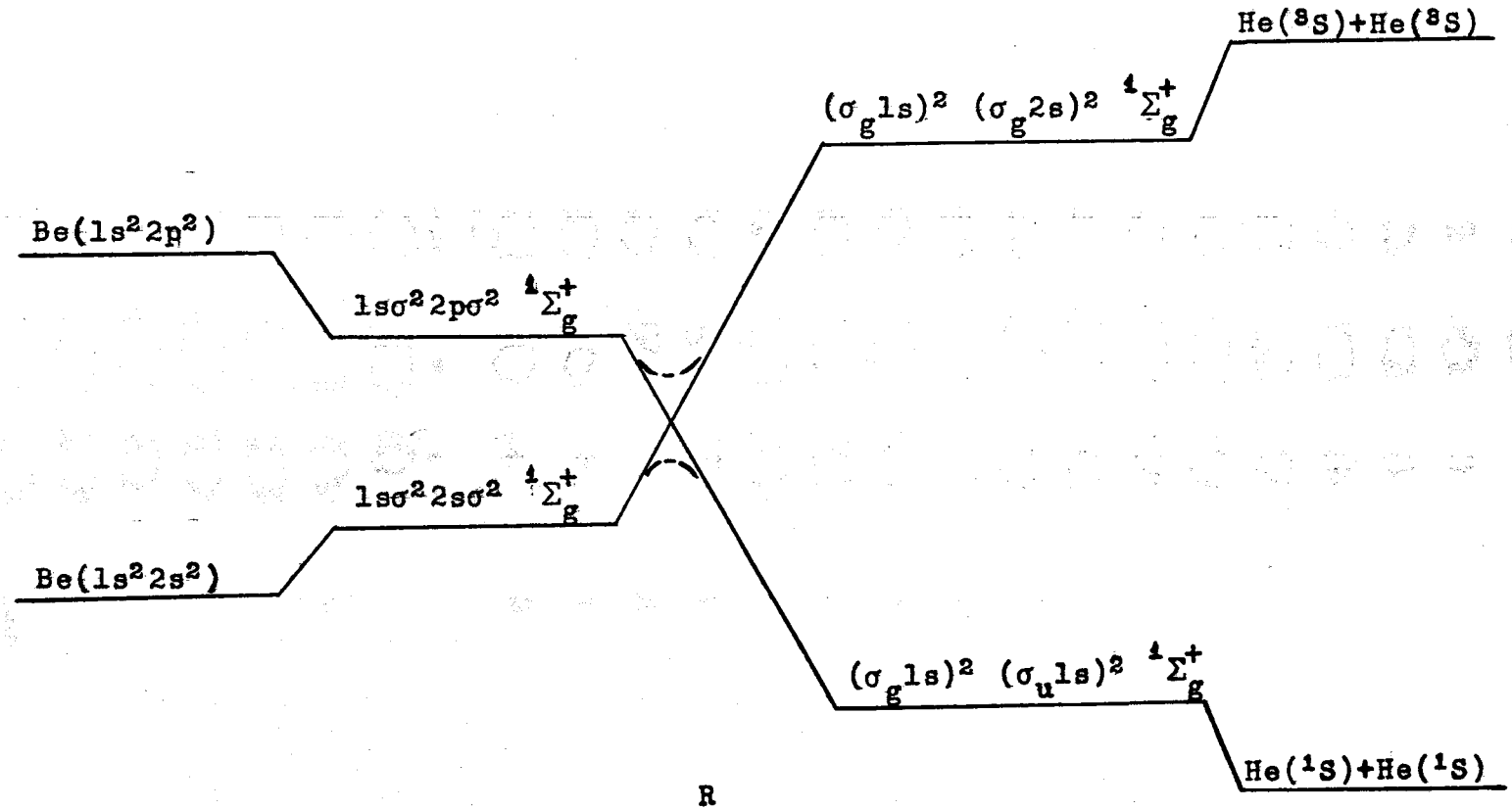
From Fig. 1 it is readily seen that the four 1s electrons possessed by two separate helium atoms in the ground state pass into the excited united atom configuration ($1s^2 2p\sigma^3$). On the other hand, if the two separate helium atoms are each in the excited state ($1s2s, {}^3S$), the ground state configuration ($1s^2 2s^2$) of beryllium may be attained. In either case the molecular state is ${}^1\Sigma_g^+$. The crossing of



The scales of energy E and of separation R are relative.

FIGURE 1

CORRELATION OF LOWEST STATES FOR ELECTRONS IN A HOMONUCLEAR DIATOMIC MOLECULE



The scales of energy E and separation R are relative.

FIGURE 2

CORRELATION OF STATES
FOR HE-HE

the molecular states with the same symmetry will not occur for the actual system. The Schrödinger equation for the system is not separable in the coordinates of each electron, and the concept of electronic orbitals is only applicable to an independent particle model which ignores the Coulomb interaction between electrons. The dotted lines of Fig. 2 indicate the actual correspondence between states with a crossing of levels of the same symmetry avoided.

Thus the united atom configuration corresponding to the lowest energy state of the molecule with small internuclear separation is $(1s^2 2s^2)$. On the other hand the lowest energy level at large separations correlates with the united atom configuration $(1s^2 2p\sigma^2)$. A united atom configuration change is therefore associated with the lowest energy level as the separation of the nuclei is decreased. The molecular symmetries remain invariant however.

III. JUSTIFICATION FOR THE UNITED ATOM METHOD

The approximate wave functions ordinarily used in theoretical calculations for diatomic molecules are considered to be the first terms in an expansion of the true wave function with respect to one or two centers. The one-center expansion is made about the center of mass of the molecular system in terms of spherical coordinates. The two-center expansion utilizes two sets of spherical

coordinates with origins located at each of the two nuclei. The two-center method is appropriate for the description of two atoms in the limit of infinite separation. In the limit of zero separation the one center method gives a good approximation to the true wave function for the united atom. Hence, one expects a diatomic molecular system to be accurately described by a one-center expansion for small internuclear separations, but a two-center expansion should be more appropriate for large internuclear separations. In this thesis the one-center expansion with united atom orbitals for the electrons has been used to obtain the interaction energy between two helium atoms at small internuclear distances.

The range of separations for which the one-center expansion is preferred over the two-center expansion may be approximately determined by a method based upon a consideration of the united atom configuration corresponding to the lowest energy level as a function of the separation of the nuclei. Previous considerations of the correlation diagrams of Fig. 1 and Fig. 2 indicated that the lowest energy level in the interaction of two helium atoms correlated with the united atom configuration ($1s^2 2p^4$) for small internuclear separations. As a result of this correlation with the united atom ground state, the wave function for the system may be said to possess an atomic

character. For large separations the lowest energy level no longer correlates with the united atom ground state, but it does correlate with the excited united atom configuration ($1s^2 2p\sigma^2$). However, in contrast to the correlation with an excited united atom configuration, this same level correlates with the ground state ($1s^2$) for each of the two separated helium atoms. Thus at large separations the molecular character of the wave function is best represented by the ($1s^2 2p\sigma^2$) configuration in terms of the united atom states. The regions of applicability of the one-center method and the two-center method may be approximately distinguished from each other by determining the separation at which the wave function for the lowest energy level changes from a function of predominantly united atomic character to a wave function more characteristic of the separated atoms. The value of R_c of the separation at which such a change occurs is determined approximately in this thesis by calculating the energies for the ($1s^2 2s^2$) and ($1s^2 2p\sigma^2$) united atom configurations with united atom wave functions for several values of the internuclear separation. The united atom method is then considered to be preferred over the two-center method for separations less than the value of R_c at which the levels for the two configurations cross. In a higher order approximation to the true wave function, one would use a linear combination of the wave functions for the two

configurations. The relative amounts of the wave functions used in the mixture would change as the separation increased such that the predominance of the ($1s^2 2s^2$) configuration at small separations would give way to the ($1s^2 2p\sigma^2$) configuration at large separation.

IV. EXPERIMENTAL METHODS

The intermolecular potential energy function for the interaction between two normal helium atoms has been determined from second virial coefficient data, viscosity data, and from the cross sections for the scattering of beams of helium atoms by helium atoms. The first two methods are limited by the magnitude of the thermal energies involved to the determination of the potential energy function in the regions of attraction and slight repulsion. The scattering experiments involve beams with energies of up to 2,000 electron volts, and these experiments are therefore suited to the determination of the interaction potential in the steeply repulsive regions at the small separations with which this thesis is concerned.

The experimental values of the potential function at small separations have been presented in a series of papers by Amdur and others (1, 3, 4, 5). The cross sections for the large angle scattering of a beam of neutral helium atoms by a helium gas target were measured as a function of the

incident beam energy. The same cross section can be calculated from classical theory provided one assumes a suitable form for the potential. To interpret the experimental results the potential was assumed by Amdur and his colleagues to have the form

$$V = K/R^s \qquad (1)$$

where R is the internuclear separation and K and s were determined by the experiments. With this potential function the resulting theoretical equation for the cross section indicated that a plot of the logarithm of the cross section against the logarithm of the energy should yield a straight line. The equation giving the best straight line fit to a given set of data when plotted with logarithmic scales was obtained. The slope of the straight line thus fitted to the experimental data was used to obtain the exponent s, and the coefficient K was determined from the intercept of the straight line. The validity of Eq. (1) with the experimental values for the parameters K and s was restricted to a small range of values of the internuclear separation. The appropriate range of separation values was determined from the minimum and maximum values of the cross section and the effective geometry of the experimental arrangement of source, scattering chamber, and detector.

The beam of neutral particles required for the scattering experiment is obtained by first accelerating helium ions produced in an arc discharge to energies

corresponding to potential differences of 150 volts to 2,000 volts between an accelerating electrode and the hot filament of the arc. Part of the ions incident upon the accelerating electrode pass through a collimating slit in the electrode. Charge exchange occurs between the fast helium ions and the background of neutral helium atoms present and between the ions and the edges of the collimating slit. As a result of charge exchange the beam contains neutral atoms with energies corresponding to the energies of the original ions. An electric field transverse to the beam direction removes ions from the beam passed by the collimating slit. The beam of neutral particles which is left passes through a small hole into a scattering chamber containing the target helium atoms. Undeflected particles and particles scattered through small angles pass through a second hole in the scattering chamber and fall upon a thermocouple. The intensities of the transmitted beams with gas in the chamber and without the scattering gas are obtained from the thermocouple readings. From these beam intensities the experimental scattering cross section may be calculated with appropriate corrections being made for the source and detector geometries.

The experimental analysis has been criticized (29) for its reliance on a theoretical expression for the scattering cross section which is derived on the basis of

classical rather than quantum theory. The use of classical theory has been justified by Amdur (2), and the quantum corrections are considered to be only a few per cent of the measured potential (3). It has also been noted (20) that while charge exchange at the edges of the collimating slit produces neutral helium atoms, the neutral atoms may be in excited metastable states. The interaction potential determined by the experiment may therefore correspond to a mixture of the interactions between target helium atoms in the ground state with ground state helium atoms and with excited helium atoms in the beam.

The interaction potentials reported by Amdur and others (1, 4, 5) and the ranges of application are as follows:

$$\varphi(R) = 4.62\ R^{-1.79} \times 10^{-12} \text{ erg.} \quad (0.52\text{A} < R < 1.02\text{A}), \quad (2)$$

$$\varphi(R) = 7.55\ R^{-5.94} \times 10^{-12} \text{ erg.} \quad (1.27\text{A} < R < 1.59\text{A}), \quad (3)$$

$$\varphi(R) = 5.56\ R^{-5.08} \times 10^{-12} \text{ erg.} \quad (0.97\text{A} < R < 1.48\text{A}). \quad (4)$$

More recent data have been given by Amdur and Bertrand (3) which give potentials approximately 75 per cent larger at small separations than the values as given by Eq. (2). A new potential function has not been presented.

An empirical potential function has been given by Buckingham (6) for the helium interaction at small separations. This potential function was selected to give the correct value of electronic energy for the united atom

beryllium in the ground state and to very closely reproduce Eqs. (2) - (4). The potential function for the interaction of helium atoms is given by

$$V(R) = 4R^{-1} e^{-2.48R} (1 + 0.265R - 2.419R^2 + 2.616R^3 - 0.436R^4) \quad (5)$$

with the internuclear distance R and the potential energy given in atomic units.

V. THEORETICAL METHODS

The basic forces responsible for the molecular interactions are well known, being simply the Coulomb forces between the electrons and nuclei of which the system is composed. The interaction is thus determined by the application of the Schrödinger equation using Coulomb potentials with the additional quantum mechanical requirement that valid solutions must be antisymmetric with respect to an interchange of any two electrons. The antisymmetry principle is fundamental to the determination of molecular interactions, not because of any modification of the Coulomb potentials, but because the wave function determines the probability density distribution of the charges. The solution of molecular problems therefore requires the determination of properly antisymmetric wave functions which satisfy the Schrödinger equation. Such solutions cannot be

readily found even for the simplest systems of charges. Recourse must therefore be made to methods which produce approximate solutions. Accompanying any basic approximate method and its variations is a large number of terminologies indicative of the procedures used. The basic methods of approximation used for molecular problems are perturbation theory and the variational method. Both of these methods require the use of ab initio wave functions. It is with respect to the procedures for establishing such wave functions that a broad terminology is used in molecular physics. Some of these terms and their abbreviations are briefly explained in the following paragraphs because of their occurrence in this thesis or in reference material.

An independent particle model is usually assumed at once and orbital functions chosen for the electrons in a manner analogous to the use of hydrogen-like orbitals in atomic physics. However, there is no simple molecular problem yielding simple analytic solutions which might be used as a basis for wave functions of more complicated molecular problems. Basic molecular orbitals (abbreviated as MO's) must be constructed. In the one-center or united atom method one simply uses an atomic orbital function. However for the two-center description of molecules MO's may be established by using a linear combination of atomic orbitals (LCAO). For example, let φ_n represent an atomic

orbital, and let φ_{nA} represent the same atomic orbital with nucleus A as a center. For a diatomic molecule with nuclei designated as A and B the LCAO-MO method may be used to form a molecular orbital $\Phi(i)$ for the i^{th} electron by means of the equation

$$\Phi(i) = \varphi_{nA}(i) \pm \varphi_{nB}(i) \quad . \tag{6}$$

The plus or minus sign is selected on the basis of whether a gerade type symmetry is desired or whether an ungerade symmetry is desired.

A suitable spin function may be associated with each MO. The MO's with spin functions for each of the electrons may then be used to form an antisymmetric wave function for the system of electrons by means of the Slater determinant method used in atomic physics. The exclusion principle must be employed, and the number of electrons characterized by a given MO limited to two electrons of opposite spin. The abbreviations are frequently employed in the literature of molecular physics without direct explanation of their significance.

In either the one-center or two-center method alternatives exist for the selection of the atomic orbitals. The hydrogen-like wave functions employed in atomic physics might be used. However, as in atomic physics, a series of nodeless hydrogen-like orbitals termed Slater type orbitals

(STO's) are quite frequently employed. For use in the variational method the Slater type orbitals are defined by

$$\varphi_{n,l,m} = N_{n,l} R_{n,l}(r) P_l^m(\cos\theta) e^{im\varphi} \quad . \tag{7}$$

$N_{l,m}$ represents the normalization constant, and $P_l^m(\cos\theta)$ represents an associated Legendre function. The nodeless radial functions $R_{n,l}(r)$ are given by

$$R_{n,l}(r) = r^{n-1} e^{-\eta_{n,l} r} \quad , \tag{8}$$

where the quantities $\eta_{n,l}$ are usually used as variation parameters. The letters n, l, and m have the usual significance, i.e. they represent the principal, azimuthal, and magnetic quantum numbers. Atomic orbitals need not be composed of a single Slater type orbital. Better approximations may be obtained by using a linear combination of Slater type orbitals (LC-STO). A linear combination of an 1s orbital and a pσ orbital has been used by a number of authors (11, 16, 25) to allow for polarization of the 1s orbital in the study of the He-He interaction.

As in atomic physics, improved wave functions may be obtained by using a linear combination of Slater determinants. Each determinant represents a particular molecular configuration, and the use of such linear combinations is referred to as the method of configuration interaction (CI).

In addition to these methods a more general formalism applicable to polyatomic molecules may be used. This method

which is termed the valence bond method (VB) requires a somewhat lengthy discussion. Since the valence bond method as applied to the interaction of helium atoms is identical (28) with the molecular orbital method in most cases, the method will not be elaborated here.

The abbreviations used in the preceding paragraphs and often found in the literature are reviewed in the following list:

MO	molecular orbital
LCAO	linear combination of atomic orbitals
STO	Slater type orbital
LC-STO	linear combination of Slater type orbitals
CI	configuration interaction
VB	valence bond

V. COMPARISON OF THEORY AND EXPERIMENT

The problem of determining the interaction between two helium atoms has received considerable attention, both experimentally (1, 3, 4, 5) and theoretically (6, 10, 11, 14, 15, 16, 19, 21, 24, 25, 26, 27), as a result of the discrepancy between theory and experiment at small separation. A brief discussion of the theoretical methods employed and the results obtained is presented in the following paragraphs. Finally some of the more significant theoretical results are compared with the experimental results and with the empirical function given by Buckingham (6).

First order perturbation theory utilizing the atomic orbitals of the separated atoms may be applied to obtain the repulsive valence energy. Such a perturbation calculation has been carried out by P. Rosen (26). The helium atom electron orbitals employed were those obtained from a variational calculation for helium (23). By a second order perturbation calculation one may include not only the repulsive valence energy but also the dispersion energy and the second order exchange energy (13). A second order perturbation calculation has been made by N. Lynn (19) with approximations for some of the integrals. In addition a parameter was introduced such that by proper choice of the parameter, agreement with experiment could be obtained at one value of the internuclear separation. These perturbation calculations used two-center wave functions. Variational calculations have improved upon the results of P. Rosen, and the work of Lynn is semi-empirical. Hence, the results of the perturbation calculations will not be presented, and emphasis will be placed upon the more successful, completely theoretical variational calculations.

Both one-center coordinates and two-center coordinates have been used with the variation method. S. Husinaga (14) has applied united atom wave functions to the determination of the interaction energy between helium atoms for the $(1s^2 2p\sigma^2)$ united atom configuration. The results of

Husinaga are presented in Fig. 3. An additional parameter has been varied for this configuration in the work of this thesis, and the improved results are presented in Chapter IV. A number of two-center calculations have been made with various forms for the trial wave functions. The two-center method with wave functions based on the valence bond procedure has been applied by M. Sakamoto and C. Ishiguro (27). The atomic orbitals used were expressed in terms of prolate spheroidal coordinates. The use of these orbitals gives a wave function which explicitly includes the internuclear separation. The results of Sakamoto and Ishiguro are displayed in Fig. 3. A modified form of the valence bond theory has been used by N. Moore (21). The product of the diagonal elements of a determinantal wave function was modified by Moore to allow for polarization of the electron orbitals. No significant improvement over the work of other authors resulted at small separations.

A number of authors (10, 11, 15, 16, 24, 25) have used the molecular orbital method in a straight-forward way to determine the interaction energy as a function of separation. These calculations differ in the types of atomic orbitals used and the number of parameters varied. The best results have been obtained by Hashino and Husinaga (11), Ransil (25), and by Phillipson (24). The results of these papers are also presented in Fig. 3.

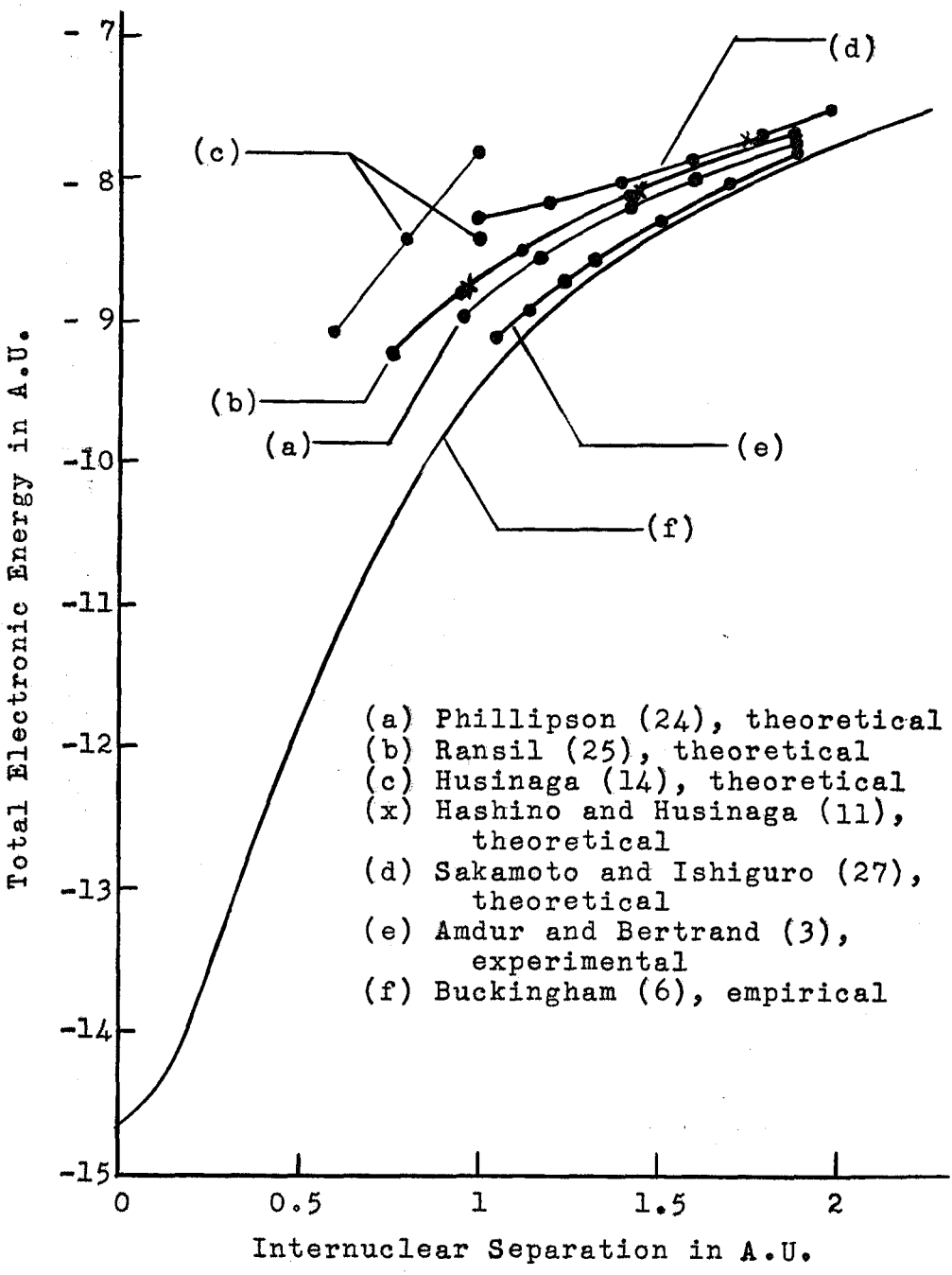


FIGURE 3

RECENT VALUES OF THE ELECTRONIC ENERGY FOR THE HE-HE INTERACTION AT SMALL SEPARATIONS

The calculations which have produced significant results at small internuclear separations are summarized by means of Table I. Some of the results are given in Fig. 3. In this figure the total electronic energy is plotted as a function of the internuclear distance. Previous papers have presented results in terms of the interaction potential energy obtained by subtracting the calculated electronic energy of two helium atoms at infinite separation from the total interaction energy of two helium atoms at a finite separation. The true value of the electronic energy for two separated helium atoms has not been used. This procedure insures that the potential energy of interaction at infinite separation is zero. Where the variational method has been used, the errors in the calculated total energies are in the same direction for both the calculation at finite separation and at infinite separation. The errors therefore tend to cancel each other when the difference is taken to determine the interaction energy. Calculations based on one-center united atom wave functions cannot utilize this procedure. In previous work with one-center methods Husinaga (14) used the calculated electronic energy as obtained by two-center methods for the separated helium atoms in order that his results might be compared with other work in terms of the potential energy of interaction. Calculated values for the separated atoms are usually close

TABLE I

SOME OF THE CALCULATIONS OF THE HE-HE INTERACTION

Author	Method	Type of Wave Function	Electron Orbitals	Comments
Rosen, P. (26)	Perturbation	VB	(1s) $e^{-Z_1 r}$ (1s') $e^{-Z_2 r}$	Z_1 and Z_2 from variational treatment of He atom
Griffing, V. and Wehner, J. F. (10)	Perturbation	LCAO-MO	STO, 1s functions Z=27/16	Variation of Z was concluded to be unnecessary
Sakamoto, M. and Ishiguro, E. (27)	Variational	VB=LCAO-MO	1s $e^{-(\alpha+\beta)r/R}$ 1s' $e^{-(\alpha-\beta)r/R}$	Orbitals contain separation distance R
Husinaga, S. (14)	Variational	One-center	STO's; $(1s^2 2p\sigma^2)$ and $[(1s+4s+4d\sigma)^2 2p\sigma^2]$ configurations	1s and $2p\sigma$ parameters assumed equal for most calculations

TABLE I (continued)

Author	Method	Type of Wave Function	Electron Orbitals	Comments
Hashino, T. (11) Husinaga (11, 14)	Variational	LCAO-MO	LC-STO ($1s+\lambda g2p\sigma$)	Different λ and STO parameters for σ_u and σg MO's
Ransil, B. J. (25)	Variational	LCAO-MO	LC-STO $1s+\lambda 2s+\gamma 2p\sigma$	Same exponential parameters for 1s,2s, and $2p\sigma$ orbitals but differing for σ_u and σ_g MO's
Phillipson, P. E. (24)	Variational	LCAO-MO, CI	$1s,2s,2p\sigma,2p\pi$ STO's in as many as 64 configurations	Different parameters for σ_u and σ_g MO's

to a value of -5.6953 a.u. (10, 14, 27) as compared to an experimental value of -5.8074 a.u. The difference between the two values is 0.1121 a.u. (3.049 e.v.). This arbitrary procedure is avoided in this thesis by making all comparisons in terms of the total electronic energy.

Figure 3 presents the results of several authors in terms of the total electronic energy. The total electronic energy is obtained by subtracting the energy due to the Coulomb interaction between nuclei from the calculated total energy. In the limit of zero separation the electronic energy then corresponds to the electronic energy of the ground state of beryllium. The electronic energy in Fig. 3 is given in terms of Hartree's atomic units. The atomic unit of energy is equivalent to 27.2 electron volts. The unit of length in atomic units corresponds to 0.529 angstroms.

For comparison with the theoretical results the electronic energies calculated from the empirical potential function of Buckingham (6) as given by Eq.(5) are also plotted in Fig. 3. The Buckingham equation closely reproduces the early experimental work (1, 4, 5). The more recent results of Amdur and Bertrand (3) are also indicated in Fig. 3. The discrepancy between the theoretical values of Phillipson (24) and the experimental values at a separation of 1.0 a.u. is seen to be about 0.40 a.u. (11 e.v.). The discrepancy

decreases at larger separations. This thesis provides additional theoretical information on the interaction energy at small internuclear separations where a united atom treatment is appropriate.

VI. MATERIAL IN SUCCEEDING CHAPTERS

In Chapter II the basic methods utilized to obtain an approximate solution to the problem of determining the interaction energy for two helium atoms at small separation are considered. The Schrödinger equation is presented in general form. The wave equation for the electronic states in terms of one-center coordinates is then obtained. The variational principle is stated as a method of obtaining approximate solutions. Consideration is then given to the concepts leading to the use of united atom orbitals and the method of constructing a suitable wave function.

The considerations of the previous chapters are applied in Chapter III to obtain the equations for the expectation value of the Hamiltonian. The resulting equations are functions of the variation parameters and of the internuclear separation. Wave functions representing several single configurations and a linear combination of configurations are used. Equations are presented for the various kinetic energy, potential energy, coulomb energy, and exchange energy terms which occur in the general energy expression.

The results of calculations leading to the minimization of the energy expressions are given in Chapter IV. The point at which the lowest energy level changes from the $(1s^2 2s^2)$ united atom configuration to the $(1s^2 2p\sigma^2)$ united atom configuration is approximately determined. The improved results are given which are obtained with configuration interaction between the $(1s^2 2s^2)$ configuration and the $(1s3d\sigma\ 2s^2, {}^1\Sigma_g^+)$ configuration. Conclusions based upon the results of the calculations are then presented.

A graph is given in the appendix to display the minimization procedure. Additional equations utilized in evaluating Coulomb and exchange integrals are listed. The variationally determined screened charges are compared with the empirical screened charges for Be. Finally a bibliography of references used in the thesis is included.

CHAPTER II

BASIC PRINCIPLES AND APPLIED APPROXIMATIONS

The complete Schrödinger equation for two interacting molecules includes the nuclear motions and therefore the vibrational and rotational motions of the complete system. The vibrational and rotational motions are not considered in determining the electronic states of the molecule. The Schrödinger equation for electronic states is discussed in this chapter using one-center coordinates. The variational principle used to obtain approximate solutions is stated. Finally the united atom wave functions are constructed.

I. THE SCHRÖDINGER EQUATION

The Equation for Electronic States

The time-independent Schrödinger equation for a molecule composed of n electrons and N nuclei is given by

$$\left(-\frac{\hbar^2}{2m} \sum_{\mu=1}^{n} \nabla_\mu^2 - \frac{\hbar^2}{2} \sum_{A=1}^{N} \frac{1}{M_A} \nabla_A^2 + V \right) \Psi = W \Psi \ , \qquad (9)$$

where V represents the sum of the electrostic potentials for the interactions between all pairs of charges, m is the electronic mass, and the M_A represent the masses of the nuclei. Due to the electrostatic potential term which involves both nuclear and electronic coordinates the equation is not

separable in the coordinates. However, the nuclear and electronic motions may be separated from one another by means of the Born-Oppenheimer approximation (13). In this approximation the electronic probability density distribution is assumed to be a slowly varying function of the nuclear coordinates, and the approximation is good because the nuclear motions are very slow compared to the electronic motions. The equation for the electronic wave function ψ obtained by making the Born-Oppenheimer approximation is

$$\left(-\frac{\hbar^2}{2m}\sum_{\mu=1}^{n}\nabla_\mu^2 + V\right)\psi = E(R)\psi\,, \qquad (10)$$

where E is the electronic energy plus the nuclear repulsion energy. The total energy W includes the nuclear rotational and vibrational energy. The nuclear coordinates which appear in Eq. (10) are considered as parameters which are held fixed while solving the equation for the wave functions of the electronic states. The solution of the electronic equation yields wave functions and energy eigenvalues which are functions of the nuclear coordinates.

Thus the wave equation for the electronic states of two interacting helium atoms involving four electrons and the two helium nuclei is given by

$$H\psi = -\frac{\hbar^2}{2m}\sum_{\mu=1}^{4}\nabla_\mu^2\psi - 2e^2\sum_{\mu=1}^{4}\left(\frac{1}{r_{\mu A}} + \frac{1}{r_{\mu B}}\right)\psi$$

$$+ e^2\sum_{\mu<\nu=1}^{4}\left(\frac{1}{r_{\mu\nu}}\right)\psi + \left(\frac{4e^2}{R}\right)\psi = E(R)\psi\,, \qquad (11)$$

where e and m refer to the charge and mass of the electron. The distance between the μ^{th} amd ν^{th} electrons is designated by $r_{\mu\nu}$. The distances $r_{\mu A}$ and $r_{\mu B}$ are the distances of the μ^{th} electron from the nuclei A and B, respectively, and the internuclear separation is represented by R. The relationship between coordinates is shown in Fig. 4. The spherical coordinates to be used in the development of the united atom treatment of the problem are designated for the μ^{th} electron by r_μ, θ_μ, and φ_μ. The angles φ_μ are measured in a plane perpendicular to the internuclear axis, and r_μ and θ_μ are specified in Fig. 4. For convenience the substitution $\rho = 1/2\ R$ will be made in the equation. The equation may also be simplified by the introduction of atomic units of length and energy. The unit of length adopted is the Bohr radius given by

$$a_o = \frac{\hbar^2}{me^2} = 1 \text{ a.u. of length} = 0.529 \text{ A.} \qquad (12)$$

The unit of energy is

$$\frac{e^2}{a_o} = \frac{me^4}{\hbar^2} = 1 \text{ a.u. of energy} = 27.2 \text{ e.v.} \qquad (13)$$

With these simplifications Eq. (11) yields

$$H\psi = \left[-\frac{1}{2} \sum_{\mu=1}^{4} \nabla_\mu^2 - 2 \sum_{\mu=1}^{4} \left(\frac{1}{r_{\mu A}} + \frac{1}{r_{\mu B}} \right) + \sum_{\mu<\nu=1}^{4} \sum^{4} \frac{1}{r_{\mu\nu}} + \frac{2}{\rho} \right] \psi = E\psi . \qquad (14)$$

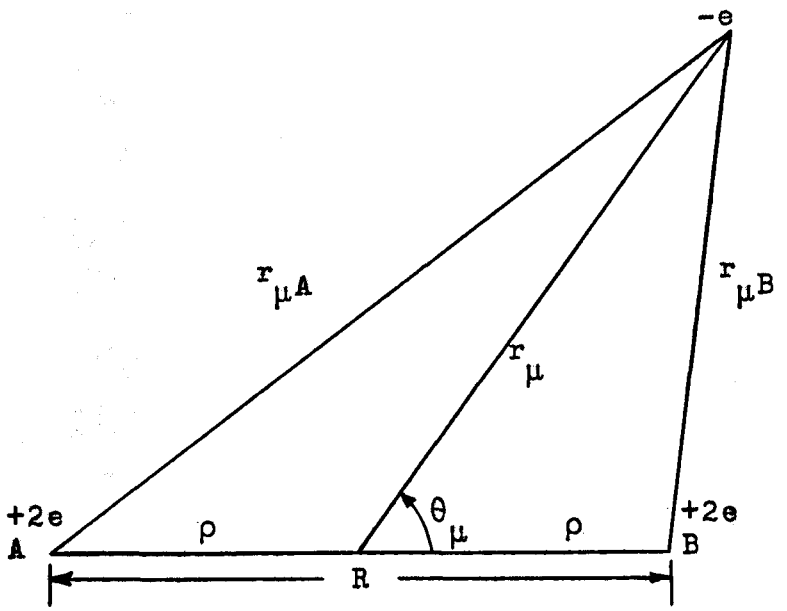


FIGURE 4

COORDINATES OF THE μ^{th} ELECTRON
FOR THE HE-HE PROBLEM

Both the one-center and the two-center methods utilize Eq. (14) by the substitution of the coordinates and operators appropriate to the given method.

The potential terms in the Hamiltonian are not affected by a rotation of the entire system about the internuclear axis. The coordinates φ_μ for the four electrons may be replaced by the set of coordinates composed of three relative azimuthal angles and the azimuthal angle of one electron relative to a fixed plane. The potential term then depends only upon the relative angles φ_{12}, φ_{13}, and φ_{14}. The Schrodinger equation is thus separable in the angle φ_1 of the system of electrons relative to a fixed plane. The solution of the equation in terms of φ_1 is

$$\Phi = N_\varphi \, e^{i\Lambda\varphi_1} \quad , \tag{15}$$

where Λ takes on integral values. The quantum number Λ corresponds to the component of angular momentum along the internuclear axis. The method is applicable to a molecular system of any number of electrons. In this thesis the main interest lies in the lowest states. Hence, only the Σ states with $\Lambda = 0$ are considered. The Schrödinger equation is not separable in the other coordinates when two or more electrons are involved, and the introduction of approximations is required to obtain solutions of the equation. It is worth noting, however, that the Schrödinger equation for a one electron system, such as the hydrogen molecule ion, is

separable in a system of confocal elliptic coordinates (23). The resultant solutions could furnish a set of electron orbitals which might be used as a basis for the study of more complex molecules in a manner analogous to the use of hydrogen-like orbitals in the study of complex atoms. However, the separated equations for the molecular ion problem are not solvable in terms of simple analytic functions. Hence the use of hydrogen molecular ion-like orbitals is not convenient for the study of molecules with several electrons.

The Use of One-Center Coordinates

The potential energy terms for the interaction between the electrons and the nuclei may be expanded in terms of one-center coordinates by using the following expressions (13)

$$\frac{1}{r_{\mu A}} = \sum_{n=o}^{\infty} \left(\frac{r_<^n}{r_>^{n+1}} \right) P_n(\cos\theta_\mu) , \qquad (16)$$

$$\frac{1}{r_{\mu B}} = \sum_{n=o}^{\infty} \left(\frac{r_<^n}{r_>^{n+1}} \right) P_n(-\cos\theta_\mu) . \qquad (17)$$

The symbols $r_>$ and $r_<$ indicate the larger and the smaller respectively of the two quantities r_μ and ρ. These symbols have been used, as the expansion assumes different forms when r_μ is larger than ρ and when r_μ is smaller than ρ. Taking into account that the Legendre polynomials $P_n(\cos\theta)$

are odd or even functions as n is odd or even, the sum of Eq. (15) and Eq. (16) yields

$$\frac{1}{r_{\mu A}} + \frac{1}{r_{\mu B}} = 2 \sum_{n=o}^{\infty} \left(\frac{r_<^{2n}}{r_>^{2n+1}} \right) P_{2n}(\cos\theta_\mu) . \qquad (18)$$

Likewise the expression for the mutual interaction between electrons may be expanded in one-center coordinates (13).

$$\frac{1}{r_{\mu\nu}} = \sum_{n=o}^{\infty} \sum_{m=-n}^{+n} \frac{(n-|m|)!}{(n+|m|)!} \frac{r_<^n}{r_>^{n+1}} P_n^{|m|}(\cos\theta_\mu) P_n^{|m|}(\cos\theta_\nu) \times e^{im(\varphi_\mu - \varphi_\nu)} . \qquad (19)$$

In Eq. (18) $r_>$ and $r_<$ indicate the larger and the smaller respectively of r_μ and r_ν. The Hamiltonian operator in terms of one-center coordinates then becomes

$$H = -\frac{1}{2} \sum_{\mu=1}^{4} \nabla_\mu^2 - 4 \sum_{\mu=1}^{4} \sum_{n=o}^{\infty} \left(\frac{r_<^{2n}}{r_>^{2n+1}} \right)_{r_\mu, \rho} P_{2n}(\cos\theta_\mu)$$

$$+ \sum_{\mu<\nu=1}^{4} \sum_{n=o}^{\infty} \sum_{m=-n}^{+n} \frac{(n-|m|)!}{(n+|m|)!} \left(\frac{r_<^n}{r_>^{n+1}} \right)_{r_\mu, r_\nu} \times P_n^{|m|}(\cos\theta_\mu) P_n^{|m|}(\cos\theta_\nu) e^{im(\varphi_\mu - \varphi_\nu)}$$

$$+ \frac{2}{\rho} . \qquad (20)$$

The term $2/\rho$ is constant for a given internuclear separation. Subtracting this term from Eq. (20) yields the Hamiltonian for the electronic energy without the nuclear repulsion energy.

II. THE VARIATIONAL PRINCIPLE

The energy of a system may be calculated with an accuracy limited only by the choice of the approximate wave functions used in the application of the variation method. The variational principle states (23) that the energy value obtained by taking the expectation value of the Hamiltonian operator with approximate wave functions is an upper limit to the lowest energy eigenvalue for the system represented by the Hamiltonian operator. It is therefore convenient to use as a wave function a general form containing arbitrary parameters. The expectation value of the Hamiltonian is calculated with such a function, and the parameters in the resulting expression are then varied to obtain a minimum value for the energy. The effectiveness of the method in providing energy values approaching the true value is dependent upon the skill with which the general forms of the wave function are chosen. The accuracy can always be improved by modifying a function to include a larger number of variational parameters. However, the work involved in the minimizing process may become prohibitive.

A convenient method of modifying a trial wave function is to add to the original function a second function multiplied by a variation parameter. Particular use will be made in this thesis of a linear combination of orthogonal

wave functions. The equations applicable to a linear combination of orthogonal functions will be developed here.

Let $\psi_1, \psi_2, \ldots \psi_n$ be orthogonal normalized wave functions. As a trial wave function one may use

$$\varphi = c_1\psi_1 + c_2\psi_2 + \ldots c_n\psi_n \,, \tag{21}$$

in which $c_1, c_2, \ldots c_n$ are real parameters to be varied to give the lowest value for the energy. The value of the energy obtained by using the wave function φ of Eq. (21) is given by

$$E = \frac{\int \varphi^* H \varphi \, d\tau}{\int \varphi^* \varphi \, d\tau} = \frac{\sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j H_{ij}}{\sum_{i=1}^{n} c_i^2} \,, \tag{22}$$

where H_{ij} is defined by

$$H_{ij} = \int \psi_i^* H \psi_j \, d\tau \,. \tag{23}$$

The values of the coefficients c_i which give an extremum are found from the equations obtained by equating to zero the derivative of the energy expression with respect to each of the coefficients. Taking the derivatives one obtains

$$\frac{\partial E}{\partial c_k} \sum_{i=1}^{n} c_i^2 + E \frac{\partial}{\partial c_k} \sum_{i=1}^{n} c_i^2 = \frac{\partial}{\partial c_k} \sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j H_{ij} \tag{24}$$

for k = 1 to n. Setting $\frac{\partial E}{\partial c_k}$ equal to zero and noting that $H_{ij} = H_{ji}$ for real trial functions, one obtains

$$2 \sum_{i=1}^{n} c_i H_{ik} - 2c_k E = 0 , \quad k = 1 \text{ to } n , \qquad (25)$$

or

$$\sum_{i=1}^{n} c_i (H_{ik} - E\delta_{ik}) = 0 , \quad k = 1 \text{ to } n . \qquad (26)$$

This set of n homogeneous equations in the n independent parameters $c_1, \ldots, c_n$ has a solution only if the determinant of the coefficients is equal to zero. Hence, there are n values of the energy E corresponding to the roots of

$$\begin{vmatrix} H_{11} - E & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22} - E & \cdots & H_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} & H_{n2} & \cdots & H_{nn} - E \end{vmatrix} = 0 . \qquad (27)$$

The root of lowest value is then an upper limit to the true energy value.

The general forms of the functions suitable as trial wave functions are usually determined by using appropriate coordinates and suitable approximations in the Hamiltonian such that the Schrödinger equation is separable and approximate solutions obtainable in terms of one electron orbitals. The complete wave function is then constructed of functions similar to the one electron orbitals by means of a Slater determinant. This approach is used in applying the united atom method.

III. UNITED ATOM WAVE FUNCTIONS

The wave equation utilizing the Hamiltonian previously presented is not separable in the coordinates of the individual electrons. The potential term for the mutual interaction between electrons couples the motion of one electron to that of all the other electrons. Two distinct effects are ascribed to the presence of the mutual interaction term. First, the presence of several electrons results in a decrease in the net electric field attracting a single electron towards a nucleus relative to the electric field of the nucleus with only one electron present. Hence, when the net electric field acting upon a particular electron considered to be in a fixed position is averaged over all positions of the other electrons, the resultant average field is less than the field produced by the nucleus alone. The effective nuclear charge is termed the screened charge of the nucleus. In applications of the variation method the nuclear charge may be taken as a variation parameter in the wave function. The process of minimizing the energy is then one of determining the values for the screened nuclear charges.

Secondly, since the electrons interact with each other, the detailed motion of one electron is dependent upon the motions of all of the other electrons. The electrons tend to avoid each other due to their mutual repulsion. This effect is termed the correlation effect, since the electronic

probability densities are correlated and will not be the same as the probability densities for independent electrons.

The separability of Eq. (20) is also prevented as a result of the non-central field due to the two nuclei. As a step toward attaining separability, one makes the united atom approximation by considering the equation for the electronic wave functions which is obtained by allowing the internuclear separation to become zero. The potential term corresponding to the repulsion between nuclei is dropped in making this approximation, as the interest lies in the electronic states of the united atom, and the details of coalescence of the nuclei are of no concern. With the united atom approximation the Hamiltonian becomes

$$H = -\frac{1}{2}\sum_{\mu=1}^{4}\nabla_{\mu}^{2} - \sum_{\mu=1}^{4}\frac{4}{r_{\mu}} + \sum_{\mu<\nu=1}^{4}\sum^{4}\left(\frac{1}{r_{\mu\nu}}\right) . \qquad (28)$$

This is the Hamiltonian for the electronic states of the Be atom, and the solution of the corresponding Schrodinger equation should yield a good approximation to the electronic wave function for two interacting helium atoms at small internuclear separation. However, analytic solutions to the corresponding Schrödinger equation are not obtainable. In order to obtain simple analytic solutions a further approximation is made by neglecting the potential due to the interaction of the electrons with each other. Separability is then attained with respect to the coordinates of each

electron. The approximate Schrödinger equation for the μth electron then becomes

$$\left(-\frac{1}{2} \nabla_\mu^2 - \frac{4}{r_\mu} \right) \psi_\mu = E_\mu \psi_\mu \,. \qquad (29)$$

This equation is separable in the spatial coordinates r_μ, θ_μ, φ_μ of the electron, and the resulting solutions are hydrogen-like orbitals corresponding to the united atom beryllium. For calculations based upon hydrogen-like orbitals it is convenient to use the Slater type orbitals of Eq. (7) and Eq. (8). The approximate antisymmetric wave function for a singlet state is then obtained by the use of the determinantal form of the wave function with two electrons of opposite spin assigned to each of two electron orbitals.

The simple wave functions which are obtained by the preceding procedures may be applied with refinements which provide some correction for the approximations made. Thus, the use of the charges in the exponents of the Slater type orbitals as variational parameters permits correction for screening of the nuclei. Correction for the correlation effect may be accomplished by using a large number of configurations with the method of configuration interaction (18). Finally, the non-central field character of the problem may be accounted for by using configurations such that the contributions of the angular dependent terms in

the potential expansion as given by Eq. (18) are non-zero when the expectation value of the Hamiltonian is determined.

The united atom approximation is not the only one-center method which has been applied to molecular problems. Cohen and Coulson (8) have obtained approximate solutions for the hydrogen-molecular ion problem without making the united atom approximation. By means of a series expansion for the wave function approximate solutions were sought for the Hamiltonian

$$H = -\frac{1}{2}\nabla^2 - 2\sum_{n=0}^{\infty}\left(\frac{r_<^{2n}}{r_>^{2n+1}}\right)_{r,\rho} P_{2n}(\cos\theta) + \frac{1}{2\rho} \quad . \quad (30)$$

Chen (7) has discussed the possibility of using solutions for a Hamiltonian which excludes the inter-electronic potential energy and all but the first term in the expansion for the potential energy of the electrons in the field of the nuclei. Thus, the Hamiltonian discussed by Chen would have the following form for the problem of two helium atoms

$$H = \begin{cases} \sum_{\mu=1}^{4}\left(-\frac{1}{2}\nabla_\mu^2 - \frac{4}{r_\mu} + \frac{2}{\rho}\right), & (r_\mu > \rho), \quad (31) \\ \sum_{\mu=1}^{4}\left(-\frac{1}{2}\nabla_\mu^2 - \frac{4}{\rho} + \frac{2}{\rho}\right), & (\rho > r_\mu). \quad (32) \end{cases}$$

The field of the two nuclei is thus replaced by a form of a potential well.

The methods of Cohen and Coulson (8) and Chen (7) represent attempts to use approximate wave functions which

account for the non-central field character of the potential due to the nuclei and for the finite separation of the nuclei. These methods are in contrast to the united atom approximation which assumes a central field arising from a single nuclear charge equal to the sum of the charges on the separate nuclei.

CHAPTER III

THE EXPECTATION VALUE OF THE HAMILTONIAN

Approximate energy values are obtained by evaluating the expectation value of the exact Hamiltonian with approximate wave functions. The standard procedure for constructing approximate wave functions has been described.

In this chapter the expectation values of the Hamiltonian for different electronic configurations of the united atom are expressed in terms of the standard kinetic energy, potential energy, Coulomb, and exchange integrals. These expressions are valid for any set of orthonormal electronic orbitals. The specific electron orbitals used in this thesis are listed, and the explicit expressions are then given for the various integrals with these orbitals. Finally, integrals and energy expressions introduced by a consideration of configuration interaction are given.

I. GENERAL FORMS WITH SINGLE CONFIGURATION WAVE FUNCTIONS

The expectation value of the Hamiltonian may be expressed in terms of a number of integral expressions of simple form if the wave function is composed of orthonormal one-electron orbitals. For a system of four electrons placed in two one-electron orbitals the singlet wave function in the form of a Slater determinant is given by

$$\psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} \varphi_a(1)\alpha(1) & \varphi_a(1)\beta(1) & \varphi_b(1)\alpha(1) & \varphi_b(1)\beta(1) \\ \varphi_a(2)\alpha(2) & \varphi_a(2)\beta(2) & \varphi_b(2)\alpha(2) & \varphi_b(2)\beta(2) \\ \varphi_a(3)\alpha(3) & \varphi_a(3)\beta(3) & \varphi_b(3)\alpha(3) & \varphi_b(3)\beta(3) \\ \varphi_a(4)\alpha(4) & \varphi_a(4)\beta(4) & \varphi_b(4)\alpha(4) & \varphi_b(4)\beta(4) \end{vmatrix} . \quad (33)$$

φ_a and φ_b represent the electron orbital functions while α and β are the conventional spin functions. Utilizing the permutation notation for the Slater determinant, the expectation value of a Hamiltonian with the wave function of Eq. (33) is given by

$$\langle \psi^*, H\psi \rangle = \frac{1}{4!} \sum_{\text{spin}} \iiiint \sum_{P} (-1)^P P[\varphi_a(1)\alpha(1)\varphi_a(2)\beta(2)\varphi_b(3)\alpha(3)$$

$$\times \varphi_b(4)\beta(4)]^* H \sum_{P'} (-1)^{P'} P'[\varphi_a(1)\alpha(1)\varphi_a(2)\beta(2)$$

$$\times \varphi_b(3)\alpha(3)\varphi_b(4)\beta(4)]d\tau_1 d\tau_2 d\tau_3 d\tau_4 . \quad (34)$$

The quantum numbers of the orbital functions are indicated by the Latin subscripts, while the numbers in parentheses enumerate the electrons which are to be permuted. The general integral may be decomposed into the sum of a number of integrals of standard form by methods given in many texts (9, 23).

The expectation value for the Hamiltonian of Eq. (14) with the wave function given by Eq. (33) yields for the energy of two interacting helium atoms

$$\langle \psi^*, H\psi \rangle = E = 2T_{aa} + 2T_{bb} - 2V_{aa} - 2V_{bb} + J_{aa}$$

$$+ J_{bb} + 4J_{ab} - 2X_{ab} + 2/\rho \ , \qquad (35)$$

where

$$T_{kk} = -\frac{1}{2}\int \varphi_k(\mu)\nabla_\mu^2 \varphi_k(\mu)\, d\tau_\mu \qquad (36)$$

$$V_{kl} = 2\int \varphi_k(\mu)\left(\frac{1}{r_{\mu A}} + \frac{1}{r_{\mu B}}\right)\varphi_l(\mu)\, d\tau_\mu \ , \qquad (37)$$

$$J_{kl} = \iint \varphi_k(\mu)\varphi_l(\nu)\left(\frac{1}{r_{\mu\nu}}\right)\varphi_k(\mu)\varphi_l(\nu)\, d\tau_\mu d\tau_\nu \ , \qquad (38)$$

$$X_{kl} = \iint \varphi_k(\mu)\varphi_l(\nu)\left(\frac{1}{r_{\mu\nu}}\right)\varphi_k(\nu)\varphi_l(\mu)\, d\tau_\mu d\tau_\nu \ . \qquad (39)$$

The last four integrals are termed kinetic energy integrals, potential energy integrals, Coulomb integrals, and exchange type integrals, respectively. The X_{kl} differ from the exchange integrals as usually defined only in that spin sums have already been taken. The orbitals to be used are real functions, and complex conjugate notations have therefore been dropped.

Calculations have also been made with a singlet configuration which places the four electrons in three different orbitals designated by subscripts i, j, and k. With paired electrons in orbital k the expectation value of the Hamiltonian is given by:

$$\langle\psi^*,H\psi\rangle = E = T_{ii} + T_{jj} + 2T_{kk} - V_{ii} - V_{jj} - 2V_{kk}$$
$$+ 2J_{ik} + 2J_{jk} + j_{ij} + J_{kk} - X_{ik}$$
$$- X_{jk} + X_{ij} \quad . \qquad (40)$$

II. ELECTRONIC ORBITAL FUNCTIONS

Values of the interaction energy are to be calculated for configurations involving 1s, 2s, 2pσ, and 3dσ electron orbitals. The orbitals may be formed from Slater type orbitals so that they are orthonormal by defining them in the following way:

$$\varphi_{1s} = \varphi_1 = (a\eta)^{3/2}\pi^{-1/2}e^{-a\eta r} \quad , \qquad (41)$$

$$\varphi_{2s} = \varphi_2 = \eta^{3/2}(3\pi N)^{-1/2}(\eta r e^{-\eta r} - 3Ae^{-a\eta r}) \quad , \qquad (42)$$

$$\varphi_{2p\sigma} = \varphi_3 = \eta^{5/2}\pi^{-1/2}re^{-\eta r}\cos\theta \quad , \qquad (43)$$

$$\varphi_{3d\sigma} = \varphi_6 = \sqrt{2}(\eta d)^{7/2}(9\pi)^{-1/2}r^2e^{-d\eta r}P_2(\cos\theta) \quad , \qquad (44)$$

where a, d, and η shall be used as variational parameters. The notation used corresponds in many ways to the notation employed in published tables of integrals based upon Slater type orbitals (22). The notations φ_4 and φ_5 are reserved for the two 2pπ orbitals which are not used in this thesis. The quantities N and A are defined through orthogonality and normalization conditions by

$$A = 8a^3(1+a)^{-4} \quad , \tag{45}$$

$$N = 1-192a^3(1+a)^{-8} \quad . \tag{46}$$

Published tables of the integrals to be employed must be used with care, as some authors use an atomic unit of energy half as large as the Hartree unit used here. Inasmuch as only σ type electrons are to be considered, the orbitals are not required to contain a dependence on the angle φ.

The orbitals given are to be used to form wave functions corresponding to the united atom configurations $(1s^2 2s^2)$, $(1s^2 2p\sigma^2)$, $(1s^2 3d\sigma^2)$, and $(1s3d\sigma 2s^2; {}^1\Sigma_g^+)$. The parameters a, η, and d shall be used without subscript for any one of the single configurations. When two configurations are mixed by the method of configuration interaction, there will be two sets of parameters which will be distinguished by Roman numeral subscripts. Thus, the subscript I will designate a parameter for the $(1s^2 2s^2)$ configuration, II for the $(1s^2 2p\sigma^2)$ configuration, III for the $(1s3d\sigma 2s^2; {}^1\Sigma_g^+)$ configuration, and IV for the $(1s^2 2d\sigma^2)$ configuration.

III. EQUATIONS FOR BASIC INTEGRALS

Kinetic Energy Integrals

Use of the orbitals given by Eqs. (41-46) yields for the expectation values of the kinetic energy the formulas

$$T_{11} = \frac{1}{2} a^2 \eta^2 \ , \tag{47}$$

$$T_{22} = (6N)^{-1} \eta^2 [1-48Aa(a-2)(1+a)^{-4}+9A^2 a^{-1}] \ , \tag{48}$$

$$T_{33} = \frac{1}{2} \eta^2 \ , \tag{49}$$

$$T_{66} = \frac{1}{2} d^2 \eta^2 \ . \tag{50}$$

Potential Energy Integrals

The potential energy integrals corresponding to the interaction between the electrons and nuclei may be evaluated by means of Eq. (37) and Eq. (18). The resulting equations are

$$V_{11} = -4\rho^{-1}[1-e^{-2a\eta\rho}(1+a\eta\rho)] \ , \tag{51}$$

$$V_{22} = -32A(N\rho)^{-1}(a+1)^{-4}\{6-e^{-(a+1)\eta\rho}[6+4(a+1)\eta\rho + (a+1)^2\eta^2\rho^2]\} + 2(3N\rho)^{-1}[6-e^{-2\eta\rho}(2\eta^3\rho^3 + 6\eta^2\rho^2+9\eta\rho+6] + 12(N_\rho)^{-1}(a)^{-3/2}A^2[1 - e^{-2a\eta\rho}(1+a\eta\rho)] \ , \tag{52}$$

$$V_{33} = 2\eta^{-2}\rho^{-3}[6+\eta^2\rho^2-e^{-2\eta\rho}(6+12\eta\rho+14\eta^2\rho^2+11\eta^3\rho^3 + 6\eta^4\rho^4+2\eta^5\rho^5] \ , \tag{53}$$

$$V_{66} = 4(\eta d)^{-4}\rho^{-5}[d^4\eta^4\rho^4+4d^2\eta^2\rho^2+90-(9)^{-1}e^{-2\eta\rho} \times(2d^9\eta^9\rho^9+10d^8\eta^8\rho^8+36d^7\eta^7\rho^7+108d^6\eta^6\rho^6$$

$$+279d^5\eta^5\rho^5+621d^4\eta^4\rho^4+1,152d^3\eta^3\rho^3+1,656d^2\eta^2\rho^2$$
$$+1,620d\eta\rho+810)] \ . \qquad (54)$$

When the method of configuration interaction is used, the off-diagonal matrix elements of the Hamiltonian may contain the off-diagonal elements for the potential energy V. These elements for the configurations used are given by

$$V_{16} = 16(15)^{-1}[2(a_I\eta_I)^8(\eta_{III}d_{III})^7]^{+1/2}\rho^{-3}(a_I\eta_I+d_{III}\eta_{III})^{-7}$$
$$\{720-e^{-(a_I\eta_I+d_{III}\eta_{III})\rho}[5(a_I\eta_I+d_{III}\eta_{III})^5\rho^5$$
$$+30(a_I\eta_I+d_{III}\eta_{III})^4\rho^4+120(a_I\eta_I+d_{III}\eta_{III})^3\rho^3$$
$$+360(a_I\eta_I+d_{III}\eta_{III})^2\rho^2+720(a_I\eta_I+d_{III}\eta_{III})\rho+720]\}, \qquad (55)$$

$$V_{26} = 16(15)^{-1}(3N_I)^{-1/2}[2\eta_I^3(\eta_{III}d_{III})^7]^{1/2}\rho^{-3}\eta_I(\eta_I$$
$$+d_{III}\eta_{III})^{-8}\{5040-e^{-(\eta_I+d_{III}\eta_{III})\rho}[5(\eta_I+d_{III}\eta_{III})^6\rho^6$$
$$+40(\eta_I+d_{III}\eta_{III})^5\rho^5+210(\eta_I+d_{III}\eta_{III})^4\rho^4+840(\eta_I$$
$$+d_{III}\eta_{III})^3\rho^3+2520(\eta_I+d_{III}\eta_{III})^2\rho^2+5040(\eta_I+d_{III}\eta_{III})\rho$$
$$+5040]\} -16(15)^{-1}(3N_I)^{-1/2}[2\eta_I^3(\eta_{III}d_{III}^7)]^{1/2}\rho^{-3}$$
$$(3A_I)(a_I\eta_I+d_{III}\eta_{III})^{-7}\{720-e^{-(a_I\eta_I+d_{III}\eta_{III})\rho} \times$$

$$[5(a_I\eta_I+d_{III}\eta_{III})^5\rho^5+30(a_I\eta_I+d_{III}\eta_{III})^4\rho^4$$

$$+120(a_I\eta_I+d_{III}\eta_{III})^3\rho^3+360(a_I\eta_I+d_{III}\eta_{III})^2\rho^2$$

$$+720(a_I\eta_I+d_{III}\eta_{III})\rho+720]\Big\} \quad . \tag{56}$$

Coulomb and Exchange Type Integrals

In the evaluation of the Coulomb and exchange type integrals use is made of Eq. (19), Eq. (38), and Eq. (39). The factors used in the integration over angles have been tabulated in the literature (23). The complete integrals may be expressed in terms of integral functions $I_p(m,\alpha|n,\beta)$ defined by

$$I_p(m,\alpha|n,\beta) = \int_0^\infty\int_0^\infty \left(\frac{r_<^P}{r_>^{P+1}}\right)_{r_\mu,r_\nu} r_\mu^m\, r_\mu^n$$

$$e^{-\alpha r_\mu} e^{-\beta r_\nu} r_\mu^2 r_\nu^2 dr_\mu dr_\nu \quad . \tag{57}$$

The functions $I_p(m,\alpha|n,\beta)$ may be evaluated (14) by means of the equation

$$I_p(m,\alpha|n,\beta) = \alpha^{P-m-2}(\alpha+\beta)^{m-n-4}(m-P+1)\,!(n+P+2)\,!$$

$$\sum_{k=0}^{m-P+1} \binom{m+n+4}{k+n+P+3} \alpha^{m-P+1-k}\beta^k$$

$$+\beta^{P-n-2}(\alpha+\beta)^{-m-n-4}(n-P+1)\,!(m+P+2)\,! \times$$

$$\sum_{k=0}^{n-P+1} \binom{m+n+4}{k+m+P+3} \beta^{n-P+1-k} \alpha^{k} \quad . \tag{58}$$

Numerical values for the Coulomb and exchange integrals with the orbitals given in Eqs. (41-46) may be obtained from tables given in the literature (22) over a limited range of the parameters. For arbitrary values of the parameters the integrals may be evaluated using the following expressions:

$$J_{11} = \left(\frac{5}{8}\right) a\eta \quad , \tag{59}$$

$$J_{22} = \left(\frac{16}{9}\right) \eta N^{-2} [I_o(2,2|2,2) - 12AI_o(2,2|1,1+a) + 36A^2 I_o(1,1+a|1,1+a) + 18A^2 I_o(2,2|0,2a) - 108A^3 I_o(1,1+a|0,2a) + 81A^4 I_o(0,2a|0,2a)] \quad , \tag{60}$$

$$J_{33} = \left(\frac{501}{1280}\right) \eta \quad , \tag{61}$$

$$J_{66} = 0.27638\eta d \quad , \tag{62}$$

$$J_{12} = \left(\frac{16}{3}\right) \eta a^3 N^{-1} [I_o(2,2|0,2a) - 6AI_o(1,1+a|0,2a) + 9A^2 I_o(0,2a|0,2a)] \quad , \tag{63}$$

$$J_{13} = \left(\frac{1}{24}\right) \eta a^3 I_o(2,1|0,a) \quad , \tag{64}$$

$$J_{16} = \left(\frac{d}{3}\right) \eta [1 - d^6 (4a+d)(a+d)^{-7}] \quad , \tag{65}$$

$$J_{26} = \left(\frac{32}{135}\right) N^{-1}d^7[I_o(2,2|4,2d)-6AI_o(1,1+a|4,2d)$$

$$+9A^2I_o(0,2a|0,2d)] , \qquad (66)$$

$$X_{12} = \left(\frac{16}{3}\right) N^{-1}a^8[I_o(1,1+a|1,1+a)-6AI_o(1,1+a|0,2a)$$

$$+9A^2I_o(0,2a|0,2a)] , \qquad (67)$$

$$X_{18} = \left(\frac{28}{3}\right) \eta a^8(1+a)^{-7} , \qquad (68)$$

$$X_{16} = \left(\frac{36}{5}\right) \eta a^8d^7(a+d)^{-9} , \qquad (69)$$

$$X_{28} = \left(\frac{16}{27}\right) \eta N^{-1}[I_1(2,2|2,2)-6AI_1(2,2|1,a+1)$$

$$+9A^2I_1(1,1+a|1,1+a)] , \qquad (70)$$

$$X_{26} = \left(\frac{32}{675}\right) N^{-1}d^7[I_2(3,1+d|3,1+d)-6AI_2(2,a+d|3,1+d)$$

$$+9A^2I_2(2,a+d|2,a+d)] . \qquad (71)$$

Additional equations for the $I_p(m,\alpha|n,\beta)$ functions are given in the appendix.

Integrals for Configuration Interaction

When a given orbital is used in each of the Slater determinants in a linear combination of determinants corresponding to different configurations, the parameters characterizing the orbital may differ from one configuration to the next. The orthogonality and normalization conditions may no longer hold for two orbitals in which the parameters

differ. Upon using a linear combination of the wave functions for the $(1s^2 2s^2)$ and $(1s3d\sigma 2s^2, {}^1\Sigma_g^+)$ configurations the following integrals are required:

$$\langle \varphi_1(a_I,\eta_I), \varphi_1(a_{III}\eta_{III})\rangle = \int \varphi_1(a_I,\eta_I)\varphi_1(a_{II},\eta_{II})d\tau$$

$$= 8(a_I\eta_I + a_{III}\eta_{III})^{-3}(a_I^3\eta_I^3 a_{III}^3\eta_{III}^3)^{1/2} \quad , \qquad (72)$$

$$\langle \varphi_1(a_I,\eta_I), \varphi_2(a_{III},\eta_{III})\rangle = \int \varphi_1(a_I,\eta_I)\varphi_2(a_{III},\eta_{III})d\tau$$

$$= 24[3N_{III}]^{-1/2}[a_I^3\eta_I^3\eta_{II}^3]^{1/2}[\eta_{II}(a_I\eta_I+\eta_{II})^{-4}$$

$$- A_{III}(a_I\eta_I + a_{II}\eta_{II})^{-3}] \quad , \qquad (73)$$

$$\langle \varphi_2(a_I,\eta_I), \varphi_1(a_{III},\eta_{III})\rangle = \int \varphi_2(a_I,\eta_I)\varphi_I(a_{III},\eta_{III})d\tau$$

$$= 24[3N_I]^{-1/2}[\eta_I^3 a_{III}^3\eta_{III}^3]^{1/2}[\eta_I(\eta_I + a_{III}\eta_{III})^{-4}$$

$$- A_I(a_I\eta_I + a_{II}\eta_{II})^{-3}] \quad , \qquad (74)$$

$$\langle \varphi_2(a_I,\eta_I), \varphi_2(a_{III},\eta_{III})\rangle = 8[N_I N_{III}]^{-1/2}[\eta_I^3\eta_{III}^3]^{1/2}$$

$$[4\eta_I\eta_{III}(\eta_I+\eta_{III})^{-5} - 3\eta_I A_{III}(\eta_I + a_{III}\eta_{III})^{-4}$$

$$-3\eta_{III}A_I(a_I\eta_I+\eta_{III})^{-4} + 3A_I A_{III}(a_I\eta_I + a_{II}\eta_{II})^{-3}] \quad . \qquad (75)$$

The terms in the Hamiltonian which contribute to the off-diagonal matrix element of the Hamiltonian are determined by the nature of the operator and the angular dependence of the orbitals used. The basic configuration used in this thesis is the $(1s^2 2s^2)$ configuration in which all of the orbitals have spherical symmetry. Hence, the angular dependence of the orbitals used in the wave function for the additional configurations determines the terms of the Hamiltonian contributing to the off-diagonal element.

For the $(1s^2 2p\sigma^2)$ configuration the wave function is composed of terms which contain as factors two first order Legendre polynomials characterizing two different electrons. Due to the orthogonality of the Legendre polynomials, the only terms which can contribute to the off-diagonal matrix element must contain the product of two first order Legendre polynomials when the $(1s^2 2s^2)$ and $(1s^2 2p\sigma^2)$ configurations are mixed. The two first order functions must characterize two different electrons. The only terms contributing in this case must arise from two-electron operators, i.e. operators involving two electrons. Thus, the kinetic energy operator and the nuclear potential terms as given by Eq. (18) cannot contribute. On the other hand, the potential term for the interaction between two electrons may contribute. It is readily seen that the term in Eq. (19) with n equal to one and m equal to zero will

contain two first order Legendre polynomials and therefore make a contribution to the off-diagonal matrix element. All of the other terms will not contribute due to orthogonality conditions.

The $(1s3d2s^2; {}^1\Sigma_g^+)$ configuration contains only one non-spherical orbital. Hence, only the one-electron operators may contribute to the off-diagonal matrix element of the Hamiltonian when this configuration is mixed with the $(1s^2 2s^2)$ configuration. The kinetic energy operator does not contain a second order Legendre function to match the function due to the 3d orbital, and by orthogonality the kinetic energy terms do not contribute. However, the term for n equal one in equation (18) contains exactly one second order Legendre function, and therefore the terms for the potential of an electron in the field of the nuclei do contribute. The terms for the interaction between electrons contain two Legendre functions. As the terms in the wave function contain only one second-order Legendre function, no contribution to the off-diagonal matrix element can be made by the terms in Eq. (19).

With these considerations the off-diagonal matrix elements may be evaluated. Indicating by $H_{I,II}$ the off-diagonal element resulting from the admixture of $(1s^2 2s^2)$ with $(1s^2 2p\sigma^2)$, one has

$$H_{I,II} = [\langle\varphi_1(a_I,\eta_I),\varphi_1(a_{II},\eta_{II})\rangle]^2[16/27]N^{-1}\eta_{II}^5\eta_I^{-4}$$

$$\left[69.375\left(1+\frac{\eta_{II}}{\eta_I}\right)^{-9} - 6A_I I_1\left(2,1+\frac{\eta_{II}}{\eta_I}\quad 1,a_I+\frac{\eta_{II}}{\eta_I}\right)\right.$$

$$\left. +47.25A_I^2\left(a_I+\frac{\eta_{II}}{\eta_I}\right)^{-7}\right] . \qquad (76)$$

The off-diagonal matrix element $H_{I,III}$ obtained with the admixture of $(1s3d\sigma 2s^2, {}^1\Sigma_g^+)$ with $(1s^2,2s^2)$ gives

$$H_{I,III} = [2]^{1/2}[\langle\varphi_2(a_I,\eta_I),\varphi_2(a_{III},\eta_{III})\rangle\ V_{16}$$

$$- \langle\varphi_1(a_I,\eta_I),\varphi_2(a_{III},\eta_{III})\rangle\ V_{26}]$$

$$[\ \langle\varphi_2(a_I,\eta_I),\varphi_1(a_{III},\eta_{III})\rangle\langle\varphi_1(a_I,\eta_I),$$

$$\varphi_2(a_{III},\eta_{III})\rangle - \langle\varphi_1(a_I,\eta_I),\varphi_1(a_{III},\eta_{III})\rangle$$

$$\langle\varphi_2(a_I,\eta_I),\varphi_2(a_{III},\eta_{III})\rangle\ ] . \qquad (77)$$

IV. THE ENERGY FOR CONFIGURATION INTERACTION

With a linear combination of two wave functions in the manner indicated by Eq. (21) the resultant expression for the energy is obtained from Eq. (27) with $H_{12} = H_{21}$ as the electron orbitals are real functions. The two roots of the resulting determinantal equation in the notation of Eq. (23) are given by

$$E = \frac{1}{2}\left\{ H_{11}+H_{22} \pm [H_{11}-H_{22}][1+4H_{12}^2(H_{11}-H_{22})^{-2}]^{1/2}\right\} . \qquad (78)$$

The energies corresponding to a mixture of $(1s^2 2s^2)$ and $(1s^2 2p\sigma^2)$ configurations may be obtained by using Eqs. (23, 35, 76, and 78). The fundamental equations required for the evaluation of the energy with configuration interaction between the $(1s^2 2s^2)$ and $(1s3d\sigma 2s^2, {}^1\Sigma_g^+)$ configurations may be obtained by utilizing Eqs. (23, 35, 40, 77, and 78).

CHAPTER IV

RESULTS OF THE CALCULATIONS AND CONCLUSIONS

I. SINGLE CONFIGURATION ENERGY VALUES

The equations for the total energies corresponding to the single configurations $(1s^2 2s^2)$, $(1s^2 2p\sigma^2)$, and $(1s^2 3d\sigma^2)$ involve two variation parameters and the internuclear separation. The internuclear separation was held fixed while each of the two variation parameters was varied to obtain minimum values for the energy. This procedure was followed for internuclear separations of 0.50 a.u., 0.75 a.u., and 1.00 a.u. In the case of the $(1s^2 2s^2)$ configuration the parameters were varied over an exceptionally large range and two minima obtained. For other configurations only the minima corresponding to screened nuclear charges intermediate between the screened charges of helium and the screened charges of beryllium were examined. An example of the minimization procedure indicating two minima for the $(1s^2 2s^2)$ configuration at an internuclear separation of 0.50 a.u. is given in a graph in the appendix. Results for the $(1s^2 2s^2)$ configuration are summarized in Table II. In the united atom limit of zero separation an electronic energy of -14.56 a.u. was obtained. The electronic energy of the beryllium ground state is -14.67 a.u. (6), which is 0.11 a.u. (3.0 e.v.) lower than the calculated value.

TABLE II

MINIMA OF THE INTERACTION ENERGY FOR THE $(1s^2 2s^2)$ CONFIGURATION OF HE-HE

R(a.u.)	a_I	η_I	$a_I\eta_I$	$(E-\frac{4}{R})$(a.u.)	E(a.u.)
0.00	3.75	0.980	3.675	-14.56	∞
0.50	0.75	1.27	0.95	- 9.887	-1.887
	2.75	0.84	2.31	-10.136	-2.136
0.75	2.50	0.76	1.90	- 8.510	-3.177
1.00	0.75	0.92	0.69	- 7.322	-3.322
	2.20	0.72	1.58	- 7.345	-3.345

Data for the ($1s^2 2p\sigma^2$) configuration have been given by Husinaga (14) with the approximation of assuming identical exponential parameters for the two orbitals used. The work of Husinaga for this configuration has been improved by separately varying each of the two parameters used for the two electronic orbitals. The resultant values for the energy are given in Table III. As given by Eq. (41) and Eq. (44), the orbitals for the ($1s^2 3d\sigma^2$) configuration contain three parameters. However, it is readily seen from the form of the orbitals that the parameters occur in such a way as to represent two screened nuclear charge parameters; and no loss of generality occurs upon setting the parameter d in Eq. (47) equal to one. Data for the ($1s^2 3d\sigma^2$) configuration are given in Table IV.

It should be noted from Tables II, III, and IV that the product $a\eta$ which corresponds to the screened nuclear charge for a 1s orbital is almost identical for all three configurations at a given internuclear separation. The optimum 1s orbital thus appears to be independent of the orbitals chosen for the outer two electrons. This suggests that the radial dependence is substantially correct. Polarization of the 1s orbit would lead to an angular dependence. The use of configurations with angular dependent orbitals in configuration interaction is thus suggested for further improvement.

TABLE III

MINIMA OF THE INTERACTION ENERGY FOR THE $(1s^2 2p\sigma^2)$ CONFIGURATION OF HE-HE

R(a.u.)	a_{II}	η_{II}	$a_{II}\eta_{II}$	$(E-\frac{4}{R})$(a.u.)	E(a.u.)
0.50	2.25	1.04	2.34	-10.081	-2.081
0.75	1.40	1.35	1.89	- 8.690	-3.357
1.00	1.00	1.60	1.60	- 7.821	-3.821

TABLE IV

MINIMA OF THE INTERACTION ENERGY OF THE $(1s^2 3d\sigma^2)$ CONFIGURATION OF HE-HE

R(a.u.)	a_{IV}	η_{IV}	$a_{IV}\eta_{IV}$	$(E-\frac{4}{R})$(a.u.)	E(a.u.)
0.50	4.50	0.52	2.34	-9.601	-1.601
1.00	3.50	0.48	1.68	-6.926	-2.926

The results for the $(1s^2 2s^2)$ and $(1s^2 2p\sigma^2)$ configurations are displayed in Fig. 5. From this figure the value of R_c at which the $(1s^2 2s^2)$ and $(1s^2 2p\sigma^2)$ configurations yield the same energy is seen to be approximately 0.56 a.u.

II. CONFIGURATION INTERACTION RESULTS

A significant improvement over the energy value for the $(1s^2 2p\sigma^2)$ configuration was obtained at an internuclear separation of 1.0 a.u. by Husinaga (14) as a result of using a linear combination of 1s, 4s, and 4dσ Slater type orbitals in place of the original 1s orbital. Only the single calculation was made. The determinantal wave function with electronic orbitals consisting of a linear combination of Slater orbitals may be decomposed into a sum of determinants representing single configurations. By using the method of configuration interaction with a linear variational parameter for each configuration one may obtain greater generality than if a linear combination of orbitals is used. In view of this fact and the improvement obtained by Husinaga, the method of configuration interaction has been applied to the original $(1s^2 2s^2)$ configuration of this thesis to obtain improved energy values.

A linear combination of $(1s^2 2s^2)$ and $(1s^2 2p\sigma^2)$ configuration wave functions was first considered, and Eq. (76) and Eq. (78) used to determine the energy. Parameters were

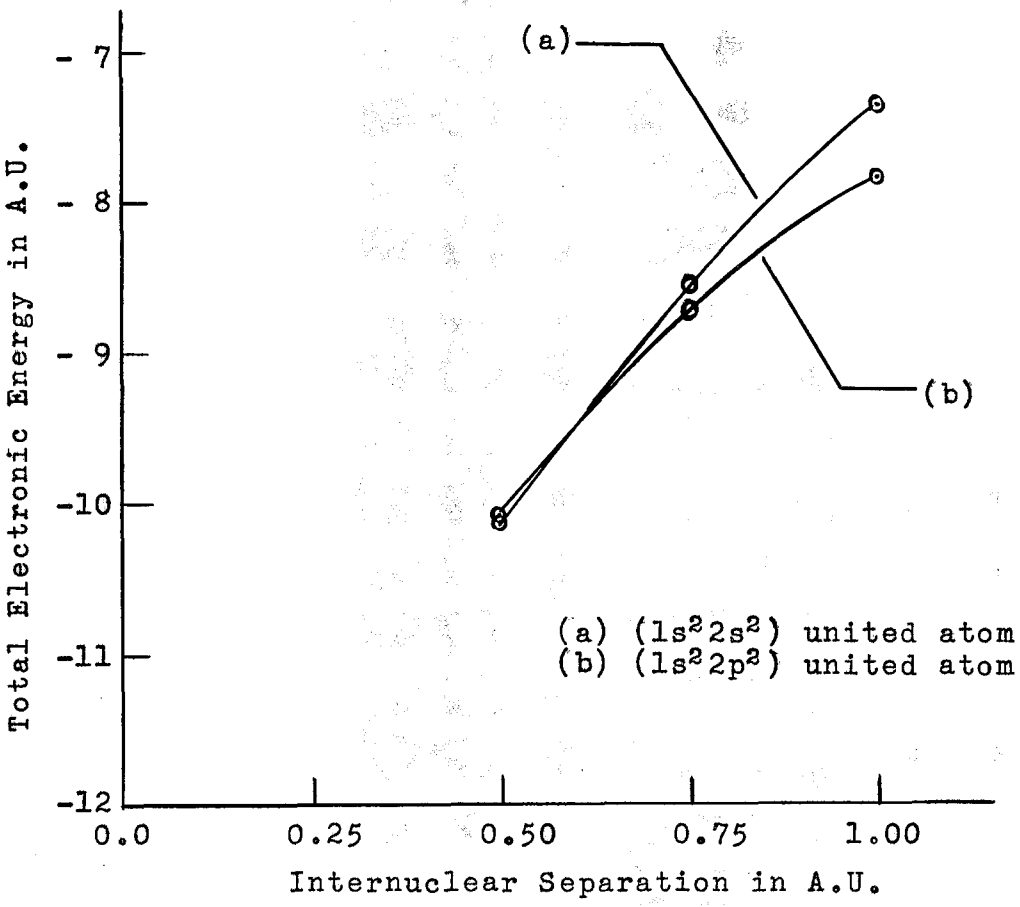


FIGURE 5

THE TRANSITION OF UNITED ATOM CONFIGURATIONS

chosen to correspond to parameters used in previous single configuration calculations. The best energy obtained was with parameters corresponding to the minima of the single configurations. The off-diagonal matrix element as given by Eq. (76) consists of the square of a normalization type integral multiplied by a function which is a generalization of X_{23} as given by Eq. (70). The normalization type integral has a maximum value of one. The generalization of the integral X_{23} is tabulated by Morse and Yilmaz (22). By inspection of the tabulated values related to X_{23} it was observed that the upper limit on the value of the off-diagonal matrix element as given by Eq. (76) was not significantly greater than the value obtained using parameters corresponding to the minima. It was therefore concluded that further work toward obtaining a lower energy value was not justified for this mixture of configurations. The data used are given in Table V. The total energy obtained was -2.175 at a separation of 0.50 a.u. This represented an improvement of 0.039 a.u. (1.1 e.v.) over the value for the single configuration ($1s^2 2s^2$) wave function. The improvement at larger separation was negligible.

A linear combination of the configurations ($1s^2 2s^2$), ($1s^2 2p\sigma^2$), and ($1s^2 3d\sigma^2$) was tried. The inclusion of the ($1s^2 3d\sigma^2$) configuration gave only a minute improvement. A consideration of the numerical tables of Morse and Yilmaz (22) indicated that the off-diagonal matrix element

TABLE V

INTERACTION ENERGIES OBTAINED FOR
HE-HE USING THE WAVE FUNCTION
$A\psi(1s^2 2s^2)+B\psi(1s^2 2p\sigma^2)$

R(a.u.)	A	B	a_I	η_I	a_{II}	η_{II}	$(E-\frac{4}{R})$(a.u.)	E(a.u.)
0.50	0.842	-0.541	2.75	0.84	2.25	1.04	-10.175	-2.175
0.75	0.190	-0.982	2.50	0.76	1.40	1.35	- 8.697	-3.364
1.00	0.032	-0.999	2.25	0.70	1.00	1.60	- 7.822	-3.822

contributions due to the $(1s^2 3d\sigma^2)$ configuration were very small, and work using this configuration was discontinued.

The configurations $(1s^2 2p\sigma^2)$ and $(1s^2 2d\sigma^2)$ correspond to the promotion of two electrons to higher electron orbitals relative to the $(1s^2 2s^2)$ configuration. As a result of the promotion of two electrons, the off-diagonal matrix element for the Hamiltonian involves only two-electron operators when configuration interaction is applied with these configurations. Thus the off-diagonal elements contain exchange integrals as factors. The values of the exchange integrals are small in comparison to the expectation value of the one-electron operators for kinetic energy and potential energy. This fact strongly suggests the use of configurations containing one promoted electron to be mixed with the ground state configuration in establishing wave functions by the method of configuration interaction. Calculations were therefore made with the configurations $(1s^2 2s^2)$ and $(1s3d\sigma 2s^2, {}^1\Sigma_g^+)$. The off-diagonal matrix element then involves the operator for the Coulomb potential of the electrons in the field of the nuclei. This matrix element is given by Eq. (77). The $3d\sigma$ function also allows for polarization effects.

With the addition of the determinant for the $(1s3d\sigma 2s^2, {}^1\Sigma_g^+)$ configuration to that of the $(1s^2 2s^2)$ configuration four new variational parameters are introduced: one linear parameter and parameters for each of the 1s, 2s,

and $3d\sigma$ orbitals in the added configuration. The minimization was first carried out with identical parameters for the 1s and 2s orbitals; that is, the parameters a and η were the same in both configurations. The linear parameter was optimized by differentiation as given by Eqs. (21 - 27). Variation of the parameter d corresponding to the 3d function of Eq. (47) then gave a minimum of -2.362 a.u. for the total energy at 0.50 a.u. separation. This value represents an improvement of 6.15 e.v. in the energy relative to the total energy for the single configuration ($1s^2 2s^2$). As a result of this substantial improvement in the total energy value with the variation of a single parameter, it seemed desirable to vary the other parameters in the ($1s3d\sigma 2s^2, {}^1\Sigma_g^+$) configuration. Accordingly the problem was programmed for the IBM 1620 computer at the University of Tennessee.[1] The three parameters for the ($1s3d\sigma 2s^2$) configuration were designated a_{III}, η_{III}, and d_{III} and varied while holding fixed the parameters a_I and η_I corresponding to the optimum energy for the single ($1s^2 2s^2$) configuration. The computer was used to more accurately determine data for the ($1s^2 2s^2$) configuration since these data were used as inputs for the calculations with configuration interaction.

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[1] Copies of the computer program are available from the author.

These calculations were carried out for internuclear separations of 0.50, 0.75, and 1.0 a.u. The final results are given in Table VI, and may be compared with previous calculations by reference to Fig. 6. As an example of the improvement obtained, the difference between the energy value for the ($1s^2 2s^2$) configuration and the empirical potential of Buckingham is 1.8 a.u. (49 e.v.) at a separation of 0.50 a.u. The energy obtained with the ($1s3d\sigma 2s^2, {}^1\Sigma_g^+$) configuration admixed differs from the Buckingham value by 1.6 a.u. (43 e.v.) at the same separation. This represents an improvement of about 11 per cent in the value of the difference.

While data are not available for two-center calculations in the neighborhood of 0.50 a.u. separation, the magnitudes of the energy values and the relative slopes of the best one-center energy curve and the curve for the best two-center calculations indicate the superiority of the one-center calculations at small internuclear separations.

III. CONCLUSIONS

The results of this thesis do provide new theoretical information of a quantitative nature on the interaction between two helium atoms at small internuclear separation. The quantitative information indicates the range of separations within which a united atom treatment should surpass

TABLE VI

INTERACTION ENERGIES OBTAINED FOR HE-HE AS A FUNCTION OF THE SEPARATION FOR CONFIGURATION INTERACTION BETWEEN $\psi(1s^2 2s^2; a_I, \eta_I)$ AND $\psi(1s3d\sigma 2s^2, {}^1\Sigma_g^+; a_{II}, \eta_{II}, d_{II})$

R(a.u.)	a_I	η_I	a_{III}	η_{III}	d_{III}	$(E-\frac{4}{R})$(a.u.)	E(a.u.)
0.50	2.75	0.84	3.00	0.84	9.0	-10.365	-2.365
0.75	2.50	0.76	3.00	0.76	7.0	- 8.822	-3.489
1.00	2.20	0.72	2.50	0.70	6.0	- 7.705	-3.705

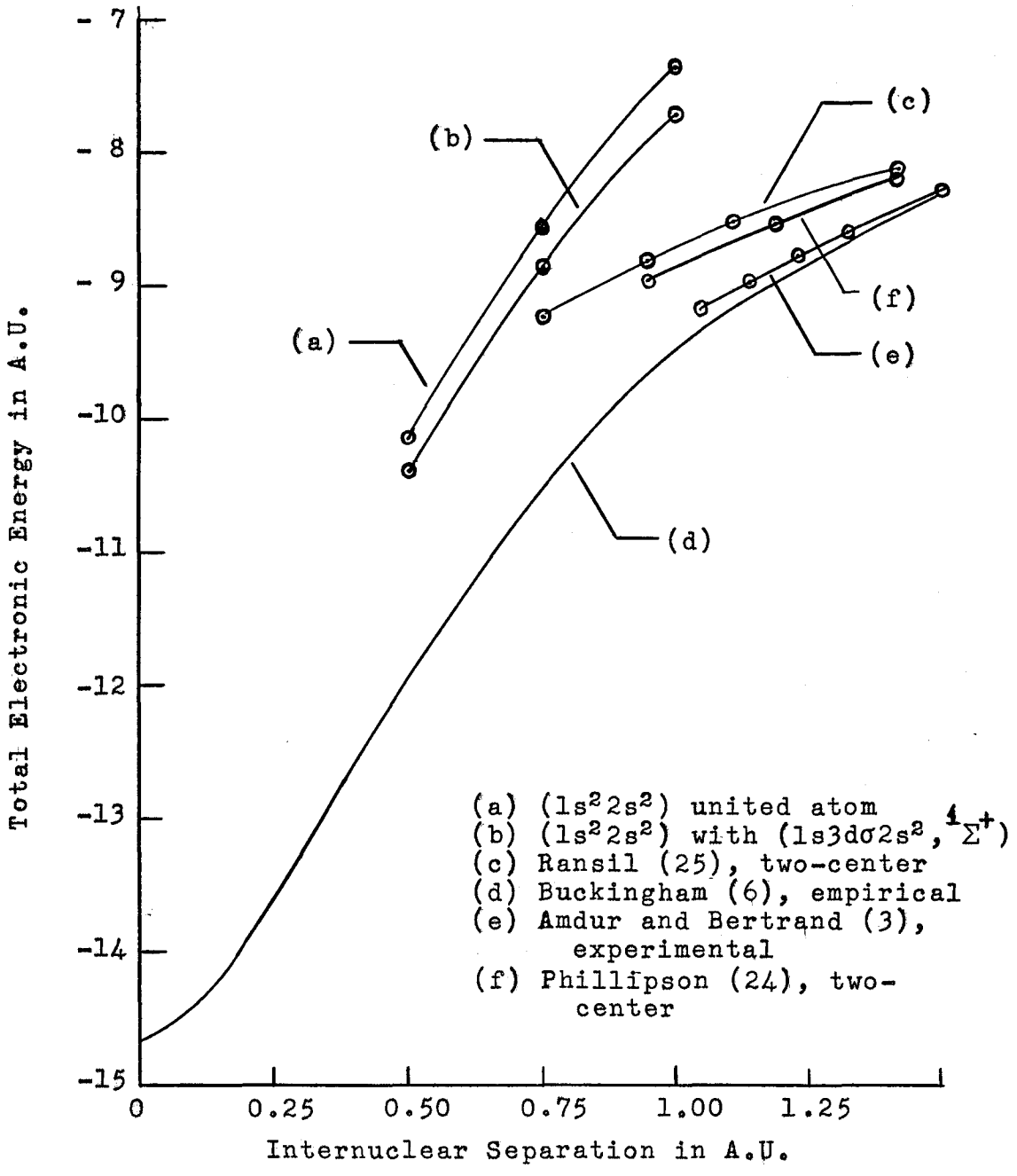

FIGURE 6

THEORETICAL AND EMPIRICAL VALUES
FOR THE HE-HE ELECTRONIC
INTERACTION ENERGY

a two-center treatment in yielding accurate theoretical data. By the use of sufficiently elaborate wave functions, e.g. by using a large number of configurations in configuration interaction, each method may be extended to cover larger ranges of the separation than is indicated by the point R_c at which the ground state configuration changes. One therefore would like to have a qualitative indication as to what might be expected of the united atom method in an extension of the present work.

The work of Ransil (25) used a linear combination of Slater type orbitals to improve upon the simple 1s orbital. This was done by the addition of a 2s and a 2pσ orbital with linear variation parameters (Table I). The results of Phillipson (24) using the molecular orbital method were obtained by using configuration interaction with a total of sixty-four configurations. The work of Ransil may be compared with the best results of this thesis. A glance at Fig. 6 and a reasonable extrapolation of the data of Ransil indicates that the one-center method with only two configurations gives lower energy values for separations less than about 0.65 a.u. This is in good agreement with the value of 0.56 a.u. found for R_c by determining the configuration transition point with single configuration united atom wave functions. Furthermore the large improvement over the simple ($1s^2 2s^2$) results obtained with the use of

one additional configuration suggests that the use of several configurations should give results as good as or better than the two-center calculations at 0.75 a.u. The one-center method is therefore capable of supplying a good extension of previous theoretical results in toward small internuclear separations.

A consideration of the united atom results and the empirical function of Buckingham at a separation of 0.50 a.u. shows that the use of configuration interaction does much to reduce the difference between the theoretical results with a single configuration and the empirical function. However the difference which remains is very large compared to the improvement resulting from one additional configuration. The recent results of Amdur and Bertrand (3) have revised the experimental data obtained from scattering experiments in a direction tending to give closer agreement between theory and experiment. Correspondingly, the empirical function of Buckingham should be revised in the same direction, as it was originally devised (6) with the use of the results of the early scattering data. It therefore seems possible that the use of additional configurations with the united atom method could produce close agreement with a revised empirical function.

Qualitatively the large improvement obtained by the use of an additional configuration in the united atom method

indicates that a single united atom configuration is not a good approximation to the true wave function at finite separations. This is not surprising in view of the automatic cut-off of multipole terms in the potential of Eq. (18) when calculating the expectation value of the Hamiltonian. With the addition of higher configurations to the wave function the expectation value of the Hamiltonian acquires additional terms corresponding to new multipole contributions from the potential function. Finally the admixture of additional configurations also gives some correction for correlation effects (18).

Husinaga (14) obtained considerable improvement in his original treatment of the He-He problem by the united atom method when he included a $4d\sigma$ type orbital. The work of this thesis has indicated that the largest contributions to the off-diagonal matrix element for the Hamiltonian are a result of the use of configurations which differ from each other by one promoted electron. It would therefore seem advisable to include in an extension of the united atom method the following configurations:

$$(1s4d\sigma 2s^2; {}^1\Sigma_g^+),$$
$$(1s^2 2s3d\sigma; {}^1\Sigma_g^+),$$
$$(1s^2 3d\sigma^2; {}^1\Sigma_g^+),$$
$$(1s3d\sigma 2s3d\sigma; {}^1\Sigma_g^+).$$

The admixture of $(1s^2 2p\pi_+ 2p\pi_-; {}^1\Sigma_g^+)$ with the $(1s^2 2p\sigma^2; {}^1\Sigma_g^+)$ configuration is suggested for separations greater than R_c.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Amdur, I., J. Chem. Phys. 17, 844 (1949).

2. Amdur, I., J. Chem. Phys. 28, 987 (1958).

3. Amdur, I. and R. R. Bertrand, J. Chem. Phys. 36, 1078 (1962).

4. Amdur, I. and A. L. Harkness, J. Chem. Phys. 22, 664 (1954).

5. Amdur, I., J. E. Jordan, and S. O. Colgate, J. Chem. Phys. 34, 1525 (1961).

6. Buckingham, R. A., Trans. Faraday Soc. 54, 453 (1958).

7. Chen, T. C., J. Chem. Phys. 29, 347 (1958).

8. Cohen, M. and C. A. Coulson, Proc. Cambridge Phil. Soc. 57, Pt. 1, p. 96 (1961).

9. Eyring, H., J. Walter, and G. E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944).

10. Griffing, V. and J. F. Wehner, J. Chem. Phys. 23, 1024 (1955).

11. Hashino, T. and S. Husinaga, Progr. Theoret. Phys. 20, 631 (1958).

12. Herzberg, G. Spectra of Diatomic Molecules, (Vol. I of Molecular Spectra and Molecular Structure, D. Van Nostrand Co., New York, 1950).

13. Hirschfelder, J. O., C. F. Curtis, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc., New York, 1954).

14. Husinaga, S., Progr. Theoret. Phys. 17, 169 (1957).

15. Husinaga, S., Progr. Theoret. Phys. 18, 139 (1957).

16. Husinaga, S., Progr. Theoret. Phys. 20, 15 (1958).

17. Landau, L. D. and E. M. Lifschitz, Quantum Mechanics, Non-Relativistic Theory (Addison-Wesley Pub. Co., Inc., Reading, Mass., 1958), pp. 262-266.

Lowdin, Per-Olov, "Correlation Problem in Many-Electron Quantum Mechanics," Advances in Chemical Physics, Vol. II, ed. I. Prigogine, (Interscience Publishers, Inc., New York, 1959), pp. 274-277.

Lynn, N., Proc. Phys. Soc. (London) 72, Pt. 2, 201 (1958).

Massey, H. S. W. and E. H. S. Burhop, Electronic and Ionic Impact Phenomena, (Clarendon Press, Oxford, 1952), p. 494.

Moore, N., J. Chem. Phys. 33, 471 (1960).

Morse, P. M. and H. Yilmaz, Tables for the Variational Determination of Atomic Wave Functions (M.I.T. Technology Press, Cambridge, Mass., 1956).

Pauling, L. and E. B. Wilson, Introduction to Quantum Mechanics (McGraw-Hill Book Co., New York, 1935).

Phillipson, P. E., Phys. Rev. 125, 1981 (1962).

Ransil, B. J., J. Chem. Phys. 34, 2109 (1961).

Rosen, P., J. Chem. Phys. 18, 1182 (1950).

Sakamoto, M. and E. Ishiguro, Progr. Theoret. Phys. 15, 37 (1956).

Seitz, F., Modern Theory of Solids (McGraw-Hill Book Co., New York, 1940), p. 263.

Wu, Ta-You, J. Chem. Phys. 28, 986 (1958).

APPENDICES

APPENDIX A

EQUATIONS FOR SOME OF THE FUNCTIONS $I_p(m,\alpha \mid n,\beta)$

From the definition of the functions in Eq. (63) it may be shown that

$$I_p(n,k\alpha \mid m,k\beta) = k^{-(m+n+5)} I_p(n,\alpha \mid m,\beta) . \qquad (84)$$

Eq. (84) is very useful in establishing values of the functions over a range of parameters after calculations have been made for a few parameters. Equations for some of the functions used in the calculations for this thesis have been determined from Eq. (63) and are given in the following list:

$$I_o(0,\alpha|0,\beta) = 2\alpha^{-2}\beta^{-2}(\alpha+\beta)^{-4}(\alpha^3+4\alpha\beta^2+4\beta\alpha^2+\beta^3), \qquad (85)$$

$$I_o(0,\alpha|1,\beta) = \alpha^{-2}\beta^{-3}(\alpha+\beta)^{-4}(6\beta^3+24\alpha\beta^2+16\alpha^2\beta+4\alpha^3) \qquad (86)$$

$$I_o(0,\alpha|2,\beta) = 12\alpha^{-2}\beta^{-4}(\alpha+\beta)^{-5}(2\beta^4+10\beta^3\alpha + 10\alpha^2\beta^2+5\beta\alpha^3+\alpha^4) , \qquad (87)$$

$$I_o(0,\alpha|4,\beta) = 240\alpha^{-2}\beta^{-6}(\alpha+\beta)^{-8}(3\beta^7+24\alpha\beta^6+56\alpha^2\beta^5 + 70\alpha^3\beta^4+56\alpha^4\beta^3+28\alpha^5\beta^3+8\alpha^6\beta+\alpha^7) , \qquad (88)$$

$$I_o(1,\alpha|1,\beta) = 12\alpha^{-3}\beta^{-6}(\alpha+\beta)^{-5}(\beta^4+5\alpha\beta^3+10\alpha^2\beta^2 + 5\alpha^3\beta+\alpha^4) , \qquad (89)$$

$$I_o(1,\alpha|2,\beta) = 12\alpha^{-3}\beta^{-4}(\alpha+\beta)^{-7}(4\beta^6+28\alpha\beta^5+84\alpha^2\beta^4 + 105\alpha^3\beta^3+62\alpha^4\beta^2+21\alpha^5\beta+3\alpha^6) , \qquad (90)$$

$$I_o(1,\alpha|4,\beta) = 720\alpha^{-3}\beta^{-6}(\alpha+\beta)^{-9}(2\beta^8+18\alpha\beta^7+72\alpha^2\beta^6$$
$$+126\alpha^3\beta^5+126\alpha^4\beta^4+84\alpha^5\beta^3+36\alpha^6\beta^2$$
$$+9\alpha^7\beta+\alpha^8) \quad , \tag{91}$$

$$I_o(2,\alpha|2,\beta) = 144\alpha^{-4}\beta^{-4}(\alpha+\beta)^{-7}(\beta^6+7\alpha\beta^5+21\alpha^2\beta^4$$
$$+35\alpha^3\beta^3+21\alpha^4\beta^2+7\alpha^5\beta+\alpha^6) \quad , \tag{92}$$

$$I_1(1,\alpha|1,\beta) = 24\alpha^{-2}\beta^{-2}(\alpha+\beta)^{-5}(\beta^2+5\alpha\beta+\alpha^2) \quad , \tag{93}$$

$$I_1(1,\alpha|2,\beta) = 24\alpha^{-2}\beta^{-3}(\alpha+\beta)^{-6}(5\beta^3+30\alpha\beta^2+2\alpha^3$$
$$+12\beta\alpha^2) \quad , \tag{94}$$

$$I_1(2,\alpha|2,\beta) = 240\alpha^{-3}\beta^{-3}(\alpha+\beta)^{-7}(\beta^4+7\alpha\beta^3+21\alpha^2\beta^2$$
$$+7\alpha^3\beta+\alpha^4) \quad , \tag{95}$$

$$I_2(2,\alpha|2,\beta) = 720\alpha^{-2}\beta^{-2}(\alpha+\beta)^{-7}(\beta^2+7\alpha\beta+\alpha^2) \quad , \tag{96}$$

$$I_2(2,\alpha|3,\beta) = 720\alpha^{-2}\beta^{-3}(\alpha+\beta)^{-9}(7\beta^4+63\alpha\beta^3$$
$$+72\alpha^2\beta^2+18\alpha^3\beta+2\alpha^4) \quad , \tag{97}$$

$$I_2(3,\alpha|3,\beta) = 1008\alpha^{-3}\beta^{-3}(\alpha+\beta)^{-10}(\beta^5+10\alpha\beta^4$$
$$+45\alpha^2\beta^3+45\alpha^3\beta^2+10\alpha^4\beta+\alpha^5) \, . \tag{98}$$

APPENDIX B

AN EXAMPLE OF THE MINIMIZATION PROCEDURE

The minima of the energy expressions for the various configurations were found numerically. The energy for a given configuration was calculated for various values of η for a given value of the parameter a. This process was repeated for various values of a until a minimum with respect to both a and η was defined. Data used in the determination of two minima for the $(1s^2 2s^2)$ configuration are presented in Fig. 7 for an internuclear separation of 0.5 a.u. Similar curves were obtained for other separations and for the other configurations.

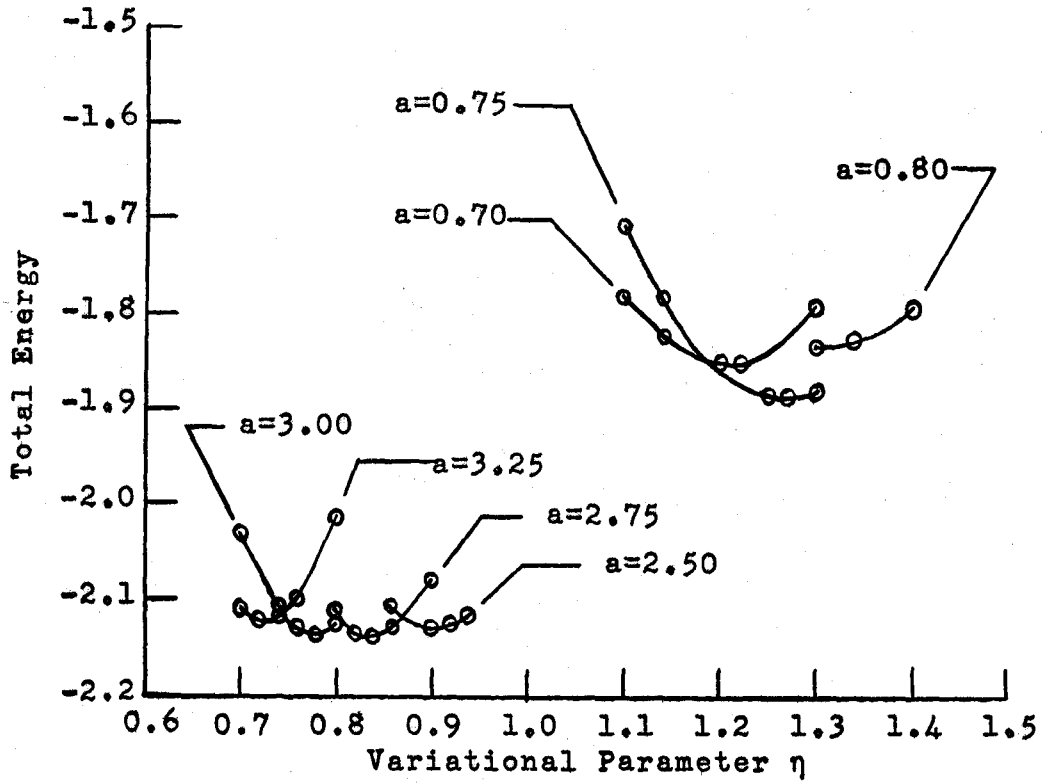

FIGURE 7

DATA USED IN THE MINIMIZATION OF THE TOTAL ENERGY FOR THE ($1s^2 2s^2$) CONFIGURATION AT R=0.5 A.U. AS A FUNCTION OF THE PARAMETERS a AND η

APPENDIX C

SCREENING CONSTANTS

A set of empirical rules (13) has been devised for determining the exponential parameters in the nodeless Slater type orbitals for use in atomic calculations. The effective exponential constant for an atomic orbital is given by the quantity $(Z-S)(1/n^*)$, where Z is the nuclear charge of the atom, S is a screening constant determined by means of the empirical rules, and n^* is an effective quantum number. For the first three shells of electrons the effective quantum number is equal to the principal quantum number.

As the work of this thesis has been based upon the united atom approximation, the comparison of these empirically determined screened charges with the screened charges obtained by means of the variational calculations is of some interest. The screened charges (Z-S) have been calculated for beryllium using the empirical rules (13) and are compared with the values determined by the variational method in Table VII for an internuclear separation of 0.5 a.u.

In the cases of all the 1s orbitals the variational values are much less than the screened charges for beryllium. This indicates that at an internuclear distance of 0.5 a.u. the separation of the nuclei is effective in

TABLE VII

COMPARISON OF SLATER SCREENED CHARGES FOR BE WITH THE VARIATIONAL RESULTS AT A SEPARATION OF 0.5 A.U.

Configuration	Orbital	Slater Screened Charge (Z-S)	Variational Screened Charge
$(1s^2 2s^2)$	1s	3.70	2.31
	2s	1.95	1.68
$(1s^2 2p\sigma^2)$	1s	3.70	2.34
	2p	1.95	2.08
$(1s^2 3d\sigma^2)$	1s	3.70	2.34
	3d	1.65	1.04
$(1s3d\sigma 2s^2; {}^1\Sigma_g^+)$	1s	4.00	2.52
	2s	2.80	1.68
	3d	1.0	7.56

pushing the probability density distribution for the electronic charge out to larger radii. This effect is naturally greatest for 1s electrons. The 2s orbital in the ($1s^2 2s^2$) configuration is characterized by a screened charge not too different from the Slater value for beryllium, and the 2p orbital in the ($1s^2 2p\sigma^2$) configuration provides good agreement. The most striking difference lies in the values for the 3d orbital in the ($1s3d\sigma 2s^2; {}^1\Sigma_g^+$) configuration. The variational wave function in this case provides an angular dependence not taken into account in the ($1s^2 2s^2$) function. This correction is very large in the neighborhood of the nuclei, and as a result the 3d orbital is pulled in to effect such correction. This is indicated by the exceptionally large value found for the screened charge.

Thus for very small internuclear separations it appears that one may expect the screened charges to closely approach the screened charges for beryllium in the case of outer shell electrons in basic configurations. For configurations that are admixed in order to supply corrections to the angular dependence of the wave functions, one may expect the correcting orbital to be strongly distorted toward the positions of the nuclei.